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RESEARCH ARTICLE

Spatial distribution, ecological risk assessment, and potential sources of heavy metal(loid)s in surface sediments from the Huai River within the Bengbu section, China

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Abstract The Huai River is one of the major drinking water resources in Bengbu City of China's eastern Anhui Province. The study focused on extracting information for spatial distributions of heavy metal(loid)s (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) based on the contents of pollutants in 20 surface sediments. Geoaccumulation index and Hakanson potential ecological index were used to calculate the ecological risk of sediment environment in this paper. The I_{geo} results indicated that the sediments were moderately contaminated by Hg and Pb. The potential ecological risk sequence of the metals was Hg > Cd > Pb > Cu > Ni > Cr > Zn > As. Among the metal(loid)s, Hg was the main source of pollution that contributed ~76% towards the potential ecological risk, followed by Cd. Finally, multivariate statistical analysis methods were conducted to identify the potential causes of pollution and provide basis for environment treatment in Bengbu Reach. The results depicted that Pb may be mainly derived from the traffic emission and manufacturing industry, while Hg may be originated from agricultural emissions.

Introduction

The Huai River is one of the seven largest rivers in China, which flows through five provinces and encompass 36 cities. It has a total drainage area of 270,000 km^2 (Zhang et al. 2010), which nurtures more than 170 million people. The Huai River is the most densely inhabited river basin whose average population density is approximately five times of the national average (Xia et al. 2011). Along with the acceleration of the urbanization and industrialization, an increasing number of enterprises have emerged over the basin, such as paper making, textiles, and chemical production (Hua et al. 2007). As a result, more than 8.6 billion m^3 of untreated water was discharged into the Huai River in year 2009, which caused serious water pollution and ecological damage (Yang et al. 2012). The water quality in more than 83% of the Huai River could not reach to the national standard, among which pollution from heavy metal(loid)s served as the major contributor to environmental hazard for humans (Uluturhan and Kucuksezgin 2007).

Heavy metal has been acknowledged as being a huge threat to the environmental quality and human health due to its toxicity, persistence, bioaccumulation, and non-degradability in the environment. A lot of research has been done to investigate concentrations and fates of heavy metals in dissolved form, with much less attention given to sediment-associated contaminants. Significant quantities of heavy metal(loid)s from industrial and agricultural sources were discharged into rivers that ultimately accumulated in the river bed sediments (Yi et al. 2011). These metal(loid)s are deposited onto

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**Fig. 1** Map of sampling sites in the Huai River (Bengbu Reach)
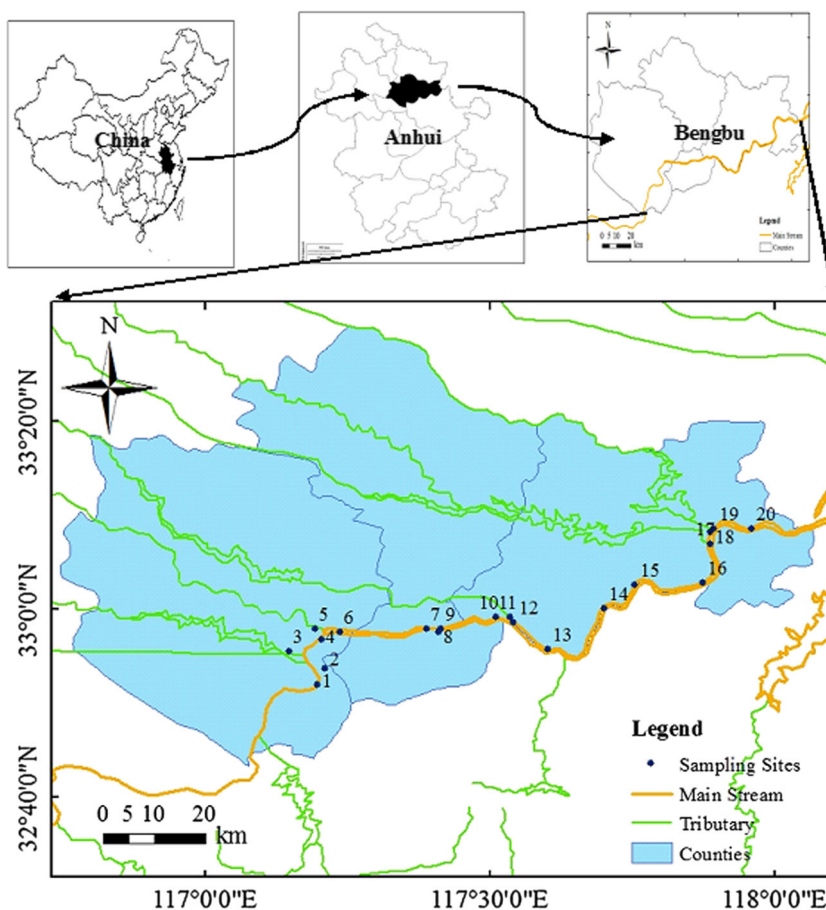
sediment surfaces and interact with sediment matrix through different binding mechanisms such as adsorption, coagulation, or flocculation (Wang et al. 2015). They can combine with carbonates, Fe/Mn oxyhydroxides, organic matter, sulfides, and refractory crystalline minerals and incorporated into the lattice structure of minerals (Bermejo et al. 2003). More than 99% of the metal contaminants are stored in the sediment,

while less than 1% is dissolved in the water (Filgueiras et al. 2004). Nevertheless, heavy metal(loid)s can also be released into the water through natural and anthropogenic processes. Camargo et al. stated that several trace metals, for example, Pb and Hg, may be transformed in sediment to organometallic compounds having increased bioavailability and toxicity (Camargo et al. 2014). This has an adverse effect on the

Table 1 Comparison of heavy metal(loid) concentrations in sediments of the mainstream of the Huai River (Bengbu Reach) and those for other rivers in China (mg/kg) (Luo et al. 2010; Wei 1991; Zhu et al. 2013)

Sample sites	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
This work								
Min.	0.00300	0.0350	63.8	14.6	ND	16.6	17.1	43.2
Max.	0.0480	0.0940	114	32.8	0.786	36.3	203	90.6
Mean	0.0240	0.0680	89.6	21.6	0.156	26.4	88.2	64.4
Background	9.00	0.0970	66.5	20.4	0.0330	29.8	26.6	62.0
EQSS (grade I)	15.0	0.200	90.0	35.0	0.150	40.0	35.0	100
Yangtze River	10.0	0.200	76.0	28.0	0.0500	33.9	22.0	73.0
Yellow River	12.9	0.310	51.3	21.8	0.0200	–	21.4	75.7
Songhuajiang River	6.50	0.290	53.1	21.0	0.240	–	21.6	112
Pearl River Estuary	5.20	0.340	56.4	39.0	1.40	–	59.4	111
Haihe River	20.0	2.64	57.3	139	–	–	66.0	382
Liao River	8.50	0.110	52.6	16.2	0.0800	26.5	17.4	–

ND not detected
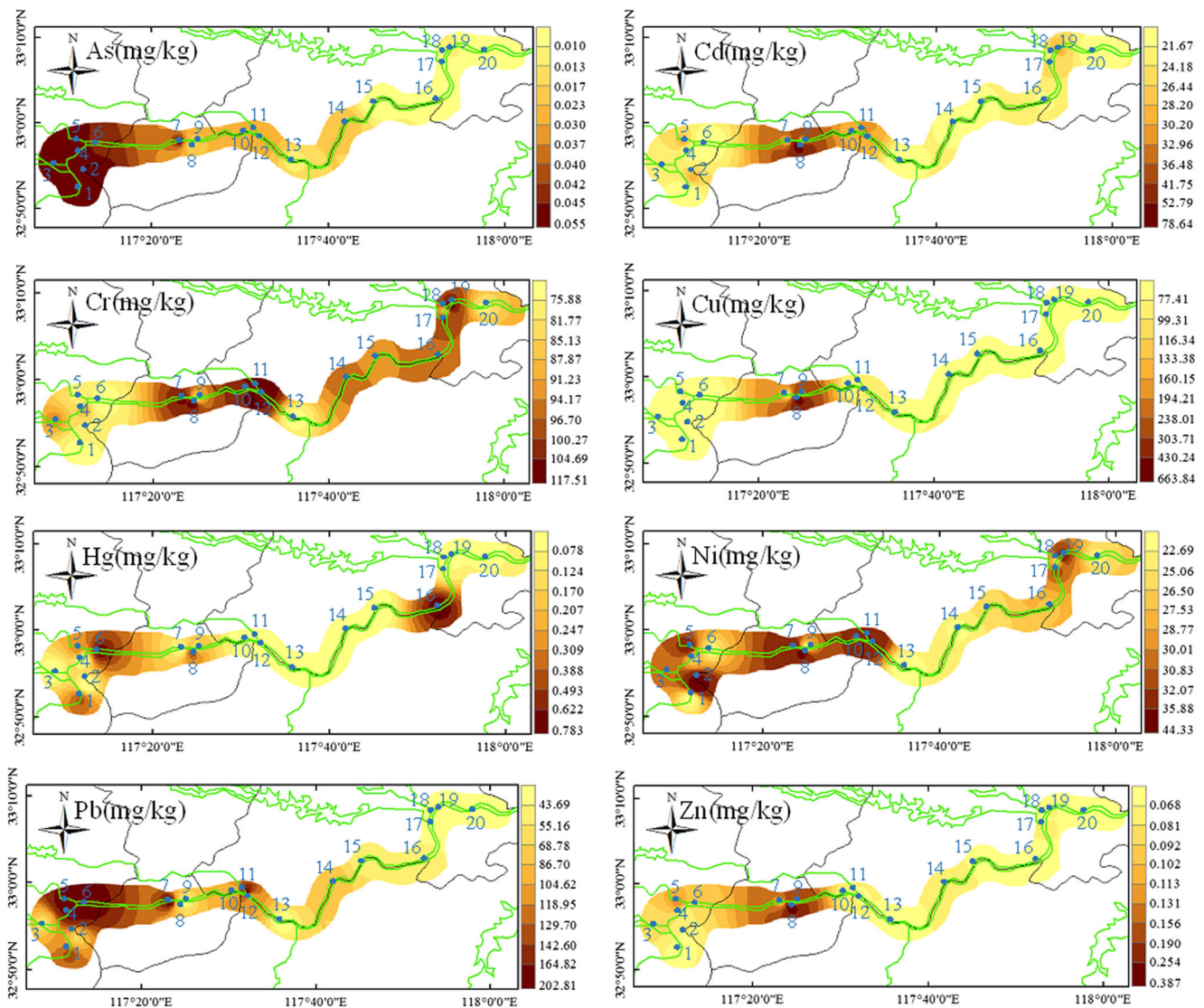
Fig. 2 Spatial distribution maps of the concentrations of eight hazardous heavy metal(loid)s

drinking water quality and thus leads to potential ecological risks to the aquatic system (Jiang and Sun 2014). So, sediments become the main repositories of heavy metal(loid)s and act as a secondary pollution source.

In view of the complexity of heavy metal(loid)s in sediments, total metal concentration alone is not sufficient enough to evaluate the environmental risk of sediments. Therefore, the following objectives were identified in the present study: (1) to characterize the content and contamination level of heavy metal(loid)s by comparison with the Environmental Quality Standard for Soils (EQSS) and other different rivers in China, (2) to determine the spatial distributions of heavy metal(loid)s in the surface sediments of the Huai River (Bengbu Reach), (3) to assess the ecological significance of measured heavy metal(loid)s by geoaccumulation index (I_{geo}) and potential

ecological risk index (RI), and (4) to investigate the possible pollution sources of heavy metal contamination using multivariate statistical analysis methods, thereby permitting prioritization and ordering of sites and metals of concern. The results presented herein will provide a scientific basis for controlling and preventing heavy metal(loid) contamination in the Huai River.

Materials and methods

Study area

The study was conducted along the Huai River and its tributaries in Bengbu City of Anhui Province, which extends from 32° 44″ N to 32° 30″ N and 116° 40″ E to 118° 04″ E.

Table 2 Geoaccumulation index of heavy metal(loid)s in surface sediments

Sample	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
S1	−8.20	−1.43	−0.61	−1.02	3.07	−1.15	1.78	−0.62
S2	−7.94	−1.18	−0.33	−0.07	−5.63	−0.04	0.66	−0.64
S3	−8.14	−0.74	−0.08	−0.40	−5.63	−0.56	0.39	−0.62
S4	−8.20	−1.23	−0.15	−0.72	−5.63	−0.80	2.21	−0.75
S5	−8.17	−0.22	−0.32	−0.07	2.57	−0.35	2.30	−0.19
S6	−8.33	−0.66	−0.64	−1.07	3.91	−0.95	2.35	−1.11
S7	−8.14	−0.63	0.10	−0.12	−0.87	−0.37	2.23	−0.29
S8	−10.26	1.51	0.28	1.45	3.51	0.05	0.69	2.94
S9	−9.14	−0.86	−0.51	−0.97	−5.63	−1.43	−1.22	−0.44
S10	−8.86	−1.01	0.05	−0.14	−0.50	−0.49	1.21	−0.38
S11	−9.02	−1.14	0.23	0.14	−0.77	−0.30	2.17	−0.14
S12	−8.81	−1.14	0.10	−0.12	−0.63	−0.43	1.30	−0.04
S13	−10.40	−2.06	−0.52	−0.97	−3.31	−1.30	−0.38	−0.84
S14	−9.33	−0.90	−0.06	−0.68	−5.63	−1.04	1.03	−0.68
S15	−11.40	−1.10	−0.11	−0.53	−5.63	−0.80	0.26	−0.67
S16	−10.72	−1.46	−0.06	−0.53	3.99	−0.72	0.41	−0.64
S17	−10.72	−0.83	0.02	−0.25	0.60	−0.50	−0.61	−0.28
S18	−10.91	−1.57	−0.26	−0.67	0.78	−0.86	−0.69	−0.84
S19	−10.02	−0.90	0.19	0.10	−1.63	−0.30	0.42	−0.18
S20	−12.14	−1.76	−0.32	−0.76	−0.14	−0.89	−0.79	−0.93
Average	−9.00	−0.72	−0.13	−0.24	1.67	−0.61	1.19	0.07

The mainstream of the Huai River in the study area originates from Macheng Zhen, flows easterly through Huaiyuan County, the center of Bengbu City, and Wuhe County (Liu et al. 2012). The distance was approximately 21 km from the north to the south and 28 km from the west to the east. The area has a subtropical monsoon type climate, and its mean annual temperature is 15.1 °C (Yang et al. 2012). The average rainfall of the area is about 905.4 mm, and the area enjoys 2167.5 h of sunshine annually. The Bengbu City is located at a transitional area between the Huang-Huai-Hai Plain and Jianghuai Hilly Region. Territory lying tilted from northwest to southeast, the three major types of land forms are plains, hills, and plateaus (Liu et al. 2012). According to the 2015 Anhui Statistical Yearbook, the Bengbu City occupies a total land area of 595.07 khm^2, among which agricultural land and building land occupy 75.68 and 15.66%, respectively (Bureau of Statistics of Anhui 2015). In 2014, a total of 301,324 t of inorganic fertilizer was used at an average rate of 798.51 kg/hm^2, which is 1.64-fold greater than the national average (Liu et al. 2015). The pesticide is also widely used in the agriculture of Bengbu, and the unit cultivated land area usage of pesticide has reached 16.71 kg/hm^2 (Bureau of Statistics of Anhui 2015). That may pose a huge threat to the local ecological environment.

Sediment sampling and analysis

The sediment samples were collected from 20 different sites (S1–S20) distributed in the mainstream of the Huai River and its tributaries in November 2015 (Fig. 1). The distribution of the sampling points was mainly chosen to reflect the typical pollution characteristics of the Huai River. The S2, S3, S5, S8, S11, and S18 sampling sites were located in the tributaries, and pollutants at these six sites were mainly from industrial wastewaters. The S1, S4, S7, S10, and S17 sampling sites were situated in the mainstream before mixing with tributaries. The S6, S9, S12, and S19 sampling sites were located in the mixed zone of the mainstream and tributaries. The remaining sampling sites were selected according to the hydraulic characteristics of the Huai River. The global positioning system (GPS) (model: GARMINGPS-12) was used to record the sampling locations in the present study. The Petersen grab sampler was used to collect the upper 0–20-cm depth of surface sediment samples. The samples were then placed into polyethylene bags and labeled. When returned to the laboratory, all the samples were air-dried at the room temperature, ground to pass through a 100-mesh sieve, and kept at −20 °C until analysis (Liang et al. 2015).

For the determination of the total concentrations of Cr, Cu, Ni, and Zn in sediments, 0.2–0.5 g samples were weighed accurately into 50-ml Teflon vessels and add a little water for wetting samples. Then, 10 ml hydrochloric acid was added, and it was placed on an adjustable electric heating plate (SD404-2-4, Jiangsu Dongtai Instruments Co., China) at low temperature until the solution was reduced to 3 ml. Subsequently, samples were digested with a combination of concentrated HNO_3-HF-$HClO_4$ (i.e., 5 ml HNO_3, 5 ml HF, 3 ml $HClO_4$, State Environmental Protection Administration of China) at 150 °C for 1 h. Cool it and add 3 ml hydrochloric acid or 1 ml nitric acid, transfer them to 50-ml volumetric flask, and dilute to the mark with deionized water. For the analysis of total concentrations of Cd and Pb, 0.1–0.3 g of each sample was weighed and placed in 50-ml Teflon vessels; then, 5 ml hydrochloric acid was added. Afterwards, the vessel was heated until the volume of solution was about 2–3 ml. After cooling at room temperature, sample was digested with 5 ml HNO_3, 2 ml HF, and 2 ml $HClO_4$ for 1 h. Then, the sample solution was transferred to a volumetric flask (25 ml); 3 ml of diammonium phosphate solution was added into each flask and diluted to the full volume. For determination of As and Hg, 0.2–1.0 g of each sediment sample was weighed into a 50-ml colorimeter tube. After which, 10 ml aqua regia (HCl/HNO_3 3:1) was added (Wu et al. 2010); the tubes were placed in a boiling water bath for 2 h and shaken for an interval of 30 min (Huang et al. 2009). Immediately next, the solution was transferred into a volumetric flask (50 ml), and quantitative saving reagent was added into each flask; then, flasks were diluted to required volume. All

Table 3 Potential ecological risk indices of heavy metal(loid)s in sediments

Sample	E_r^i								RI	Pollution grade
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn		
S1	0.05	16.70	1.97	3.70	504.24	3.37	25.75	0.97	556.76	Considerable
S2	0.06	19.79	2.38	7.16	1.21	7.28	11.84	0.96	50.69	Low
S3	0.05	26.91	2.84	5.69	1.21	5.08	9.85	0.98	52.60	Low
S4	0.05	19.18	2.71	4.56	1.21	4.31	34.77	0.89	67.69	Low
S5	0.05	38.66	2.40	7.13	356.36	5.89	37.03	1.31	448.84	Considerable
S6	0.05	28.45	1.92	3.58	901.82	3.88	38.16	0.70	978.55	High
S7	0.05	29.07	3.22	6.89	32.73	5.81	35.15	1.23	114.14	Low
S8	0.01	128.04	3.64	20.51	681.21	7.79	12.12	11.5	864.83	High
S9	0.03	24.74	2.10	3.82	1.21	2.79	3.21	1.10	39.01	Low
S10	0.03	22.27	3.10	6.81	42.42	5.34	17.37	1.16	98.50	Low
S11	0.03	20.41	3.52	8.26	35.15	6.09	33.83	1.36	108.66	Low
S12	0.03	20.41	3.22	6.91	38.79	5.57	18.44	1.46	94.84	Low
S13	0.01	10.82	2.09	3.82	6.06	3.04	5.77	0.84	32.45	Low
S14	0.02	24.12	2.88	4.68	1.21	3.64	15.34	0.93	52.83	Low
S15	0.01	21.03	2.78	5.20	1.21	4.31	9.00	0.94	44.48	Low
S16	0.01	16.39	2.88	5.20	952.73	4.56	9.94	0.96	992.67	High
S17	0.01	25.36	3.04	6.30	90.91	5.32	4.92	1.23	137.09	Low
S18	0.01	15.15	2.51	4.71	103.03	4.14	4.64	0.84	135.03	Low
S19	0.01	24.12	3.43	8.04	19.39	6.09	10.04	1.32	72.45	Low
S20	0.00	13.30	2.41	4.44	54.55	4.04	4.34	0.79	83.86	Low
Average	0.03	27.25	2.75	6.37	191.33	4.92	17.08	1.57	251.30	Moderate

procedures were carried out according to the instructions of the technical specification for soil environmental monitoring of China (HJ/T 166-2004) (MEP 2004).

The solutions prepared above were used to determine Cr, Cu, Ni, and Zn using a flame atomic absorption spectrometry (AAS, Vario 6, Analytik Jena AG, Jena, Germany) at wavelength 357.9, 324.8, 232.0, and 213.8 nm, respectively. Concentrations of Pb and Cd were calculated using graphite furnace atomic absorption spectrophotometry (PerkinElmer SIMAA 6000, Norwalk, CT, USA) at 283.3 and 228.8 nm

of wavelength, respectively. The concentrations of As and Hg were measured using atomic fluorescence spectrometry (HG-AFS, AFS-8230, Beijing Jitian Instruments Co., Beijing, China). The same procedure was used for the blank solutions.

All glass and plastic wares used were previously soaked overnight in HNO_3 (10% v/v) and rinsed thoroughly with Milli-Q water. The HNO_3 used throughout the entire process of determination for heavy metal(loid)s was of guaranteed reagent grade, while the other chemicals were all analytical reagent grade. For quality control, analytical blanks, duplicate samples, and standard reference materials GSD-5 (GBW 07305a, from National Research Center for Certified Reference Materials, Beijing, People's Republic of China) were used to verify the accuracy and precision. Three reagent blanks and three analytical duplicates were analyzed with the sediment samples during the course of the analysis to ensure the accuracy. The effect of blank subtraction was relatively small. Duplicate analysis also indicated a good precision as the mean RSD was less than 6.3%. Percent recoveries of the selected heavy metal(loid)s from standard reference materials were in the range of 80 to 120% for all samples. The detection limits of heavy metal(loid)s were 0.009 mg/kg for As, 0.013 mg/kg for Cd, 2.7 mg/kg for Cr, 0.87 mg/kg for Cu, 0.002 mg/kg for Hg, 0.95 mg/kg for Ni, 0.025 mg/kg for Pb, and 1.35 mg/kg for Zn.

Table 4 Pearson's correlation matrix for the metal(loid) concentrations in sediments

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
As	1							
Cd	−0.075	1						
Cr	−0.224	0.422	1					
Cu	−0.124	0.922**	0.658**	1				
Hg	−0.008	0.378	−0.154	0.22	1			
Ni	0.188	0.564**	0.678**	0.781**	0.035	1		
Pb	0.674**	0.034	0.010	−0.008	0.249	0.159	1	
Zn	−0.193	0.973**	0.458*	0.940**	0.343	0.545*	−0.077	1

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

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

Table 5 Total variance explained and component matrices for metal(loid) concentrations (principal component analysis with varimax rotation)

Component	Initial eigenvalues			Rotation sums of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	3.889	48.613	48.613	3.889	48.613	48.613
2	1.788	22.353	70.966	1.788	22.353	70.966
3	1.292	16.144	87.110	1.292	16.144	87.110
4	0.547	6.838	93.948			
5	0.341	4.258	98.206			
6	0.118	1.479	99.685			
7	0.022	0.274	99.959			
8	0.003	0.041	100.000			
Element	Rotated component matrix			Communalities		
	PC1	PC2	PC3			
As	0.961	−0.073	0.242	0.849		
Cr	0.867	0.258	−0.134	0.788		
Cu	0.827	−0.184	0.469	0.987		
Cd	0.817	−0.059	0.502	0.922		
Ni	0.810	−0.083	−0.353	0.837		
Pb	−0.067	0.918	−0.042	0.827		
Zn	0.035	0.897	0.147	0.937		
Hg	0.047	0.116	0.898	0.823		

Assessment of sediment contamination

Geoaccumulation indices

The contamination levels of heavy metal(loid)s in sediments are assessed by using geoaccumulation index (I_{geo}) introduced by Muller since the late 1960s (Muller 1969). The I_{geo} is computed using the following equation:

$$I_{geo} = \log_2\left(C_n \big/ 1.5 B_n\right) \tag{1}$$

where measured concentration of the element n in environment is denoted by C_n and B_n denotes the geochemical background value of the element in the fossil argillaceous sediment. In this study, B_n is the background content of element n in the local soil. The average background content for soil in the Anhui Province (As 9.0, Cd 0.097, Cr 66.5, Cu 20.4, Hg 0.033, Ni 29.8, Pb 26.6, and Zn 62.0 mg/kg) was adopted for the present study (Chinese Environmental Protection Administration 1990). The constant 1.5 is introduced to minimize the effect of possible variations which may be attributed to lithologic variations in the sediments (Nikolaidis et al. 2010). According to Muller (Muller 1969), the I_{geo} for every metal can be calculated and classified as under practically uncontaminated ($I_{geo} \leq 0$, class 0), uncontaminated to moderately contaminated ($0 < I_{geo} \leq 1$, class 1), moderately contaminated ($1 < I_{geo} \leq 2$, class 2), moderately to strongly contaminated ($2 < I_{geo} \leq 3$, class 3), strongly contaminated ($3 < I_{geo} \leq 4$, class 4), strongly to extremely contaminated ($4 < I_{geo} \leq 5$, class 5), and extremely contaminated ($I_{geo} > 5$, class 6).

Potential ecological risk index

The potential ecological RI is frequently used to give a comprehensive assessment of potential ecological risks from metal(loid)s in the environment, including soils and sediments (Hakanson 1980). The equation for calculating the RI was according to the toxicity of heavy metal(loid)s and response of the environment, proposed by Hakanson (Hakanson 1980):

$$C^i_r = \frac{C^i_s}{C^i_n} \tag{2}$$

$$E^i_r = T^i_r \times C^i_r \tag{3}$$

$$RI = \sum_{i=1}^{n} E^i_r \tag{4}$$

where C^i_r is the pollution factor of an individual element, C^i_s is the concentration of metal i in the samples, and C^i_n is a reference value for the metal i. E^i_r is the potential ecological risk factor, and T^i_r is the toxic response factor of the single element i, which indicates its toxicity levels and the sensitivity towards bio-organism. The values of T^i_r for common heavy metals have been reported to be As = 10, Cd = 30, Cr = 2, Cu = Pb = Ni = 5, Hg = 40, and Zn = 1 (Hakanson 1980; Madiseh et al. 2009). The character RI depicts the potential ecological risk caused by the overall contamination. Hakanson (Hakanson 1980) distinguished five classes of E_r^i and four classes of RI—low risk ($E_r^i < 40$, RI < 150), moderate risk ($40 \leq E_r^i < 80$, $150 \leq$ RI < 300), considerable risk ($80 \leq E_r^i < 160$, $300 \leq$ RI < 600), high risk ($160 \leq E_r^i < 320$, RI ≥ 600), and very high risk ($E_r^i \geq 320$).

Statistical analysis

Relationships among the eight heavy metal(loid)s were determined using the Pearson's correlation with statistical significance at $p < 0.05$ and $p < 0.01$. Principal component analysis (PCA) was used to reduce the dimensionality and collinearity of large-scale data sets. It was further used to identify pollution sources and distinguish natural versus anthropogenic contributions (Liang et al. 2015). The eigenvalues higher than 1 were selected as the significant principal components on the basis of a Kaiser criterion. All the statistical analyses were conducted by using SPSS 13.0 for Windows. Maps of the sampling locations and the spatial distributions of the eight metal (loid)s were produced using ArcGIS 10.2 by the simple point kriging interpolation (Lee et al. 2006).

Results and discussion

Evaluation on heavy metal(loid) contamination in surface sediments

Our investigation of the Huai River (Bengbu Reach) clearly revealed that the mean concentrations of Cr, Cu, Hg, Pb, and Zn in contaminated sediments were higher than Anhui background values. The mean concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in mainstream were about 0.003, 0.70, 1.35, 1.06, 4.73, 0.89, 3.32, and 1.04 times greater than their background values in Anhui Province of China, respectively. However, in Anhui Province of China, the percentages of the sediment samples, which had values exceeding the background value of heavy metal concentrations, fell in the order of Cr (85.7%) > Pb (78.6%) > Cu (50.0%) > Hg (42.9%) = Zn (42.9%) > Ni (35.7%) > Cd (0.0%) = As (0.0%). In order to evaluate the sediment pollution caused by heavy metal(loid)s, the concentrations of eight heavy metal(loid)s were compared to the EQSS in China (Chinese Environmental Protection Administration 1995). The result indicated that the concentrations of As, Cd, Cu, Ni, and Zn were consistently lower than the critical values in EQSS. Approximately 62.3% of Cr sediment samples surpassed the corresponding grade I value, and about 71.4% of Pb and 28.6% of Hg sediment samples also exceeded their grade I values.

The measured metal contents in this paper were compared with results from studies of other different rivers in China (Table 1) (Luo et al. 2010; Wei 1991; Zhu et al. 2013). The amounts of heavy metal(loid)s have been calculated on the basis of dry weight. According to the data from Table 1, the concentrations of As and Cd in sediments of the Huai River were extremely low suggesting practically unpolluted. The mean values of Cu in this area were lower than those detected in the Yangtze River, the Yellow River, the Pearl River Estuary, and the Haihe River, indicating Cu pollution was

not severe in this area. The average metal loads of Cr and Pb were quite higher in the sediments of the Huai River compared to other rivers, which illustrated that the sediments were severely polluted by Cr and Pb. The concentration of Ni in the Yangtze River and the Liao River and concentration of Hg in the Songhuajiang River and the Pearl River Estuary have higher values, and all the other rivers have lower values when compared with present corresponding values. Most of the rivers except the Liao River have higher values of Zn than the river in the present study. As stated above, the surface sediments in the Huai River were heavily polluted by Hg and Pb, moderately polluted by Cr, slightly polluted by Cu, and unpolluted by As, Cd, Ni, and Zn compared with other rivers in China. Other comparisons are clearly presented in Table 1.

Distribution maps of heavy metal(loid)s

The spatial distribution patterns of the eight measured heavy metal(loid)s in the Huai River sediments are presented in Fig. 2. The varied spatial distributions suggested that the sediment metal(loid)s may be attributed to different types of pollution source and were regulated by multiple factors (Yin et al. 2011). As and Pb had similar spatial distributions; sediment samples from certain subareas (e.g., S5, S7) had much higher concentrations than other subareas, which indicated an obvious input of heavy metals in those subareas (Du et al. 2015). The spatial distributions of As and Pb suggested that pollutions from tributaries were key pollutant sources. Heavy metals inevitably accumulate in aquatic sediments as a consequence of long-term industrial effluent discharge from urban area. However, in other areas, their concentrations were found to be relatively low.

Cd, Cu, and Zn had similar spatial distributions; the concentrations were low except for some sites at the middle west part of the study area. Concentrations of Cd, Cu, and Zn were elevated at S8, which were mainly due to the collection of sewage from the drains. According to the sewage outlet distribution map of BengBu City, there is a Longzihe drain outlet around the S8, which receives the effluent discharged by the chemical dye, filter manufacturing, and wool textile industry nearby. Nevertheless, the study area appears almost no pollution of Cd, Cu, and Zn. A relatively high Cr concentration was observed in the mid-eastern area of mainstream except for S1, S6, S9, S13, and S20, which would pose certain threats to the ecological environment. Sediments in the vicinity of the tributary contained high levels of Cr (Fig. 2), which were obviously caused due to anthropogenic effects. The highest concentration of Ni was found in the river inlets of the S2 and S8. This was similar to the findings of previous analysis that high concentrations of heavy metals were always present at the confluence of the mainstream and tributaries (Branco et al. 2005). Hg concentrations varied from west to east, while high Hg concentrations were distributed at the mainstream of S1, S5, S6, and S16 and

the river inlets of S8. The results indicated that most of the high concentrations of Hg occurred in the upper mainstream sites of the Huai River, which were probably due to the sewage discharge by the pollution source in the upper reaches of the Huai River (Bengbu Reach). Huainan, an important riverside industrial city about 60 km upstream of Bengbu, is one of the main storage sites of coal mine (Wang et al. 2016). The average content of Hg in sediments of the Huai River (Huainan section) was 0.46 mg/kg, and the maximum content of it was 0.90 mg/kg (Mei et al. 2010). That may be the main reason for the high contributions of Hg in sediments of the upper mainstream of the Huai River in Bengbu section.

Heavy metal(loid) pollution

I_{geo} values of the heavy metal(loid)s

In order to assess the contamination level of the sediment, the I_{geo} values for metal(loid)s in sediments of the Huai River were calculated (Table 2). The mean I_{geo} values for all metals decreased in the order of Hg > Pb > 1 > Zn > 0 > Cr > Cu > Ni > Cd > As. According to the ranking criteria, the mean I_{geo} values of Hg and Pb in sediments were placed into the category of moderately contaminated. The sediments in these stations were uncontaminated to moderately contaminated by Zn and practically unpolluted by other metal(loid)s. The I_{geo} values were below 0 for As in sediments extracted from all of the sampling sites. This suggests that all of them were altogether uncontaminated. The I_{geo} values for Cr ranged from <0 to 1, suggesting uncontaminated to moderately contaminated levels of pollution at the sample sites (such as S8, S11, S19) in the case study area. The I_{geo} values for Cd, Cu, Ni, and Zn were all below 0 with the exception of the sediment from S8. It has an average I_{geo} value of 1.51, 1.45, 0.05, and 2.94 for Cd, Cu, Ni, and Zn, respectively. The branch of the Longzi River which has degenerated to urban drains was located here. Therefore, the tributary of the Huai River was an important contamination source in the local environment of this region. The I_{geo} values ranged from <0 to 3.99 for Hg at all sampling sites, and the average value was 1.67. The I_{geo} values for Pb ranged from <0 to 2.35 with an average value of 1.19, suggesting spatial variation in the Pb contamination. Thus, Hg and Pb were identified as the main contributors for metal(loid) contamination.

Potential ecological risk of the metal(loid)s

According to Hakanson's ecological risk index method, eight polluted heavy metal(loid)s (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) in sediment samples were analyzed and evaluated. Table 3 lists the calculated potential ecological risk of an individual element along with the comprehensive potential ecological index. The mean values of E_r^i for As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn were 0.03 (0.01–0.06), 27.25 (10.82–128.04), 2.75 (1.92–3.64), 6.37 (3.58–20.51), 191.33 (1.21–952.73), 4.92 (2.79–7.79), 17.08 (3.21–38.16), and 1.57 (0.70–11.50), respectively. As shown in Table 3, it was evident that Hg has the largest potential ecological risk index value, demonstrating a moderate ecological risk for the Huai River within Bengbu section. The average E_r^i values for the other elements studied in this investigation were less than 40, suggesting a low ecological risk for the water body. The average E_r^i of heavy metal decreased in the order of Hg > Cd > Pb > Cu > Ni > Cr > Zn > As. The RI values for the sediments in the area under study varied from 32.45 to 992.67 with a mean value of 251.30. The percentages of sampling sites that were classified as low risk, moderate risk, considerable risk, high risk, and very high risk were 75, 0, 10.0, 15, and 0%, respectively. This indicated that most of the sediments from the Huai River showed low potential ecological risk. According to Table 3, the sampling sites S6, S8, and S16 suffered the most serious pollution with a RI value in the range of 864–993, which posed a high risk and may be attributed to the industrial and traffic activities (Yin et al. 2011). The sampling sites S1 and S5 depicted a considerable ecological risk, while other sampling sites reflected a low risk of the heavy metals. Among the metals considered, Hg was the most serious polluting element in the present sediments, which contributes largely (~76%) to the RI in all sampling sites due to its high E_r^i. According to these evaluations, the largest ecological risk was contributed by Hg, followed by Cd. Thus measures should be taken to control both of these metals.

Result comparison of two methods

The results of I_{geo} values for heavy metal(loid)s were basically consistent with that calculated by RI method except for Pb and Zn. The I_{geo} values depicted that the sediments were moderately contaminated and uncontaminated to moderately contaminated by Pb and Zn, respectively. However, the average E_r^i values suggested that a low ecological risk was caused by Pb and Zn. The reason causing the difference may be that the former mainly considers the enrichment degree of exotic heavy metals, while RI also takes into consideration the sensitivity of various biological communities to toxic substances. The small toxic response factor of Pb and Zn should be responsible for the low potential ecological risk index value. After the comparison, the results of Hakanson's ecological risk index method were more comprehensive and rational. Nevertheless, there are still some disadvantages of RI method, such as the subjectivity of toxic response factor and the negligence of the interaction among metals. Therefore, the appropriate relationships of these two methods are complementary and cross reference each other.

Source identification

Correlation coefficient

Table 4 indicates the values for obtained correlation coefficients as the linear correlation matrix. The results of correlation analysis suggested a significant correlation between Zn and Cr and Zn and Ni at the 0.05 level. In addition, a highly positive correlation was observed between As and Pb ($r = 0.674$), Cd and Cu ($r = 0.922$), Cd and Ni ($r = 0.564$), Cd and Zn ($r = 0.973$), Cr and Cu ($r = 0.658$), Cr and Ni ($r = 0.678$), Cu and Ni ($r = 0.781$), and Cu and Zn ($r = 0.940$) at the 0.01 level. The high correlations among metals may reflect that these heavy metals have similar pollution level, identical behavior during the transport, and common sources or at least one major source (Qu and Kelderman 2001; Suresh et al. 2011). There was a significant correlation among Cd, Cu, Ni, and Zn, which indicated that they may have the same pollution source such as metallurgical production, electroplating industry, leather industry, abuse of fertilizer, and pesticides (Loska and Wiechuła 2003). The correlation between Cd, Cu, Ni, Zn, and Hg was low, which indicated that the adsorption capacity of Hg may be inhibited due to the competitive adsorption of other coexisting heavy metal(loid)s in sediments (Zhang and Zheng 2007). These results suggested that the contamination sources or controlling factors of heavy metal(loid)s from the Huai River were complicated.

Factor analysis

In order to better understand the relationship among these variables and distinguish the possible sources of the heavy metals in sediments, PCA was commonly conducted. Table 5 depicts the results of PCA for heavy metal concentrations in the studied sediments of the Huai River. As shown in Table 5, the first three principal components with eigenvalues of 3.89, 1.79, and 1.30 were extracted, which accounted for 87.11% of the total variance. Therefore, these three components play an important role in explaining the level of contamination by heavy metals along with their potential sources in the present examined area.

The first principal component (PC1, eigenvalue 3.89) accounted for 48.61% of the total variance and had high loadings of As (0.961), Cr (0.867), Cu (0.827), Cd (0.817), and Ni (0.810) and was the most important component. As shown in Table 1, the contents of As were much lower than the background value of Anhui Province and the critical value in EQSS. So, it could be considered no pollution for As. The results of correlation analysis indicated that Cr, Cu, Cd, and Ni had a highly positive correlation, suggesting that they may share a common source. According to the comparative analysis, the mean contents of Cd, Cr, Cu, and Ni in the sediments under study had no evident difference compared with that of

background values of Anhui. In addition, both I_{geo} and EI results suggested that these four metals did not cause pollution except in case of some specific sample sites (for example, S8). Based on the above analysis, PC1 may be defined as both natural erosion and point industrial pollution.

The second PC (PC2) comprised 22.35% of the total variance and revealed higher contributions of both Pb and Zn. Pb is known to originate from automobile exhausts and the introduction of Pb into gasoline (Chen et al. 2005). The anthropogenic Pb from automobile exhaust gets into the aquatic sediment through atmospheric deposition and thus source of serious sediment pollution. In general, the sources of Zn and its compounds are mainly derived from different manufactured goods such as paints, batteries, and electrical apparatus (Micó et al. 2006). Given all these considerations, the component loading of PC2 hence can be defined as traffic emission and manufacturing industry.

The third PC (PC3) depicted total variance of 16.14%, with the highest loadings of Hg. The concentration of Hg is mostly contributed by the pesticide and fertilizers, chlor-alkali production, and plastic production (Wei and Yang 2010). Anhui, a major agricultural province, has abundant grain, cotton, and food oil production every year. In 2014, a total output of grain in Bengbu City was 2.68×10^6 t, with the usage of 3.01×10^5 and 6.31×10^3 t fertilizers and pesticides, respectively (Bureau of Statistics of Anhui 2015). According to investigation statistics, the chemical pesticides and fertilizer input per unit area of cultivated land in Bengbu City were far above the Anhui Province and national average. On the basis of the abovementioned facts, PC3 indicates pollution sources from agricultural emissions.

In general, correlations between metal(loid)s agreed with the results obtained by PCA, and correlation analysis was useful to confirm some new associations between metals that were not clearly stated in previous analysis. According to correlation analysis, a highly positive correlation was observed between Pb and As, Zn and Cu, and Zn and Cd. However, As, Cu, Cd, Pb, and Zn were grouped into different principal components. The reason may be that these heavy metal(loid)s had similar behavior during the transport other than common sources. Due to the complexity of the relationship, it is difficult to draw more clear conclusions directly. PCA has been proved to be an effective tool to elucidate the latent relationships among heavy metals, to identify pollution sources, and to apportion natural versus anthropogenic contributions (Bai et al. 2011). The use of the PCA allows more successful assessment of the source of the contamination, since this multivariate analysis tool establishes and quantifies the correlations among the original variables in the dataset with no need for any linear assumption (Caeiro et al. 2005). Given that our sample sites varied from unpolluted to highly polluted and can be rated from best to worst quality, PCA allows a more accurate classification.

Conclusions

The contents of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in the 20 surface sediment samples of the Huai River within the Bengbu section were analyzed. The mean concentrations of these metals ranged from 0.003 to 4.73 times higher than their background values in Anhui Province, suggesting that heavy metal(loid)s in the Huai River suffered from different anthropogenic effects. The concentrations of Pb, Cr, and Hg in sediments exceeded their grade I values set by EQSS in China, which had a standard-exceeding rate of 71.4, 62.3, and 28.6%, respectively. The spatial distributions indicated that high concentrations of heavy metal(loid)s were always present at the confluence of the mainstream and tributaries. The mean I_{geo} values suggested that the sediments were moderately contaminated by Hg and Pb, uncontaminated to moderately contaminated by Zn, and were not polluted by other heavy metal(loid). The potential ecological risk indices of heavy metals in the sediments along the Huai River were Hg > Cd > Pb > Cu > Ni > Cr > Zn > As. The main heavy metal pollution was Hg, which posed a moderate potential ecological risk (average E_r^i = 191.33) and contributed most (~76%) to RI in all sampling sites, followed by Cd. Moreover, multivariate analysis revealed that As, Cr, Cu, Cd, and Ni were mainly derived from natural erosion and point industrial pollution, whereas Pb and Zn were predominantly originated from traffic emission and manufacturing industry. Hg may be derived from agricultural emissions. In summary, control of industrial effluent discharge and reduction of the river pollution load are the most useful measures to improve the aquatic environment. This research will be quite useful for developing strategies for pollution control and sediment remediation in the Huai River with Bengbu section.

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