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Original Research

Distribution, Bioavailability and Ecological Risk of Heavy Metals in Surface Sediments from the Wujiang River Basin, Southwest of China

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Abstract

Chemical speciation of Cu, Zn, Mn, Pb, Cd, As, and Hg in surface sediments from the Wujiang River Basin was analyzed by using modified BCR sequential extraction procedure. The results indicated that the mean total concentrations of all heavy metals except As were higher than their background values. Cu, Zn, Pb, As, and Hg mostly exist in a residual fraction. The Mn and Cd were dominated by the reducible fraction and exchangeable fraction, respectively. According to the risk assessment code (RAC) classification, Cu, Zn, Pb, As, and Hg posed a relatively low risk in this study area, while Mn and Cd posed a high risk in most sampling sites. The I_{geo} classification manifested that Cd has the highest environmental risk and the pollution levels of heavy metals in the surface sediments were generally in the sequence of Cd>Zn>Cu>Pb>Hg>Mn>As. The potential ecological risk index (*PERI*) was classified as considerable risk in two sampling sites and moderate risk in ten sampling sites. It should pay much attention to the ecological risk of heavy metals from the Wujiang River Basin which will influence the Yangtze River ecosystem eventually.

Keywords: heavy metal, the Wujiang River Basin, surface sediments, chemical speciation, ecological risk

Introduction

Heavy metal pollution is one of the most alarming environmental issues around the world due to the potential biotoxicity, persistence, accumulative characteristic, and widespread sources. It originates from the natural and anthropogenic sources. The former includes rock weathering, volcanic eruption, soil erosion, atmospheric deposition, etc. The latter includes discharge of domestic sewage and industrial wastewater, operation of mining and metal smelting, combustion of fossil fuels, utilization of agricultural fertilizer, and activities of increasing traffic [1-3]. The distribution characteristics of heavy metals in water and sediments can reflect not only the pollution status but also the potential influences on the health of aquatic ecosystems [4]. When heavy metals enter the river environment, most of them will be accumulated in the

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surface sediments through a series of physiological and biochemical processes [5]. In the meantime, the absorbed metals in sediments could be released with the changing of environmental conditions such as pH, dissolved oxygen, conductivity, redox potential, nutrient levels, as well as the stirring of deposits caused by flowing water and benthic organisms. It then poses secondary pollution to the aquatic environment [6]. Therefore, the sediments can not only be served as a major sink for heavy metal inputs but also be a potential source of metal pollution in river ecosystems, which are considered to play an important role in recording the current and historical pollution [7].

The pollution status can be reflected by the assessment of the total concentrations of heavy metals in sediments. Nevertheless, the total concentration itself cannot provide sufficient information on the mobility and bioavailability of heavy metals, as different heavy metal forms in sediments have different stabilities and biological availabilities and result in varying ecological risks [8]. So, it is necessary to determine the speciation of heavy metals. In order to understand the characteristics of metal fractions in sediments, the three-step sequential extraction procedure proposed by the European Community Bureau of Reference (BCR) was commonly used. There are four kinds of metal fractions according to BCR method: (1) exchangeable fraction (F1, species with cation exchange sites and bound to carbonates), (2) reducible fraction (F2, bound to Fe-Mn oxides), (3) oxidizable fraction (F3, bound to organic matter and sulphides), and (4) residual fraction (F4, bound to mineral matrix) [9]. On the basis of BCR sequential extraction method, the Risk Assessment Code (RAC) classification can be chosen as a suitable way to assess the mobility and biological availability of heavy metals [10, 11]. In addition, the mobile fraction calculated as the sum of exchangeable, reducible, and oxidizable fractions was also important to assess the bioavailability and potential ecological risk of heavy metals in river ecosystems [6, 12].

A lot of Hg ore deposits were found in the Wujiang River Basin, which is located in the Circum-Pacific mercuriferous belt [13]. Because of the special geological background, numerous studies were conducted to investigate the geochemical cycling of Hg in river-reservoir ecosystem in this area [14-16]. In addition, other mineral resources such as coal, zinc, iron, and manganese are also rich in the Wujiang River Basin. The mineral exploitation and discharge of sewage could result in metal contamination in the Wujiang River. The highest heavy metal evaluation index was found at Wulong where it is located in the downstream of Wujiang River compared to other sites from the Three Gorges Reservoir [17]. So, there is a necessity to concern the contamination of heavy metals due to highly background values and anthropogenic sources in the Wujiang River Basin. The main objectives of the present study were: (1) to determine the spatial distribution of seven selected heavy metals (Cu, Zn, Mn, Pb, Cd, As, and Hg) resided in surface sediments from the Wujiang River Basin; (2) to explore the relationships between heavy metals in sediments and physic-chemical properties in overlying water; (3) to assess the mobility, potential bioavailability, and environment risk of these heavy metals.

Experimental

Study Area

The Wujiang River is the largest tributary on the south bank of the upper Yangtze River. It originates from the Wumeng Mountain in Western Guizhou Province and ends at Fuling in Chongqing, with a total length of 1037 km and a drainage area of 87920 km^2 (26°10'-29°45'N, 104°05'-108°30'E) [18]. The sampling of overlying water and sediments was conducted at 26 sites from the Wujiang River Basin during January 2018. Ten of sampling sites were in the main stream of the Wujiang River, and the others were in eight tributaries, which are Liuchong River (LCR), Maotiao River (MTR), Pianyan River (PYR), Qingshui River (QSR), Xiangjiang River (XJR), Apeng River (APR), Hongdu River (HDR), and Furong River (FRR), respectively. There were two sampling sites on the middle and lower reaches of each tributary (Fig. 1).

Sampling and Sample Preparation

Surface sediment samples were collected by a Peterson grab sampler from each sampling site. Each sample was composed of six mixed sub-samples (three on the left bank and three on the right bank). The impurities such as gravel and foliage were eliminated, and then the collected sediment samples were stored in polyethylene bags. The sediment samples were air dried at room temperature, ground with agate mortars, sieved through a 200-mesh sieve, and stored in polypropylene bottles prior to analysis.

At each sampling site, the overlying water samples were collected simultaneously by a plexiglass water sampler from about 20 cm above the surface of sediment. They were immediately filtered through 0.45 μm Millipore membrane and placed in cleaned polyethylene bottles. Ultrapure nitric acid was then added until the pH became less than 2. The samples were kept in an icebox and stored at 4ºC in a refrigerator before the experiment.

Sequential Extraction

Chemical speciation of Cu, Zn, Mn, Pb, Cd, As, and Hg in surface sediments was analyzed by using the BCR sequential extraction procedure according to Nemati et al. [19] with minor modifications. It could be classified into the following four forms:

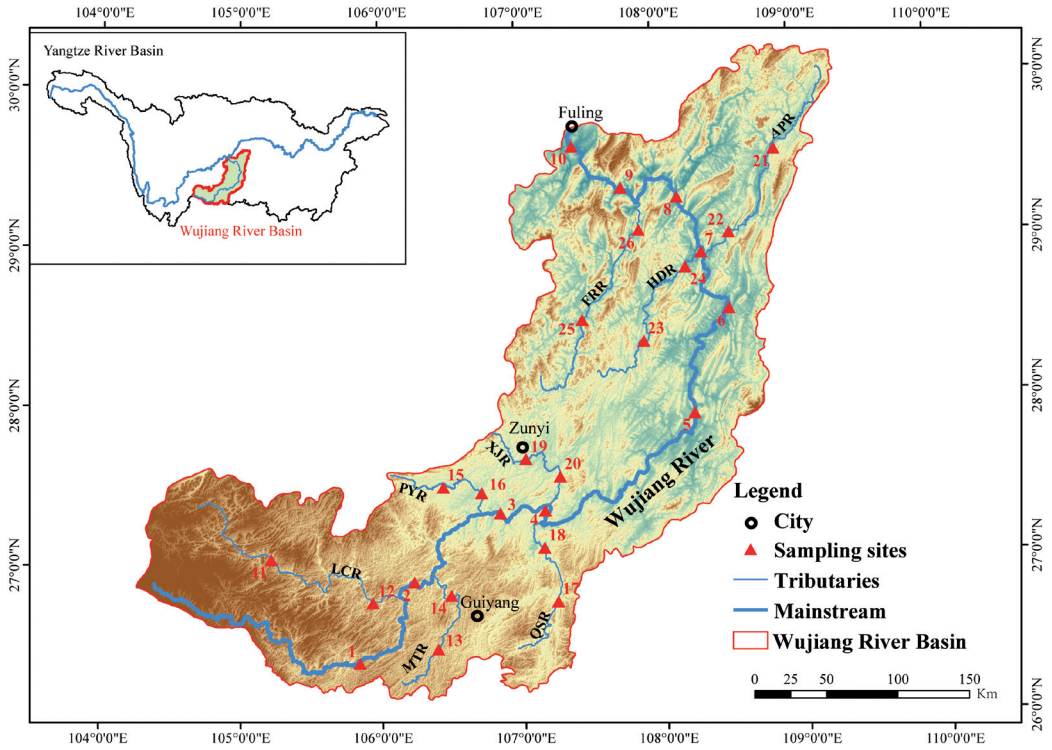

Fig. 1. Sampling sites of the surface sediments and overlying water in the Wujiang River Basin.

Exchangeable fraction (F1): 40 mL of 0.11 mol L^{-1} CH_3COOH was added to 0.500 g sediment sample in a 100 mL centrifuge tube. The tube was shaken in a shaker for 16 h at 25ºC, then centrifuged at 5000 rpm for 15 min. The supernatant was decanted gently into a glass test tube and stored at 4ºC. The residue was washed with 20 mL deionized water twice, and the supernatant was decanted and discarded.

Reducible fraction (F2): 40 mL of 0.1 mol L^{-1} $NH_2OH{\cdot}HCl$ (pH = 1.5 with HNO_3) was added to the residue from the first step in a centrifuge tube. The supernatant and residue in this step were obtained as previously described.

Oxidizable fraction (F3): 10 mL of 30% H_2O_2 was carefully added to the residue from the previous step. The digestion was proceeding at room temperature for 1 h with manual shaking at 10 min interval, and then digested at 85ºC for 1 h in a water bath until the mixture was reduced to 2-3 mL. After cooling, an additional 10 mL of 30% H_2O_2 was added and repeated the above procedure. Finally, 50 mL of 0.5 mol L^{-1} NH_4COOH (pH = 2 with HNO_3) was added to the mixture and shaken for 16 h at 25ºC, then centrifuged at 5000 rpm for 15 min. The supernatant was decanted gently into a glass test tube and stored at 4ºC.

Residual fraction (F4): The residue from previous step was digested in a Teflon crucible with an acid mixture of concentrated HCl (4.5 mL), HNO_3 (1.5 mL), and HF (2 mL) and heated at on a hot plate up to dryness. After cooling, the sample was dissolved in 2 mL of high pure HCl, and diluted with deionized water to a volume of 25 mL.

Analytical Methods

The common physico-chemical characteristics of overlying water (e.g., water temperature (T), pH, dissolved oxygen (DO), saturation percentage of dissolved oxygen (DO%), electrical conductivity (EC), and oxidation reduction potential (ORP)) were determined in situ by a portable multi-parameter water quality analyzer (YSI Professional Plus, YSI Inc., Ohio, USA). The concentrations of Ca and Mg in overlying water, and Cu, Zn, Mn, Pb, and Cd in extracted sediment solution of each steps in the BCR method were analyzed by the Shimadzu AA-6880 atomic absorption spectrophotometer. The concentrations of As and Hg in BCR solution were carried out by the KCHG AFS-9530 atomic fluorescence spectrophotometer. The total concentrations of heavy metals are expressed as the sum of the four fractions. Three replicates were carried out for all of the analyses, and the results were expressed as mean concentration. The relative standard deviations were less than 5%. The precision and accuracy of analytical procedures were assessed by recovery measurements on sediment standard reference material GSD-7 (GBW07307). The recoveries for Cu, Zn, Mn, Pb, Cd, As, and Hg in the standard reference materials ranged from 91.4% to 108.6%.

Ecological Risk Assessment

The geo-accumulation (I_{geo}) is widely used as a proxy to assess the sediment pollution state [20]. It is expressed as the following equation:

$$I_{geo} = \log_2 \frac{C_i}{1.5 \times B_i}$$

...where C_i is measured concentration of metal *i*, and the B_i is the geochemical background concentration of metal *i*. In present study, the background concentrations of Cu, Zn, Mn, Pb, Cd, As, and Hg were 29.43, 89.94, 1076.90, 29.39, 0.31, 14.89, and 0.10 mg/kg, respectively [21]. As a qualitative scale of metal pollution levels, I_{geo} is defined as following seven classes: class 1 (unpolluted, $I_{geo} \leqslant 0$); class 2 (unpolluted to moderately polluted, $0 \leqslant I_{geo} \leqslant 1$); class 3 (moderately polluted, $1 \leqslant I_{geo} \leqslant 2$); class 4 (moderately polluted to strongly polluted, $2 \leqslant I_{geo} \leqslant 3$); class 5 (strongly polluted, $3 \leqslant I_{geo} \leqslant 4$); class 6 (strongly polluted to extremely polluted, $4 \leqslant I_{geo} \leqslant 5$); class 7 (extremely polluted, $I_{geo} \geqslant 5$) [22].

In order to assess the biotoxicity and comprehensive effects of heavy metals in surface sediments, the potential ecological risk index (*PERI*) initially introduced by Hakanson [23] was employed in present study. The *PERI* is defined as shown below:

$$PERI = \sum E_r^i = \sum T_r^i \times \frac{C_s^i}{C_n^i}$$

...where C_s^i and C_n^i are the measured concentration of metal *i* and its background concentration, respectively. The T_r^i is the biological toxicity factor of an element *i* which is 5, 1, 1, 5, 30, 10, and 40 for Cu, Zn, Mn, Pb, Cd, As, and Hg, respectively [23, 24]. The E_r^i is the potential ecological risk factor of metal *i*. There are five classes according to E_r^i: low risk ($E_r^i < 40$); moderate risk ($40 \leqslant E_r^i < 80$); considerable risk ($80 \leqslant E_r^i < 160$); high risk ($160 \leqslant E_r^i < 320$); very high risk ($E_r^i \geq 320$). The *PERI* is the sum of E_r^i for all selected heavy metals. Four classes of *PERI* are as following: low risk ($PERI < 150$); moderate risk ($150 \leqslant PERI < 300$); considerable risk ($300 \leqslant PERI < 600$); very high risk ($PERI \geqslant 600$).

The assessment methods of I_{geo} and *PERI* are based on total concentrations of heavy metals in sediments, which cannot fully reflect the potential risk to water environment. Considering the mobility and biological availability of heavy metals in sediments are intensely influenced by the chemical speciation, the risk assessment code (RAC) was also used to assess the potential risk of heavy metals in this study. RAC is defined as the percentage of exchangeable fraction in the total metal concentrations (F1/(F1+F2+F3+F4)×100%). According to RAC, the sediments were categorized into five classes: no risk (RAC<1%); low risk (1%⩽RAC<10%); moderate risk (10%⩽RAC<30%); high risk (30%⩽RAC<50%); very high risk (RAC ⩾50%).

Statistical Analysis

SPSS Statistics 13.0 and Origin 8.0 were utilized to conduct statistical analyses. The physic-chemical properties of overlying water were expressed as mean±standard deviation (n = 3). Pearson correlation coefficient was conducted to determine the relationships between the total metal concentrations in surface sediments and physic-chemical parameters in the overlying water.

Results and Discussion

Physic-Chemical Properties of Overlying Water

The physic-chemical properties of overlying water from 26 sampling sites were summarized in Table 1. The water temperature (T), percentage of dissolved oxygen (DO%), dissolved oxygen (DO), pH, electrical conductivity (EC), oxidation reduction potential (ORP), Ca, and Mg concentrations were 8.9-16.3ºC, 55.8-127.9%, 5.91-12.8 mg L^{-1}, 7.72-8.71, 138.3-495.5 μS cm^{-1}, 31.4-573.6 mV, 62.6-94.1 mg L^{-1}, 9.1-15.6 mg L^{-1}, respectively. The alkalinity and high concentrations of Ca and Mg of overlying water can be attributed to the well-developed karstification and the carbonate weathering in the Wujiang River basin [25].

Distribution of Total Concentrations of Heavy Metals in Sediments

The descriptive statistics of the total concentrations of Cu, Zn, Mn, Pb, Cd, As, and Hg in surface sediments from the Wujiang River basin are listed in Table 2. The mean concentrations of the seven selected metals were decreased in the order of Mn>Zn>Cu>Pb>As>Cd>Hg, which is similar to the distribution characteristics of their background values. The mean concentration of As (11.67 mg kg^{-1}) was lower than the background value (14.89 mg kg^{-1}), and the mean concentration of Mn (1110.99 mg kg^{-1}) was comparable with its corresponding background value (1076.90 mg kg^{-1}). However, the mean concentrations of Cu (50.79 mg kg^{-1}), Zn (181.99 mg kg^{-1}), Pb (42.49 mg kg^{-1}), Cd (0.96 mg kg^{-1}), and Hg (0.16 mg kg^{-1}) were 1.73, 2.02, 1.45, 3.07, and 1.54 times higher than their background values, respectively. The total concentrations of Cu, Zn, Mn, Pb, Cd, As, and Hg in surface sediments of 26 sampling sites are shown in Fig. 2. Notably, the concentrations of Zn and Cd exceed their background values in all 26 sampling sites, and the concentration of As was higher than the background value in two sampling sites (15.57 mg kg^{-1} in site 4 and 17.57 mg kg^{-1} in site 13). It might be related to the high background of zinc mining area and zinc smelting activities in northwest Guizhou which are located in the upper reaches of Wujiang River. The high concentration of Hg in central Guizhou (site 13 and site 18) might be caused by anthropogenic source such as Guizhou organic chemical plant and high Hg background in Kaiyang section where Hg mine exist [26].

Table 1. The physic-chemical properties of overlying water from the Wujiang River Basin.

Site	T (°C)	DO%	DO (mg/L)	pH	EC (μS/cm)	ORP (mV)	Ca (mg/L)	Mg (mg/L)
1	10.6±0.1	92.6±0.9	10.30±0.10	8.50±0.01	280.0±1.0	128.4±0.4	63.1±10.9	9.1±0.8
2	12.0±0.1	80.9±1.3	8.72±0.14	8.11±0.02	260.0±2.0	491.2±0.7	62.6±12.5	9.7±0.8
3	15.3±0.0	127.9±2.4	12.50±0.42	8.71±0.10	295.6±0.7	60.9±0.9	70.6±11.0	12.7±1.0
4	13.5±0.0	94.4±0.5	9.77±0.06	8.29±0.01	288.3±1.4	447.9±1.7	64.4±1.7	11.1±1.4
5	13.2±0.0	83.2±0.9	8.72±0.10	8.07±0.02	284.0±0.4	430.7±2.7	75.4±12.0	12.7±0.9
6	13.2±0.0	90.9±0.6	9.53±0.06	8.21±0.02	279.5±0.3	32.8±0.1	75.1±13.0	13.5±2.2
7	16.0±0.1	93.9±0.3	8.99±0.06	8.42±0.02	285.4±0.3	31.4±0.2	73.1±10.9	12.6±2.5
8	13.6±0.1	80.2±0.7	8.34±0.07	8.09±0.01	269.0±1.6	185.3±0.7	92.0±5.0	13.0±2.1
9	13.3±0.1	83.7±0.8	8.74±0.08	8.12±0.01	257.7±1.8	182.4±0.8	70.0±6.2	12.0±0.5
10	13.1±0.0	83.0±0.2	8.74±0.03	8.03±0.03	262.8±0.2	181.3±0.8	75.2±3.9	15.0±0.5
11	12.3±0.0	81.0±0.5	8.66±0.05	8.42±0.14	235.2±2.6	530.4±0.4	78.2±2.6	15.1±0.2
12	12.6±0.1	83.4±0.5	8.87±0.05	8.15±0.11	267.7±7.9	142.1±6.0	72.6±1.0	11.9±0.5
13	10.0±0.0	95.8±1.6	10.80±0.06	8.26±0.01	350.2±0.2	133.5±0.9	69.4±7.8	14.8±0.4
14	11.9±0.0	93.5±1.0	10.10±0.11	8.21±0.02	364.8±0.2	129.1±0.4	69.3±2.4	12.3±0.3
15	11.2±0.0	82.9±0.7	9.08±0.08	8.14±0.04	358.3±1.1	480.8±1.8	70.5±3.8	11.9±0.4
16	12.7±0.1	79.2±2.1	8.40±0.20	8.13±0.02	286.4±1.9	51.2±1.4	83.6±2.4	14.3±0.3
17	11.5±0.1	98.4±0.1	10.70±0.01	7.72±0.03	362.4±4.0	59.9±0.7	76.4±7.0	14.8±1.2
18	13.8±0.0	108.7±0.2	11.30±0.02	8.43±0.02	294.7±0.1	44.3±0.3	71.8±1.0	12.5±0.2
19	12.6±0.0	55.8±0.4	5.91±0.05	7.82±0.03	495.5±0.1	420.7±2.3	73.2±2.5	12.2±0.3
20	12.6±0.0	120.7±1.4	12.80±0.15	8.63±0.03	286.4±1.7	429.7±1.1	76.5±2.2	13.2±0.2
21	8.9±0.1	84.9±0.6	9.79±0.04	8.33±0.02	138.3±0.4	563.0±4.6	75.1±3.0	11.7±0.9
22	9.0±0.1	85.9±0.3	9.88±0.04	8.12±0.03	149.6±0.3	573.6±2.5	66.4±1.6	12.5±0.2
23	12.5±0.1	108.5±1.7	11.60±0.22	8.22±0.03	233.4±0.2	418.1±1.7	70.4±5.1	13.1±0.6
24	16.3±0.1	88.3±0.2	8.55±0.04	8.27±0.02	283.2±0.2	32.4±0.3	72.6±4.1	13.1±0.3
25	11.6±0.0	92.1±0.9	10.0±0.10	8.04±0.02	305.3±0.7	422.6±1.3	69.8±4.9	13.0±0.6
26	11.3±0.1	94.5±0.5	11.2±0.06	8.17±0.03	330.8±0.1	343.2±1.2	94.1±2.2	15.6±0.1

Table 2. Descriptive statistics of the total concentrations of heavy metals (mg/kg) in surface sediments from the Wujiang River Basin and published mean concentrations of heavy metals from adjacent area.

	Cu	Zn	Mn	Pb	Cd	As	Hg	References
Mean	50.79	181.99	1110.99	42.49	0.96	11.67	0.16	Present study
SD	21.73	76.07	480.86	15.13	0.36	2.54	0.18	
Median	44.19	147.14	1045.15	38.82	0.87	11.63	0.11	
Max	109.66	381.98	2455.38	80.13	1.93	17.57	0.89	
Min	23.94	120.87	511.32	22.91	0.41	6.94	0.05	
Kurtosis	1.68	1.91	1.01	2.07	0.67	-0.14	12.75	
Skewness	1.49	1.66	1.05	1.55	0.90	0.25	3.51	
CV (%)	42.79	41.80	43.28	35.61	37.08	21.76	111.46	
BV	29.43	89.94	1076.90	29.39	0.31	14.89	0.10	
% Sites>BV	92 %	100 %	46 %	88 %	100 %	8 %	58 %	

Table 2. Continued.

Pengxi River	33.92	NA	324.5	20.77	0.42	NA	NA	[25]
Jinsha River	58.57	56.5	NA	22.23	0.25	12.45	0.038	[26]
Three Gorges Reservoir	97.72	177	NA	114.1	0.33	10.08	0.05	[27]
Yangtze River	82	174	NA	60	2.46	25.4	0.16	[28]

NA: not available. BV: background value.

The coefficient of variations (CVs) of Pb and As were 35.61% and 21.76%, respectively, which were classified to medium variation (15%<CV<36%) [27]. The CVs for Cu, Zn, Mn, Cd, and Hg were 42.79%, 41.80%, 43.28%, 37.08%, and 111.46%, respectively, which belong to high variation (CV > 36%). The higher CV values for these heavy metals indicated that they were unevenly distributed and probably influenced by anthropogenic sources. The skewness of the selected heavy metals followed the order of Hg>Zn>Pb>Cu>Mn >Cd>As. The skewness for Hg was also higher than that of the other metals, suggesting that the Hg in sediments may be influenced by the human activities [5]. The Hg concentration had a CV of 111.46%, skewness of 3.51 and kurtosis of 12.75, which were the largest of all heavy metals studied.

The mean concentrations of Cu, Mn, Pb, and Cd in sediments from present study area were higher than that found in sediments of Pengxi River, a tributary of the Yangtze River [28]. The mean concentrations of Cu and As in the Wujiang River Basin were comparable to those in Jinsha River, while Zn, Pb, Cd, and Hg were much higher than those in Jinsha River, a significant source of water to the Yangtze River [29]. The mean concentrations of Zn and Hg were close to the Yangtze River, and the mean concentrations of Cu, Pb, Cd, and As were lower than that found in sediments of the Yangtze River [30]. Compared with the reports about heavy metals in sediments from the Three Gorges Reservoir, the Cu and Pb were lower, but Zn, Cd, As, and Hg were higher [31]. The Wujiang River is one of the most important input rivers for the Three Gorges

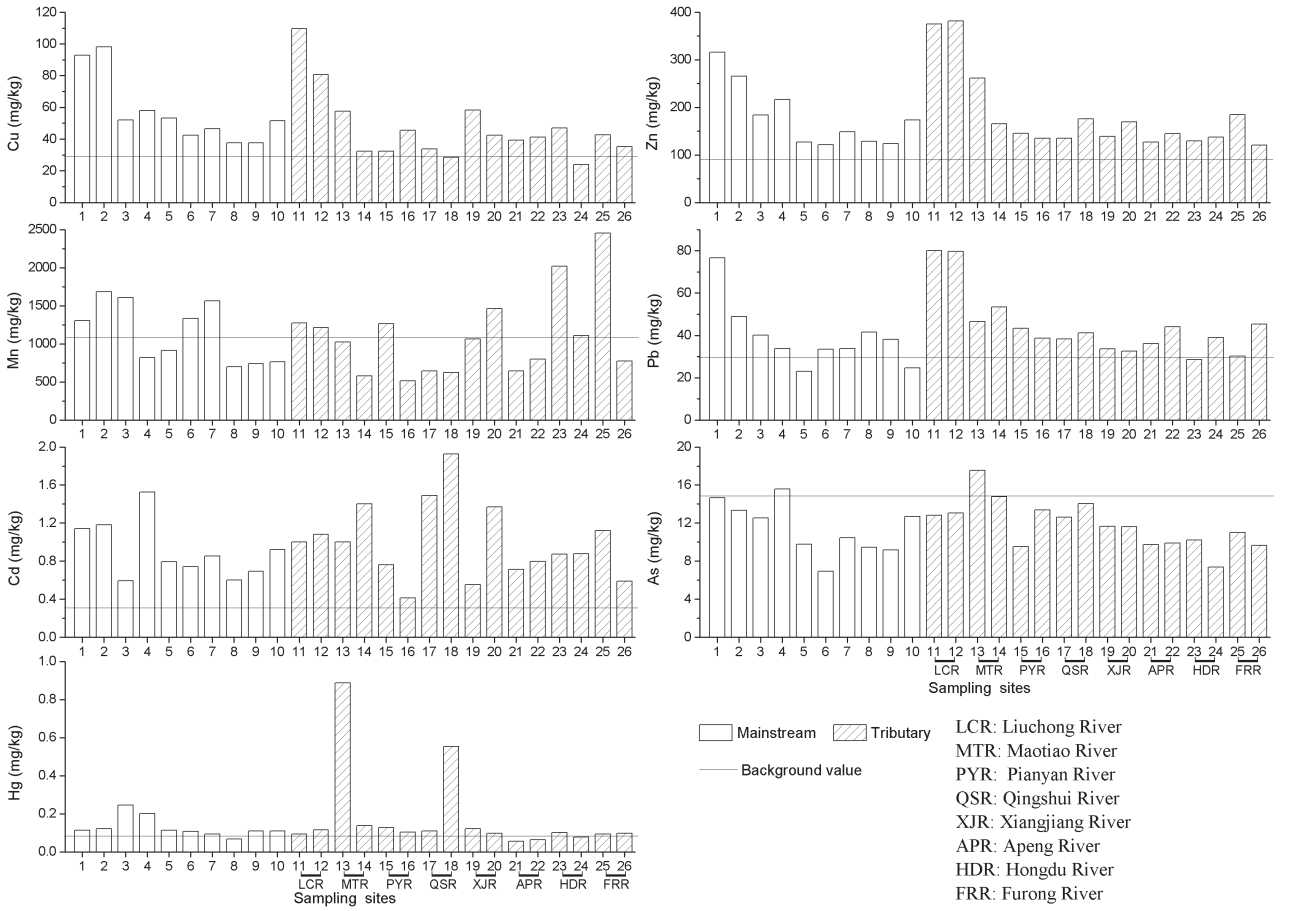

Fig. 2. The total concentrations of Cu, Zn, Mn, Pb, Cd, As, and Hg in surface sediments of 26 sampling sites from the Wujiang River Basin.

Reservoir, it could be a main pollution source of heavy metals in the Three Gorges Reservoir [17].

Correlation Analysis

The results of Pearson correlation coefficient are presented in Table 3. The correlations between overlying water physic-chemical properties and the total concentrations of heavy metals in surface sediments from 26 sampling sites were complex. Significant negative correlation was shown between water temperature (T) and ORP (p<0.01). Significant positive correlations were observed in the pairs DO%-DO (0.944, p<0.01), DO%-pH (0.658, p<0.01), DO-pH (0.566, p<0.01), and Ca-Mg (0.652, p<0.01). There was a positive correlation of p<0.05 between Cd and DO, indicating that the distribution of Cd was controlled by the concentration of dissolved oxygen in this study area. In addition, the Cd concentration was significantly negative correlated with Ca (p<0.05), indicating that the Ca may be the main factor affecting the distribution of Cd in the surface sediment of the Wujiang River Basin. However, no correlations were observed between Cd and other parameters (p > 0.05). Pearson's correlation matrix also reflected close relationships among the heavy metals (Table 3). Significant positive correlations were found between several metal pairs like Cu-Zn, Cu-Pb, Zn-Pb, As-Zn, As-Cd, and As-Hg (p<0.01). Metal pair As-Cu exhibited a significant positive correlation of p<0.05, which indicated common sources, mutual dependence, and migration behavior of these metals [32,33]. However, no significant correlation was found between Mn and other metals. In addition, no significant correlation exists among other metals, which reflected these metals might not be controlled by a single factor [34].

Chemical Speciation of Heavy Metals in Sediments

The chemical fraction percentages of Cu, Zn, Mn, Pb, Cd, As, and Hg in sediment from the Wujiang River Basin were illustrated in Fig. 3. Cu, Zn, Pb, As, and Hg appear mostly in a residual fraction with mean percentages of 79.98%, 73.00%, 67.84%, 93.72%, and 82.23%, respectively. It indicated that these heavy metals were mainly bound in the mineral lattice and could be stable under natural conditions with lower mobility and bioavailability. It is generally accepted that the sum of exchangeable fraction, reducible fraction, and oxidizable fraction is mobile fraction [6]. The relatively unstable binding forms show high bioavailability and toxicity than the residual fraction. The mean percentages of mobile fraction of heavy metals occurred in the following order: Mn (78.63%)>Cd (67.67%)>Pb (32.16%)>Zn (27.00%)>Cu (20.02%)>Hg (17.77%)>As (6.28%). Obviously, the values of Mn and Cd were much higher than other heavy metals, indicating that Mn and Cd were more mobile and bioavailable than other studied heavy metals. Mn was dominated by the reducible fraction with a mean percentage of 39.66% and a range from 12.83% to 59.64%. The exchangeable fraction of Mn was also found in a significant mean percentage of 37.05% and a range from 5.69% to 69.21%. The relatively high proportions of exchangeable and reducible Mn in present study were in agreement with Zheng et al. [35]. Mn is an active element and will exist and migrate in a dissolved form in porewater [36]. Besides, a great number of Mn could be released as the water environment acidified continuously [37]. Furthermore, high levels of Mn originated from the development and utilization of local Mn resources might be easily attached to the surface sediments, which has also been reported in the previous study [38].

The exchangeable fraction of Cd was the most dominant fraction with mean percentages of 35.00% followed by the residual fraction (32.33%), reducible fraction (30.85%), and oxidizable fraction (1.82%). Other studies also demonstrated that the predominance proportion of Cd were found in exchangeable fraction [33, 39, 40]. The ionic radius of Cd is 0.97 Å, which is similar to that of Ca (0.99 Å). It should be good for the co-precipitation of Cd with carbonates [41]. Significant negative correlation between Ca in overlying water and Cd in sediments was shown in Table 3, indicating the Ca could be easily replaced by Cd in the form of carbonate minerals. The high mobility of Cd could, at least partly, explain that the total concentration of Cd was relatively less than other heavy metals in the present studied area. On the other hand, it also suggested that the Cd is regarded as one of the most contaminated metals in the Wujiang River Basin because of its higher dispersal ability. The presence of heavy metals in the exchangeable fraction is mainly due to the anthropogenic activities, such as industrial production, mining, and utilization of agricultural fertilizer [42,43]. Considering that less source of industrial production and mining because of strict environmental protection measures, the accumulating of Cd could be as a result of runoff containing phosphate fertilizer from the agricultural farms [39, 41].

Assessment of Potential Ecological Risk

The RAC value of the selected heavy metals ranged from 0.08% to 3.67% with an average of 1.04% for Cu, 0.14% to 12.34% with an average of 4.17% for Zn, 5.69% to 69.21% with an average of 37.05% for Mn, 0.62% to 4.56% with an average of 1.76% for Pb, 10.10% to 51.47% with an average of 35.00% for Cd, 1.40% to 3.25% with an average of 2.01% for As, 0.82% and 19.04% to with an average of 8.01% for Hg (Fig. 3). According to the RAC classification, Cu, Zn, Pb, As, and Hg posed a low risk in the Wujiang River Basin. However, it cannot be ignored that the moderate risk of Hg were shown in sampling sites of 8, 21, and 22, indicating higher potential mobility and bioavailable risk than other sites. Mn and Cd posed a high risk in

Table 3. Pearson's correlation matrix between overlying water physic-chemical properties and the total concentrations of heavy metals in surface sediments from 26 sampling sites.

	T	DO%	DO	pH	EC	ORP	Ca	Mg	Cu	Zn	Mn	Pb	Cd	As	Hg
T	1														
DO%	0.197	1													
DO	-0.114	0.944**	1												
pH	0.233	0.658**	0.566**	1											
EC	0.189	-0.166	-0.204	-0.335	1										
ORP	-0.525**	-0.242	-0.085	-0.099	-0.261	1									
Ca	0.104	-0.106	-0.062	-0.155	0.071	-0.124	1								
Mg	0.052	0.090	0.129	-0.192	0.124	-0.174	0.652**	1							
Cu	-0.145	-0.224	-0.206	0.164	-0.115	0.257	-0.29	-0.292	1						
Zn	-0.136	-0.04	-0.02	0.277	-0.086	0.060	-0.322	-0.215	0.846**	1					
Mn	0.144	0.275	0.209	0.230	-0.010	0.201	-0.338	-0.193	0.293	0.226	1				
Pb	-0.233	-0.118	-0.049	0.240	-0.077	-0.047	-0.103	-0.206	0.648**	0.828**	-0.025	1			
Cd	-0.015	0.387	0.390*	0.142	0.064	-0.075	-0.415*	-0.194	0.054	0.317	-0.010	0.154	1		
As	-0.214	0.150	0.195	0.150	0.248	-0.111	-0.341	-0.098	0.424*	0.575**	-0.125	0.361	0.514**	1	
Hg	-0.095	0.271	0.297	0.193	0.249	-0.276	-0.190	0.166	-0.024	0.204	-0.110	0.034	0.323	0.591**	1

Significance at $p<0.05$ and 0.01 are represented as * and **, respectively.

more than 53% and 73% sampling sites, respectively. In addition, Mn was associated with very high risk in sites of 8, 11, 15, and 24. Cd was associated with very high risk in sites of 23 and 24, which is located in the HDR.

The I_{geo} values for the present study area are shown in Fig. 4. It can be seen that the I_{geo} values of As in all sampling sites were less than 0, indicating no pollution. Although 11.5 % and 26.9 % of sampling sites of Mn and Pb were classified as unpolluted to moderately polluted, the average values were less than 0. It suggested that the pollution degree of Mn and Pb in the Wujiang River Basin was no pollution. The average I_{geo} value of Hg was less than 0. However, it cannot be ignored that degrees of moderately polluted and moderately polluted to strongly polluted were shown in sites of 18 and 13, respectively. 38.5 % of sampling sites for Cu, 61.5 % for Zn were unpolluted to moderately polluted, and the average I_{geo} values of Cu and Zn were 0.10 and 0.34, respectively, indicating mild pollution. The I_{geo} values of Cd in all sampling sites were above 0 with the exception

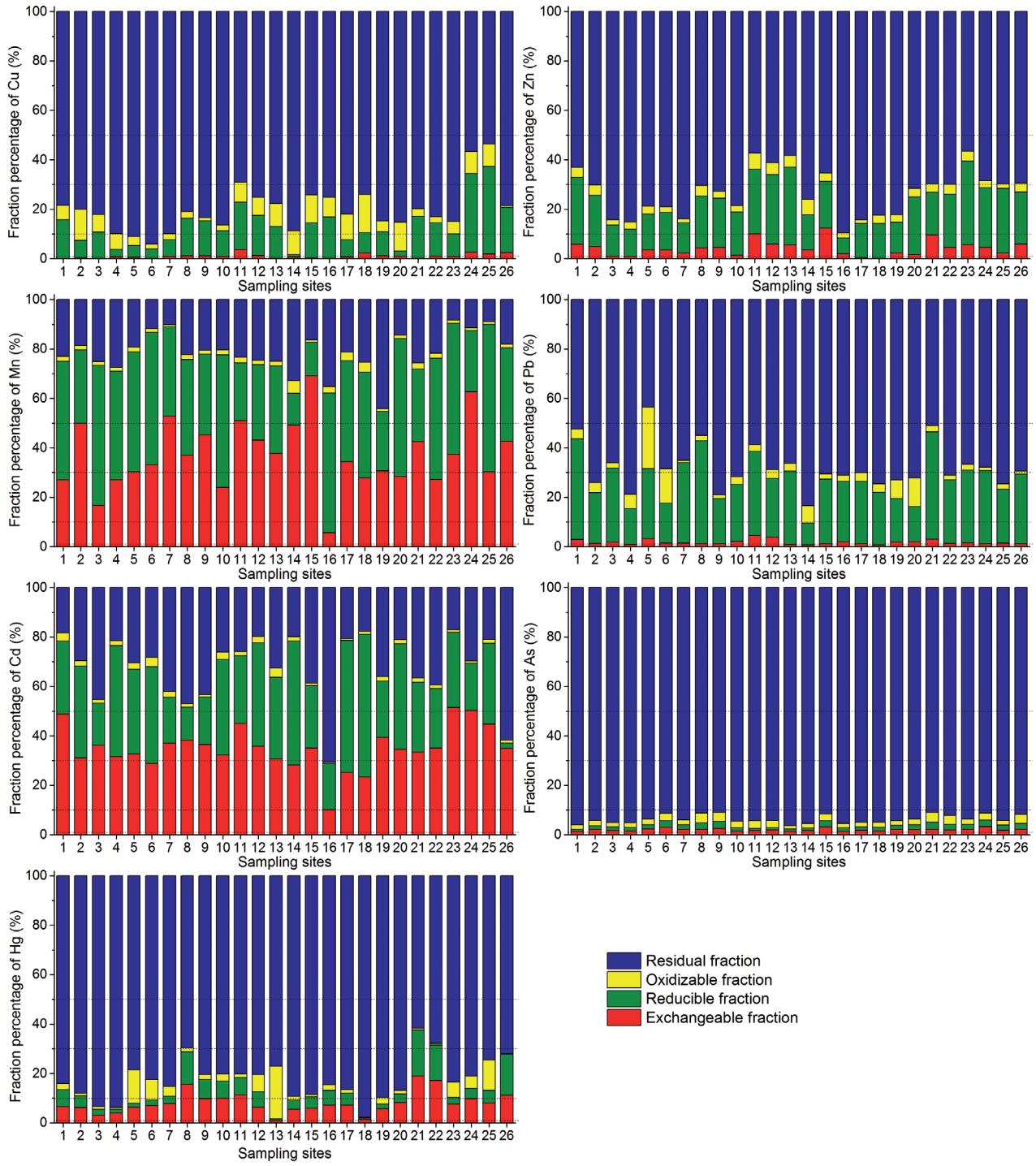

Fig. 3. The chemical fractions of Cu, Zn, Mn, Pb, Cd, As, and Hg in surface sediments of 26 sampling sites from the Wujiang River Basin.

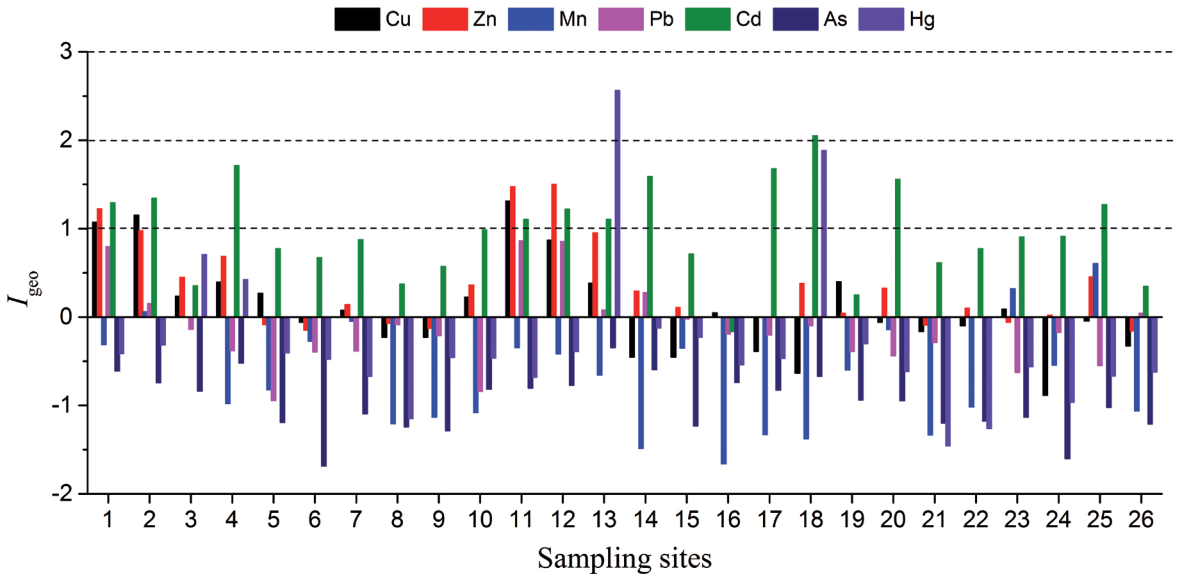

Fig. 4. The Igeo values of heavy metals in surface sediments of 26 sampling sites from the Wujiang River Basin.

of site 16. 38.5 % of sampling sites were moderately polluted, and it was moderately polluted to strongly polluted in site 18. In summary, the pollution levels of heavy metals with respect to I_{geo} classification in the surface sediments of the Wujiang River Basin were generally in the order of Cd>Zn>Cu>Pb>Hg>Mn>As.

The E_r^i and *PERI* analysis results of selected heavy metals in the sediments of the studied area are represented in Fig. 5. The values of E_r^i in each sampling site for Cu, Zn, Mn, Pb, and As were far less than 40, indicating a low potential ecological risk. The E_r^i values of Hg ranged from 21.9 to 354.9 and with an average of 63.31. A total of 22 (84.6 %) sampling sites exhibited a low or moderate risk, two sampling sites presented considerable risk, one presented high risk and one presented very high risk. The E_r^i values of Cd in all sampling sites were above 40, ranged from 41.1 to 186.3, with an average of 93.1. More than half of the sampling sites showed a considerable risk. The sampling site of 18 posing a high risk due to the high level of Cd in this site. Overall, the average *PERI* value (183.13) for all studied heavy metals in the surface sediment of the Wujiang River Basin was classified as moderate risk. Fourteen sampling sites of the *PERI* values were lower than 150,

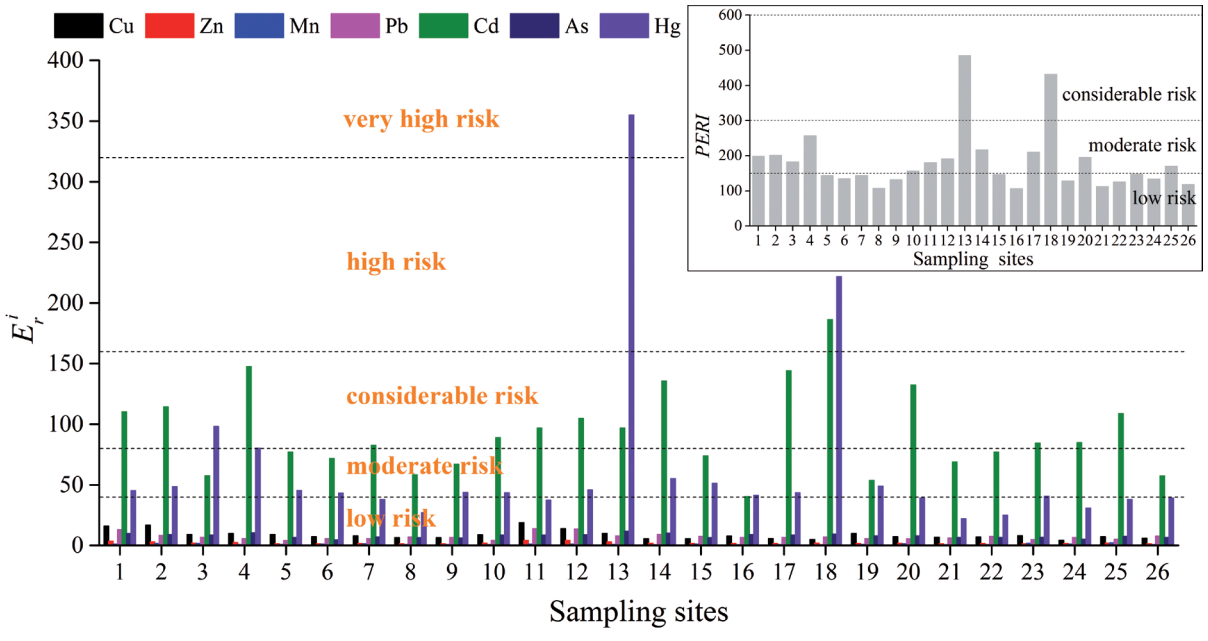

Fig. 5. The potential ecological risk index (PERI) of heavy metals in surface sediments of 26 sampling sites from the Wujiang River Basin.

suggesting that these sampling sites had low ecological risk from combined metal pollution. However, the *PERI* was classified as considerable risk in sampling sites of 13 and 18 and moderate risk in sites of 1, 2, 3, 4, 10, 11, 12, 14, 20, and 25. Therefore, it should pay more attention to the ecological risk of heavy metals from the Wujiang River Basin which will influence the Yangtze River ecosystem eventually.

Conclusions

The physic-chemical properties of overlying water and chemical speciation of Cu, Zn, Mn, Pb, Cd, As, and Hg in surface sediments from the Wujiang River Basin were studied. The results showed that the mean total concentrations of all heavy metals except As were higher than their background values. The higher CV values for selected heavy metals indicated that they were unevenly distributed and probably influenced by anthropogenic sources. The concentrations of most heavy metals in the presently studied area were relatively higher than that from the Pengxi River and the Jinsha River. It indicated that the Wujiang River could be a main pollution source of heavy metals within the Three Gorges Reservoir. No identical correlation between physic-chemical properties and heavy metal concentrations was showed, which suggested that these metals might be controlled by multiple factors. Cu, Zn, Pb, As, and Hg appear mostly in a residual fraction. The mean percentages of mobile fraction of heavy metals occurred in the following order: Mn>Cd>Pb>Zn>Cu>Hg>As. The Mn and Cd were more mobile and bioavailable than other studied heavy metals. Mn and Cd were dominated by the reducible fraction and exchangeable fraction, respectively. The most important source of Cd in the Wujiang River Basin could be as a result of runoff containing phosphate fertilizer from the agricultural farms. The potential ecological risk of heavy metals in present study area were also assessed.

According to the RAC classification, Cu, Zn, Pb, As, and Hg posed a low risk in this studied area. Mn and Cd posed a high risk in most sampling sites. However, it cannot be ignored that the moderate risk of Hg in several sampling sites. The I_{geo} classification showed that Cd has the highest environmental risk and the pollution levels of heavy metals in the surface sediments were generally in the sequence of Cd>Zn>Cu>Pb>Hg>Mn>As. The *PERI* was classified as considerable risk in two sampling sites and moderate risk in ten sampling sites. So, it should pay much attention to the ecological risk of heavy metals from the Wujiang River Basin which will influence the Yangtze River ecosystem eventually.

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Conflict of Interest

The authors declare no conflict of interest.

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