Risk Assessment of Heavy Metals in Surface Sediments after Sediment Dredging

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ABSTRACT
Concentration, distribution and risk associated with Cu, Zn and Pb in surface sediments of Xiaofu River were studied after sediment dredging. The total concentrations of metals ranged from 19.4 to 42.3 mg · kg^{-1} for Cu, from 32.4 to 64.3 mg · kg^{-1} for Zn, and from 11.1 to 32.4 mg · kg^{-1} for Pb. The degree of surface sediments contamination was computed for the Geo-accumulation index and the consensus-based sediment quality guideline values. The result determined that none of studied metals had high potential risk to water ecological of the investigated area, although those stations nearby anthropogenic influx had higher metal concentration in contrast with those of the rest stations.

Keywords
Sediment, Heavy metals, Risk assessment.

1. INTRODUCTION
Heavy metals are considered as serious inorganic pollutants because of their toxic effects on life in aquatic system, having a high enrichment factor and slow removal rate [1]. Sediment represents one of the most important sinks for heavy metals discharged into the aquatic environment [12]. Contaminants Such as heavy metals are not fixed forevermore by the sediments, and under changing environmental conditions they can be released by various processes of remobilization [7]. Therefore, in a system like a river basin, sediments could behave both as a carrier and a source of pollutants [8]. In recent years, considerable attention has been given to assessing the sediment state of the river receiving discharges of wastewater.

The study area, Xiaofu River catchment, is approximately 1733 km^2 and the discharge is about 0.44 m3/s. As the following reasons: (1) it is situated in the most urbanized and heavily populated area that more than 453.06 million people living around here. (2) Most industrial area of Zibo state is located along this river. (3) It flows into an important branch route of the Eastern Route Project of the Water Diversion Projects (a major project to channel water from the Yangtze River in the southern part of the country to the north through three canals to solve the problem of water shortage in the North, China), Xiaofu River is a crucial river for the Water Diversion Projects, and millions of inhabitants will be impacted daily by water flowing through this river. Unfortunately, rapid industrialization, immoderate mining and uncontrolled urbanization around cities have brought alarming level of pollutions to Xiaofu River ' s environments because of their anthropogenic inputs, including heavy metals[20]. Since 2003, the comprehensive management including sediment dredging has been conducted to improve the water quality of the River。

A study of the distribution, enrichment and accumulation of heavy metals in the Xiaofu River sediments is important to the assessment of the river state after sediment dredging. In the present study, we characterized the physical – chemical properties of the river sediments, namely clay, silt, sand and organic carbon (OC), and examined the distribution of heavy metals such as Cu, Zn and Pb in the sediments at 9 stations (Fig. 1) during 2009. In order to better represent and understand the chemistry and the anthropogenic pressure in the areas studied, the extent of metal contamination was assessed using background sediments, the geo-accumulation index (Igeo) and threshold values of sediment quality guidelines (SQGs).

2. MATERIALS AND METHODS

2.1 Study Area and Sample Collection
Riverine sediments were collected from 9 sample locations in the Xiaofu River during the spring of 2012 using a 0.05 m^2 polyethylene grab (Fig. 1). The river-bed sediments, which were brown to black in color, were transported to a laboratory at 4 ℃ with an acid-washed polyethylene bag and then freeze dried. All freeze-dried sediment samples were ground, homogenized, and stored at -20 ℃ before analysis. [1]

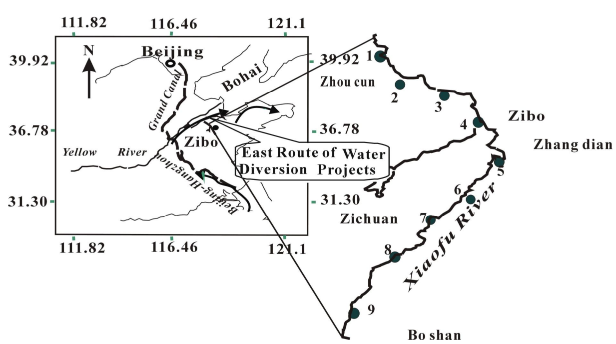

Fig.1 Sstudy area and geographical locations of sampling stations.

2.2 Chemical Parameters

To evaluate the total concentration of Cu, Zn and Pb, the EPA Method 3052 was selected for the samples digestion[17]. Briefly, the dried and ground samples (about 0.125 g) were pressure-digested in the Teflon bombs in a microwave oven (MRS60, CEM, USA) with 6 ml HNO_3, 0.5 ml HCl, and 3.0 ml HF for 15 min at 180 ± 5℃. Then, the solution and residue were transferred into a Teflon breaker; 0.5 ml $HClO_4$ and 0.25 ml H_2O_2 were added and braised nearly dried on a heating block at about 200℃. Finally, 2.5 ml HNO_3 was added and diluted to 25 ml with double-distilled water for analysis.

2.3 Metal Analysis and Quality Control

The metal concentrations in solutions prepared by digestion and extraction procedures were determined by using an ICP-MS (7500ce, Agilent, USA), completed by Analysis & Testing Center of Shandong University of Technology.

For the quality control, the reagent and procedural blank corrections were applied, and the standard reference materials (GSS-10， AMS-1) were also analyzed as a precision check. Percentage of recoveries for certified and measured concentration of those metals were ranged from 96% for Zn, 122% for Cu to 128% for Pb.

2.4 Data Analysis

Descriptive data analysis (mean, standard deviation) on different variables was applied accompanied by correlation analysis to determine relationships between individual elements and the organic carbon and the clay content of the sediment. Additionally, multivariate techniques were applied to assess the regional distribution pattern of the assemblages of the elements in the study area. Descriptive analysis was performed using Excel v.2003, while Statistical analysis was performed using Statistical Program for Social Sciences (SPSS program version 17.0 for Windows).

3. RESULTS AND DISCUSSION

3.1 Sediment Characteristics and Metal Distribution

It has been reported that the distribution of grain size and organic matter content were two critical factors influencing the metal distribution in sediments[2,10]. Table 1 presents the values of sediment characteristics for the 9 stations. The organic carbon (OC) content of the sediments ranged from 0.45% to 1.8% with the mean level of 0.8% (SD = 0.4), the peak value being recorded in the sediment sampled from the station 9, whereas the evident differences were observed among the studied area (Table1). Results also show that there exists a great granulometric variability between the studied stations, with essentially clay (＜2 μm) sediments in stations 1, 3, 6, 7,8, and 9) and typically sandy (＞63 μm) sediments with a fairly significant gravel and sand content on the other stations (4 and 5).

The range of total metal content analyzed for the sediment samples is as follows: Cu, 18.6-42.3 mg · kg^{-1}; Zn, 32.4-64.3 mg · kg^{-1} and Pb, 11.1-32.4 mg · kg^{-1} (Table 1).Variations in total metal content are largely systematic along the River with the sampling stations. All of the studied metals show higher concentration in sediments from the stations 6 to 8. In addition, compared with the background values, both Cu and Pb show a significant accumulation at the stations 6, 7 and 8; Zn shows an evident accumulation only at the station 7.

Table 1 Physiochemical properties of sediments from Xiaofu River

Sample sites	OC (%)	Clay (%＜2 μm)	Slit (%＞2-63 μm)	Sand (%＞63μm)	Cu ($mg·kg^{-1}$)	Zn ($mg·kg^{-1}$)	Pb ($mg·kg^{-1}$)
1	0.71±0.02	47.4±5.3	16.3±1.8	25.6±1.1	28.5±2.3*	32.4±2.1	12.9±1.0
2	0.52±0.01	39.7±2.1	23.4±1.2	24.6±2.2	24.7±1.9*	41.5±2.3	11.1±3.3
3	0.64±0.03	50.3±3.6	32.9±1.6	16.4±1.5	30.4±4.5*	44.6±6.4	13.2±4.5
4	0.96±0.02	38.6±1.2	16.9±2.0	43.2±2.1	19.4±5.2	34.6±8.5	15.4±2.7
5	1.06±0.04	43.7±4.1	17.9±1.4	38.9±1.8	25.4±3.2*	42.4±4.2	11.8±5.2
6	0.58±0.01	50.6±2.4	24.5±1.9	24.7±1.3	38.6±7.8*	52.8±5.1	30.4±6.2*
7	0.72±0.06	59.5±3.1	26.6±1.1	13.6±1.1	42.3±2.1*	64.3±1.9*	25.8±5.1*
8	0.45±0.04	55.4±1.8	29.4±1.3	19.8±2.3	40.3±9.5*	52.1±8.9	32.4±8.5*
9	1.8±0.04	53.6±3.5	31.3±1.2	14.8±1.4	18.6±5.7	36.8±5.4	12.5±4.5
Background values[a]					20.4±10.05	60.6±18.88	22.7±7.13

*, the value of an element is significantly higher than its background value (p<0.05).

A relationship between organic carbon and metal content has been shown in sediments at other locations and is consistent with the model of organic carbon coating on particles controlling the sorption of metals [3,6]. However, in the present study, the content of OC does not present a positive correlation with the heavy metals as was expected. It is possible that organic carbon from anthropogenic sources is not main carriers of the elements and does not affect metal binding to sediment particles in the studied area. This may be related to the sediment dredging conducted two years ago.

The spatial trends of heavy metal and clay of sediments indicate the significant role of the fine sediment (silt+clay) in binding the metals in the River sediments; this is confirmed with correlation analysis results that Cu and Pb were significantly correlated to the contents of clay in sediments (Table 2). This result corroborates the affirmation of Haque and Subramanian (1982)[9], according to which, the capacity of adsorption of metals is in increasing order, sand < silt < clay, due to the increase in the superficial area and to the content of minerals.

Table 2 Peason correlation matrix for surficial sediments (n=27)

	OC	Clay	Slit	Cu	Zn
Cu	-.677**	.484*	.012		
Zn	-.391*	.335	.346	.430*	
Pb	-.488**	.579**	.000	.871**	.261

*, Correlation is significant at the 0.05 level; **, Correlation is significant at the 0.01 level.

3.2 Geo-accumulation Index

Geo-accumulation index (Igeo) was introduced by Müller (1969)[14] and allows the contamination of the investigated sediment with organic and inorganic pollutants to be determined by comparing present concentrations with pre-industrial levels. Concentrations of geochemical background are multiplied each time by 1.5 in order to allow content fluctuations of a given substance in the environment as well as very small anthropogenic influences. Values of geo-accumulation index can be defined as follows:

$$I_{geo} = \ln[(C_n / (1.5 \times B_n)]$$

Where, C_n represents the measured concentration of the element 'n' in pelitic sediment fraction (<2μm) in unit mg · kg^{-1}; B_n is the geochemistry background value of the same element in fossil argillaceous sediment in the same unit mg · kg^{-1}; the factor 1.5 is used because of possible variations of background data due to lithogenical variability. The values of geo-accumulation index of Cu, Zn and Pb were listed in Table 3.

Table 3. Geo-accumulation index of heavy metals in sediments from Xiaofu River

Sampling sites	I_{geo}		
	Cu	Zn	Pb
1	-0.07	-1.03	-0.97
2	-0.21	-0.78	-1.12
3	-0.01	-0.71	-0.95
4	-0.46	-0.97	-0.79
5	-0.19	-0.76	-1.06
6	0.23	-0.54	-0.11
7	0.32	-0.35	-0.28
8	0.28	-0.56	-0.05
9	-0.50	-0.90	-1.00
mean	-0.07	-0.73	-0.70

3.3 Environmental Significance of Heavy Metals in Sediment

The metal concentrations at each site were compared with the consensus-based sediment quality guideline values referred to as the threshold effect concentration (TEC) and the probable effect concentration (PEC) proposed by MacDonald et al. (2000)[13]. These guidelines have been selected for comparison because various evaluations have demonstrated that the consensus-based SQGs provide a unifying synthesis of the existing SQGs, and reflect causal rather than correlative effects [4]. Comparisons of the mean metal concentrations at each site with their respective TEC and PEC values were done using a one-tailed t-test.

Table 4 Comparison of sediment quality guidelines with average values for Xiaofu River

Sediment metal concentrations (mg·kg^{-1})	Cu	Zn	Pb
TEC	31.6	121	35.8
PEC	149	459	128
Average values for the study area of concern	30.3	41.2	19.4
% samples which exceeded TEC	33	0	0
% samples which exceeded	0	0	0

Comparing the heavy metal concentrations with the consensus-based TEC and PEC values developed by MacDonald et al. (2000)[13], revealed that only 33% the samples collected exceeded the TEC for the element Cu, while the Zn and Pb contents fall below the TEC (Table 4). All sample concentrations fall below the PEC for all traces condidered (Table 4). According to the consensus-based SQGs, adverse biological effects would be not to be expected frequently. However, exceedances of SQG values do not firmly guarantee the occurrence of deleterious ecological effects, unless they are also coherent with regional background data[11,15] . In the present study, the results for Zn showed that whilst the concentrations of all the samples did not exceed even the TEC threshold, they did not exceed the regional background levels [11]. Therefore, contamination ranking of the Zn load of the sediments against the regional background values seems to be more reliable. But for Cu and Pb, whilst their concentration of all the samples did not exceed the PEC threshold, the deleterious ecological effects caused by them maybe occurrence as some samples did significantly exceed the regional background levels[11]. Based all the above statements, none of studied metals had high potential risk to water ecological of Xiaofu River.

The index of geo-accumulation includes even grades, from 0 (non-contaminate) until 6 (very strong). The Igeo values calculated for heavy metal concentrations in Xiaofu River reveal that the sediments are unpolluted with respect to the total of analysed metals. Authors that used this index evaluated sediments strongly polluted, as Chen et al. (2007) [5] at the vicinity of the mouths of major rivers that flow into Kaohsiung harbour, Taiwan. Also, Tang et al. (2009)[16] reported that the lake sediments had heavily polluted by Cd and evidently by Zn and Hg at the 8 typical lakes of Wuhan, China. Zhang et al. (2008) [20] found sediments of Liao River were uncontaminated with Ni, As, lightly contaminated with Cu, Cr, Pb and moderately contaminated with Cd and Hg.

4. CONCLUSIONS

After comprehensive managements of Xiaofu River, the concentrations of the investigated metals ranged 19.4-42.3 mg · kg^{-1} for Cu, 32.4-64.3 mg · kg^{-1} for Zn, and 11.1-32.4

mg · kg^{-1} for Pb, the higher concentrations of them were found at the sites 6, 7 and 8 among the nine investigated sites. The result determined that none of studied metals had high potential risk to water ecological of this area. This study was the first study in accordance with total concentration of metals in surface sediments of the Xiaofu River. Also, it located in the high sensitive area of the East Route Project of the Water Diversion Projects, China. It, therefore, can be informative data to control and reduce pollution in Xiaofu River.

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