



Distribution, Ecological Risk Assessment, and Source Identification of Heavy Metals in River Sediments from Hai River and Its Tributaries, Tianjin, China

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Received: 10 October 2019 / Accepted: 6 January 2020 / Published online: 18 January 2020
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Abstract Heavy metal pollution in river sediments is one of the most serious problems in the aquatic environment. In this study, thirty-two surface sediment and overlying water samples were collected to evaluate the nutrient levels and heavy metal contents (Mo, Cu, Zn, Ni, Cd, Pb, and Cr) in the Hai River and its tributaries, which is the largest river flowing into Bohai Bay. The enrichment degree and geoaccumulation value of the studied metals decreased in the same order of $Cd > Cu > Pb > Mo > Ni > Zn > Cr$, and the mean contents of Cu and Cd were 2.58 and 2.93 times as high as their background values in Tianjin. Cd contributed over 50% of the ecological risk at the thirty-two sites. Moreover, according to the results of multivariate statistical analyses, Cu and Cd were mainly derived from anthropogenic sources, the quality of overlying water except COD influenced the distribution of heavy metals, and Cd had no correlations with the other heavy metals.

Keywords Heavy metals · Sediment · Source identification · Pollution assessment · Potential ecological risk · Multivariate statistical analysis

1 Introduction

Rapid economic growth in China has resulted in serious environmental side effects. With rapid urbanization and industrialization, large amounts of pollutants are discharged into the aquatic environment (Pan and Wang 2012). Heavy metal pollutants are a severe threat to the aquatic ecosystem owing to their toxicity, persistence, hard degradation, bio-accumulation by organisms, and biomagnification through the food chain (Wei et al. 2016; Zahra et al. 2014; Zheng et al. 2013). Heavy metals in aquatic environments originate from both natural (weathering soil and rock, erosion, forest fires, and volcanic eruptions) and anthropogenic sources (domestic discharges, industrial effluents, mining tailings, agricultural fertilizers, and fossil fuel burning) (Davutluoglu et al. 2011; Karbassi et al. 2008; Malik et al. 2010). In recent years, heavy metal pollution caused by anthropogenic activities has become increasingly serious.

Over 85% of heavy metals accumulated in the sediments of aquatic environments (Bosch et al. 2016; Zhang et al. 2016). Sediments serve as both carriers and potential future sources of heavy metals and are important indicators of metal contamination and tools for assessing the health of aquatic ecosystems (Baborowski et al. 2012; Davutluoglu et al. 2011;

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s11270-020-4404-6>) contains supplementary material, which is available to authorized users.

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Silva and Rezende 2002; Yang et al. 2012). Heavy metals bind to sediments through different mechanisms, and different forms exhibit different physical and chemical behaviors in terms of their chemical interaction, mobility, biological availability, and potential toxicity (Tessier et al. 1979; Xu et al. 2017). Heavy metals may be released into the overlying water from sediments or adsorbed from the overlying water, and the mechanisms are controlled by many factors, such as salinity, pH, temperatures, redox potential, hydrodynamic condition, nutrient level, and so on (Gao and Li 2012; Kang et al. 2019; Segura et al. 2006; Singh et al. 2005; Zheng et al. 2013; Zhu et al. 2018). The nitrogen addition could promote the transformation of heavy metal speciation from bioavailable to organic bound (Li et al. 2019). The mobility of As was increased by the addition of phosphate fertilizer (Gupta et al. 2014).

Bohai Bay is the second largest bay in the Bohai Sea, a semi-closed shallow sea in Northern China. Hai River, the largest river flowing into Bohai Bay, carries large amounts of contaminants into the bay annually (Chai et al. 2014; Gao and Chen 2012; Gao and Li 2012). Due to the continuous expansions of population and economy in the surrounding area, the Hai River and Bohai Bay faces a serious heavy metal pollution problem (Ding et al. 2018; Duan and Li 2017; Feng et al. 2011; Gao and Li 2012; Wu et al. 2014). Though studies on heavy metals in sediments have been widely applied into the regulation of contaminant, the researches on the degree of heavy metals pollutants of the Hai River and its tributaries inflowing to Bohai Bay were limited (Tang et al. 2014; Tang et al. 2013). The Hai River and its tributaries mainly flow across regions with a high population density and well-developed economy and have been severely polluted by industrial and domestic wastewater, agricultural non-point pollution sources, and atmospheric deposition. The nutrient status in the overlying water and heavy metal contents in the sediments of the Hai River and its tributaries are largely unknown. Furthermore, the relationship between the contents of metals in the sediments and water physicochemical parameters is unclear. Therefore, data on the quality of sediment and water in this region are required to gain a more comprehensive understanding of this issue.

In this study, we focused on the total contents of Mo, Cu, Zn, Ni, Cd, Pb, and Cr in 32 surface sediment samples and 32 overlying water samples collected from the Hai River and its tributaries to (1) investigate the content and spatial distribution of heavy metals in

sediments; (2) investigate the contamination levels and potential ecological risks of heavy metals by EF, I_{geo} , PLI, and PERI; (3) identify the possible sources of the heavy metals in the sediments; and (4) establish relationships between the elements.

2 Materials and Methods

2.1 Study Area

The focus of this study is the Hai River and its tributaries, which is the largest river flowing into Bohai Bay. This area is densely urbanized and hosts many agricultural and industrial activities. Owing to the highly-developed economy and society, pollution has become a serious problem. The main land-use types in this area are residential, industrial, traffic, and farmland, and the main soil types include brown, cinnamon, moist, boggy, and coastal saline soil (Chorography 1997). The mean annual precipitation ranges from 520 to 660 mm, most of which is received during July to September. The average monthly maximum and minimum temperature range from 25.8 to 26.6 °C in July and - 5.5 to - 3.4 °C in January, respectively.

2.2 Sample Collection and Pre-Treatment

Thirty-one sampling sites were located in the Hai River and its ten tributaries, and at least two study sites were chosen for each river, considering different land-use types. In addition, one sampling site was located in the Bohai Bay. A total of 32 surface sediments (0–10 cm) and 32 overlying water (20 cm below the water surface) samples were collected from the Hai River, its ten tributaries, and Bohai Bay during September 2016 (Fig. 1; Table S1). Three replicate samples were collected at each site. The surface sediment samples were collected using a Peterson grab sampler (ETC-200, China), and the water samples were collected using an automatic water quality sampler (WS700, American). The water temperature, pH, and dissolved oxygen (DO) concentrations were measured in the field using a HACH HQ 30D probe.

Immediately after collection, all sediment and water samples were stored in air-sealed polyethylene bags and bottles, respectively, and were sent to the laboratory for further analysis. The sediment samples were air-dried at room temperature, ground in an agate mortar, screened

through a 100-mesh nylon sieve, and then stored at 4 °C under darkness before their metal contents were analyzed (Mo, Cu, Zn, Ni, Cd, Pb, and Cr). The water samples were also stored at 4 °C and analyzed within 48 h.

2.3 Analytical Methods

2.3.1 Water

The concentration of the total nitrogen (TN) was determined with the alkaline potassium persulfate digestion-UV spectrophotometric method; the concentration of ammonium nitrogen (NH_4^+ -N) was determined using Nessler's reagent spectrophotometric method; the concentration of total phosphorus (TP) was determined by the molybdophosphate blue spectrophotometric method after the potassium persulfate digestion (China 2002). The chemical oxygen demand (COD) was determined with a Digital Reactor Block 200 and a HACH DR 2800 spectrophotometer according to the standard calibration and operation (Wang et al. 2015b). The chemical reagents used were analytical or guaranteed reagent grade. The solutions were prepared with distilled water.

2.3.2 Sediment

The sediment samples were carefully handled to prevent the loss or introduction of trace elements during preparation and analysis. To determine the total heavy metal contents, the sediment samples were digested following the procedure reported by Wang et al. (2015a) and then analyzed using inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7700x). The chemical reagents used were analytical or guaranteed reagent grade. All the recipients used were soaked in 5% (v/v) HNO_3 for 24 h, rinsed with ultrapure water, and then air-dried. The solutions were prepared with ultrapure water.

2.3.3 Quality Control

Standard samples (GBW07 sediment, obtained from the Center of National Standard Reference Material of China) were used to verify the accuracy of the analytical procedure. The metal contents of the three replicate samples were within $\pm 10\%$ relative percent deviation of the standards. Blank samples were used throughout all the experiments, and all elemental contents in the

blanks were below the detection limits of the ICP-MS. The recovery rates of heavy metals were between 85.6 and 108.3%. The data reported in this study were calculated as the dry weight. All the water and sediment samples were analyzed in duplicate, and results were presented as the means.

2.4 Geochemical and Ecotoxicological Indexes

2.4.1 Sediment Quality Assessment Guidelines

The sediment quality guidelines (SQGs) were used to assess the quality of sediments and their adverse biological effects on the aquatic ecosystem (MacDonald et al. 2000; Sundaray et al. 2011). In the present study, two limit values were applied to evaluate the heavy metal contamination, threshold effect content (TEC), and probable effect content (PEC). When the content is below the TEC, the adverse biological effects rarely occur; however, when the content exceeds the PEC, the adverse biological effects frequently occur (Chai et al. 2014; Ke et al. 2017).

2.4.2 Enrichment Factor

The enrichment factor (EF) is widely utilized as a reference to predict the extent of metal contamination and differentiate between anthropogenic and natural metal sources (Alexander et al. 1993; Selvaraj et al. 2004). To reduce the influence of grain size and mineralogy, which would affect the heavy metals' variability, the content data should be normalized and Fe was chosen as the reference element. The EF for each element was calculated according to the following formula:

$$EF = \frac{(c_x/c_{Fe})_{sample}}{(c_x/c_{Fe})_{background}} \quad (1)$$

where $(c_x/c_{Fe})_{sample}$ is the ratio of element (x) to the normalizer element (Fe) in the sediment samples and $(c_x/c_{Fe})_{background}$ is the ratio of element (x) to the normalizer element (Fe) in the reference background conditions. The background values of Fe, Mo, Cu, Zn, Ni, Cd, Pb, and Cr in the basin were 34,100, 4.6, 28.8, 79.3, 33.3, 0.09, 21, and 84.2 mg/kg, respectively (CNEMC 1990). Six contamination categories were generally recognized based on the enrichment factor (Table 1) (Birch and Olmos 2008; Birth 2003).

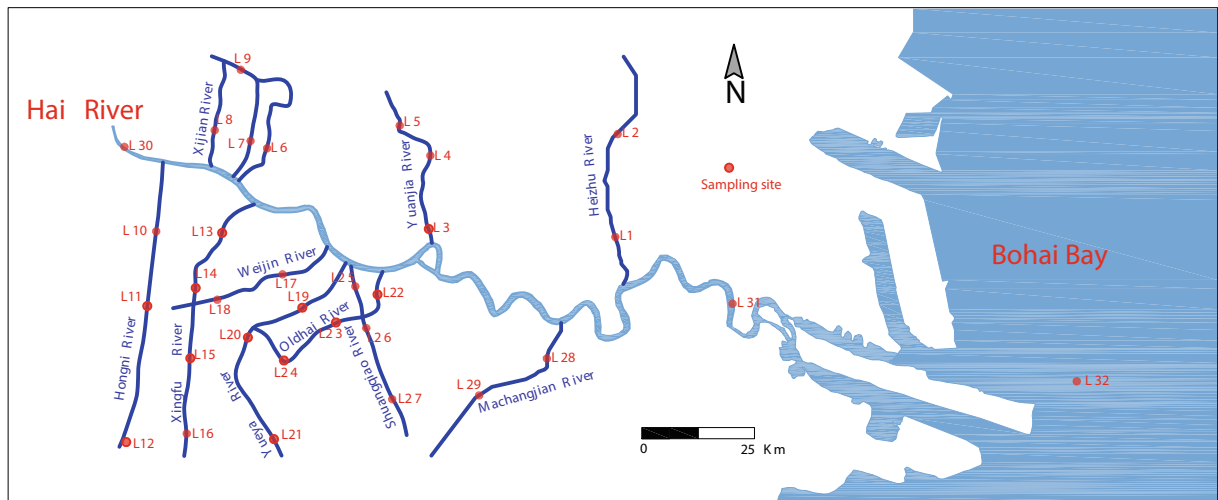


Fig. 1 Map of the sampling sites

2.4.3 Geoaccumulation Index

The geoaccumulation index (I_{geo}) is used to assess the degree of contamination from heavy metals and is widely applied in the assessment of sediment and soil contamination (Islam et al. 2015; Müller 1979; Zahra et al. 2014). To characterize the level of pollution, the I_{geo} values were calculated using the following formula:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right) \tag{2}$$

where C_n is the content of the measured metal in the surface sediment sample and B_n is the geochemical background value of the examined metal in the background sample. Factor 1.5 is introduced to minimize the possible variations in the background values that may be attributed to lithogenic effects. The I_{geo} values are classified into seven categories (Table 2).

Table 1 Enrichment factor (EF) in relation to sediment quality

EF classes	Sediment quality
$EF < 1.5$	No enrichment
$1.5 \leq EF < 3$	Minor enrichment
$3 \leq EF < 5$	Moderate enrichment
$5 \leq EF < 10$	Moderately severe enrichment
$10 \leq EF < 25$	Severe enrichment
$25 \leq EF < 50$	Extremely severe enrichment

2.4.4 Pollution Load Index

To better assess the overall environmental sediment quality and effects of the anthropogenic metals at different sedimentation ages (Guo et al. 2015), an integrated pollution load index (PLI) was calculated according to Suresh et al. (2012), which can be expressed as follows:

$$PLI = \sqrt[n]{(CF_1 \times CF_2 \times \dots \times CF_n)} \tag{3}$$

where CF_i is the contamination factor calculated as the ratio of the metal in sediment sample to that in the background sample. CF values were interpreted as follows: low contamination at $CF < 1$; moderate contamination at $1 \leq CF < 3$; considerable contamination at $3 \leq CF < 6$; and very high contamination at $CF \geq 6$ (Hakanson 1980). If the values of $PLI > 1$, heavy metal pollution exists; however, if the values of $PLI < 1$, there

Table 2 I_{geo} classes in relation to sediment quality

I_{geo}	I_{geo} class	Sediment quality
$I_{geo} < 0$	0	Unpolluted
$0 \leq I_{geo} < 1$	1	Unpolluted to moderately polluted
$1 \leq I_{geo} < 2$	2	Moderately polluted
$2 \leq I_{geo} < 3$	3	Moderately to highly polluted
$3 \leq I_{geo} < 4$	4	Highly polluted
$4 \leq I_{geo} < 5$	5	Highly to very highly polluted
$5 \leq I_{geo}$	6	Very highly polluted

may be no heavy metal pollution (Guo et al. 2015; Tomlinson et al. 1980).

2.4.5 Potential Ecological Risk

The potential ecological risk (PERI) was proposed by Hakanson (1980) and is applied to assess the comprehensive potential ecological risk posed by heavy metals in surface sediments (Liu et al. 2018b). This index emphasizes the toxicology response to heavy metals. The PERI for an individual metal (E_i) is defined by the following formula:

$$E_i = T_i \times \frac{C_i}{C_0} \quad (4)$$

The risk index (RI) of sampling sites was calculated using the following equation:

$$RI = \sum_{i=0}^n E_i = \sum_{i=0}^n T_i \times \frac{C_i}{C_0} \quad (5)$$

where C_i is the present content of heavy metals in the surface sediment, C_0 is the background content, and T_i is the toxic-response factor for the given heavy metal ($Cd = 30$, $Cu = Pb = Ni = 5$, $Cr = 2$, and $Zn = 1$) (Hakanson 1980; Mao et al. 2017). The PERI classifications are listed in Table 3.

2.5 Multivariate Statistical Analysis

Cluster analysis (CA), principal Component analysis (PCA), and the Pearson correlation analysis were conducted to explore the differences and sources of heavy metals in surface sediments. CA was used to identify spatial variability among the sites and the seven heavy metals. Euclidean distance was used as a dissimilarity matrix, whereas Ward's distance was used as a linkage method (Zahra et al. 2014). PCA is an effective tool for simplifying data and identifying factors that explain most of the variance and is widely used (Li and Zhang 2010; Wang et al. 2012; Xu et al. 2017). Factor analysis based on PCA was used to ascertain sources of contamination (natural and anthropogenic). Pearson correlation analysis is used to identify relationships between the heavy metals and other environmental parameters (such as TN or TP), which may originate from the same sources and exhibit similar geochemical behaviors (Bing et al. 2016; Skordas et al. 2014). The data were analyzed using IBM SPSS Statistics 22.0 for Windows

and OriginPro 8.6 software. Analysis of variance (ANOVA) was performed to illustrate the statistical significance ($P < 0.05$), and, prior to the ANOVA, the Levene's test for equality of variance was run ($P < 0.05$). A post hoc was carried out using the least significant difference (LSD) to assess significance.

3 Results and Discussion

3.1 Characterization of the Study Area

3.1.1 Parameters of the Overlying Water

The overlying water had temperatures of 18–21 °C, pH of 7.97–8.93, DO of 3.38–7.64 mg/l, COD of 32.0–79.7 mg/l, TN of 0.89–18.00 mg/l, NH_4^+-N of 0.17–17.30 mg/l, and TP of 0.082–2.411 mg/l (Table 4). The nutrient level in Xijian River was much higher than the other rivers and in Old Hai River was much lower. The industrial effluent and domestic sewage could be mainly responsible for the high concentrations of COD and nitrogen/phosphorus in the Xijian River. While for the Oldhai River, the good water quality may due to the large area of green land along the river.

3.1.2 Total Metal Content in the Sediments

The basic statistical parameters and total contents of heavy metals in the study area are shown in Table 5. The mean content from the sampling sites of Mo ranged from 3.52 to 9.89 mg/kg, with an average of 6.77 mg/kg, which was higher than the background value (4.6 mg/kg) and UCC (1.5 mg/kg). The Mo contents were higher than the background value at most sites, excluding L19, L20, L21, L26, L30, L31, and L32. The maximum Mo content found at L14 was two times higher than the background value and approximately six times higher than the UCC (1.5 mg/kg). The content of Cu ranged from 23.56 to 119.17 mg/kg, with an average of 74.23 mg/kg, and all the sites were higher than the background value (28.8 mg/kg) and UCC (25 mg/kg), excluding L32. The Zn content ranged from 68.27 (L22) to 109.12 (L8) mg/kg, with an average of 89.41 mg/kg, which was slightly higher than the background value (79.3 mg/kg) and UCC (71 mg/kg). The Ni content ranged from 33.36 (L31) to 57.30 (L18) mg/kg, with an average of 44.63 mg/kg, which was higher than the background value (33.3 mg/kg) and UCC (20 mg/kg).

Table 3 Category of potential ecological risk factor (E_i) and risk index (RI)

E_i	Category	RI	Category
$E_i \leq 40$	Low ecological risk	$RI \leq 150$	Low ecological risk
$40 < E_i \leq 80$	Moderate ecological risk	$150 < RI \leq 300$	Moderate ecological risk
$80 < E_i \leq 160$	Considerable ecological risk	$300 < RI \leq 600$	Considerable ecological risk
$160 < E_i \leq 320$	High ecological risk	$600 < RI$	Very high ecological risk
$320 < E_i$	Very high ecological risk		

The Cd content ranged from 0.141 (L18) to 0.478 (L32) mg/kg, with an average of 0.264 mg/kg, which was much higher than the background value (0.09 mg/kg) and the UCC (0.10 mg/kg). The content of Pb ranged from 20.65 (L32) to 53.96 (L31) mg/kg, with an average of 36.08 mg/kg, which was also higher than the background value (21 mg/kg) and the UCC (20 mg/kg). The Cr content ranged from 55.01 (L30) to 114.46 (L20) mg/kg, with an average of 92.09 mg/kg. The Cr contents were higher than the background value at most sites, excluding L5, L9, L21, L28, L29, L30, L31, and L32, and all the sites were higher than the UCC. All heavy metal average values were higher than their corresponding background values; especially Cu and Cd were 2.5 and 3.0 times greater than their background values, which indicated that the surface sediment experiences various degrees of contamination.

The heavy metal contents in this study were compared with other selected locations from the literature around the world (Table S2). The mean contents of Mo measured in this study were much higher than those in the Bohai Bay (Duan et al. 2010), the Jinjiang River (Liu et al. 2018a), and the Ruzin and Velke Kozmalovce Reservoirs (Hiller et al. 2010). The mean content of Cu was lower than the values reported by Xu et al. (2017), Zhu et al. (2018), and Varol (2011) and considerably higher than the contents measured in the other areas. Compared with the Zn content reported by the literature, the Zn content in this study were lower than in most of the basins and only exceeded the values in Bohai Bay (Hebei Province) (Ding et al. 2018), Tiaoxi River (Zheng et al. 2018), South China (Zhuang et al. 2018), Red sea coast (Nour et al. 2019), Kafue River (M'Kandawire et al. 2017), and Pra Basin (Duncan et al. 2018). Ni mean content was considerably lower than the values determined in Heer River (Zhu et al. 2018), Trgris River (Varol 2011),

and Pra Basin (Duncan et al. 2018). Nevertheless, Ni content in this study in higher levels compared with that in Yangtze (Zhang et al. 2009), Jinjiang River (Liu et al. 2018a), Laizhou Bay (Xu et al. 2017), Korotoa River (Islam et al. 2015), Red Sea coast (Nour et al. 2019), and so on. Cd mean content in this research was among the lowest found in the literature. Pb content in the basins of Hai River, Yangtze River Anqing section, Heer River, main tributaries of Dongting Lake, Tigris River, and Pra Basin (Duncan et al. 2018; Lei et al. 2016; Liu et al. 2018b; Varol 2011; Xu et al. 2018; Zhu et al. 2018) were notably higher than the content determined in this study. The mean content of Cr in this research was low compared with the levels determined in Coastal Bohai Bay (Gao and Chen 2012), Heer River (Zhu et al. 2018), and Pra River (Duncan et al. 2018); however, it was present in higher levels compared with contents determined in areas such as Yangtze River Anqing section (Liu et al. 2018b), main tributaries of Dongting Lake (Xu et al. 2018), and Kafue River (M'Kandawire et al. 2017).

3.2 Sediment Quality Guidelines

Sediment quality guidelines (SQGs) are used to evaluate sediment contamination by comparing sediment contaminant content with the corresponding quality guidelines (Islam et al. 2018). The mean total heavy metal contents in sediment from the Hai River and its tributaries and the sediment quality guidelines (SQGs) are summarized in Table 5. The mean contents of Cu were lower than the PEC values, and at site L32 was lower than TEC. At all the sites, the Zn and Cd contents were lower than TEC, which meant the adverse effects caused by Zn and Cd content in this study would occur rarely. The mean content of Ni was between the TEC and PEC

Table 4 Parameters of the overlying water in L1–L32

Sampling site	River name	T (°C)	pH	DO (mg/l)	COD (mg/l)	TN (mg/l)	NH ₄ ⁺ -N (mg/l)	TP (mg/l)
L1	Heizhu River	19.8	8.65	5.45	49.6	5.90	3.93	0.910
L2	Heizhu River	18.8	8.56	5.71	42.0	4.46	2.02	0.646
L3	Yuanjia River	19.4	8.57	5.27	57.6	2.70	2.01	0.940
L4	Yuanjia River	19.8	8.63	5.50	47.0	2.30	1.84	0.687
L5	Yuanjia River	19.3	7.97	5.01	49.7	3.70	2.48	0.580
L6	Xijian River	20.4	8.58	3.38	79.7	16.69	17.30	2.352
L7	Xijian River	20.2	8.80	3.60	60.4	18.00	15.82	1.553
L8	Xijian River	19.5	8.67	4.33	67.0	15.89	10.24	2.089
L9	Xijian River	18.5	8.34	3.70	60.8	14.96	12.79	2.411
L10	Hongni River	20.1	8.59	5.55	44.3	3.26	2.32	0.466
L11	Hongni River	19.4	8.36	5.63	38.0	2.55	1.97	0.652
L12	Hongni River	18.5	8.67	5.57	52.9	3.57	3.08	0.426
L13	Xingfu River	19.2	8.75	5.22	50.0	3.68	2.40	0.359
L14	Xingfu River	19.7	8.67	5.76	45.0	2.94	1.98	0.346
L15	Xingfu River	18.2	8.79	5.11	40.2	4.60	3.18	0.549
L16	Xingfu River	18.0	8.84	5.20	67.0	3.44	2.55	0.386
L17	Weijin River	18.4	8.87	5.17	47.5	2.99	1.85	0.277
L18	Weijin River	18.5	8.87	5.01	50.2	3.12	1.57	0.342
L19	Yueya River	18.0	8.83	5.21	68.4	4.27	1.23	0.532
L20	Yueya River	19.5	8.77	5.15	61.1	4.97	1.54	0.479
L21	Yueya River	19.6	8.83	5.29	56.0	4.08	2.20	0.239
L22	Oldhai River	20.5	8.54	5.78	36.5	1.00	0.17	0.092
L23	Oldhai River	20.7	8.67	6.07	43.0	0.89	0.19	0.083
L24	Oldhai River	19.7	8.83	6.23	49.0	1.04	0.23	0.082
L25	Shuangqiao River	19.2	8.87	6.10	50.4	2.91	2.24	0.540
L26	Shuangqiao River	19.3	8.89	7.64	62.4	3.56	2.13	0.444
L27	Shuangqiao River	21.0	8.93	6.90	64.8	3.85	3.24	0.475
L28	Machangjian River	18.5	8.92	7.01	66.1	5.94	8.99	0.420
L29	Machangjian River	19.6	8.76	7.01	72.8	5.46	8.99	0.384
L30	Hai River	18.7	8.64	5.14	39.0	2.54	0.38	0.334
L31	Hai River	18.5	8.45	6.22	49.0	3.09	0.42	0.364
L32	Bohai Bay	19.0	8.25	7.51	32.0	2.67	0.30	0.310
Max		18.0	8.93	7.64	79.7	18.00	17.30	2.411
Min		21.0	7.97	3.38	32.0	0.89	0.17	0.082
Mean		19.3	8.67	5.54	53.1	5.03	3.80	0.648
SD		0.79	0.21	0.99	11.4	4.47	4.44	0.594

values, and the Ni contents at sites L2, L3, L5, L9, L10, L11, L12, L17, and L18 were higher than the PEC value. The mean Pb content was near to TEC value, and the Pb contents at about half of the sites were below the TEC value. The content of Cr was between the TEC and PEC values, and the Cr

content at site L20 was slightly above the PEC value. In sediment, Cr was mainly present in the trivalent oxidation state, whereas in aerobic environments Cr (3+) was easily oxidized to Cr (6+), which was mobile, bio-available, and toxic (Drincic et al. 2018; Hausladen and Fendorf 2017; McClain et al.

Table 5 Descriptive statistics of the total metal contents of the sediment samples in L1–L32

	Mo (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Cr (mg/kg)
Max	9.89	119.17	109.12	57.30	0.478	53.96	114.46
Min	3.52	23.56	68.27	33.36	0.141	20.65	55.01
Mean	6.77	74.23	89.41	44.63	0.264	36.08	92.09
SD	1.99	18.16	11.79	7.01	0.076	7.52	14.02
Background values in Tianjin	4.6	28.8	79.3	33.3	0.09	21	84.2
UCC	1.5	25	71	20	0.10	20	35
TEC ^a		31.60	121.0	22.70	1.00	36.00	43.40
PEC ^b		150.0	460.0	49.00	5.00	130.0	111.0

UCC upper continental crust

^aThreshold effect concentration (MacDonald et al. 2000)

^bProbable effect concentration (MacDonald et al. 2000)

MacDonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Arch Environ Contam Toxicol* 39, 20–31

2017). The results showed that Cu, Pb, and Cr were likely to occasionally impose adverse effects on the ecosystem.

3.3 Pollution Level of Heavy Metals

To interpret and assess the pollution level of heavy metals in the surface sediment of the Hai River and its tributaries, we compared four geochemical indexes: EF, I_{geo} , PLI, and PERI in this study.

3.3.1 Enrichment Factor

The EF was calculated for each metal relative to the background values after normalization by Fe. The mean EF values of Mo, Cu, Zn, Ni, Cd, Pb, and Cr followed the order of Cd (2.63) > Cu (2.31) > Pb (1.53) > Mo (1.32) > Ni (1.20) > Zn (1.01) > Cr (0.98) (Fig. 2). Among these metals, the mean EF of Cd, Cu, and Pb were higher than 1.5, revealing anthropogenic inputs. However, the EF of the Mo, Ni, Zn, and Cr except L4, L17, and L18 for Ni remained within the range of natural variability (Wei et al. 2016). The EF values of Cd ranged from 1.37 (L18) to 4.76 (L32), which corresponded to minor to moderate enrichment, especially all the sites in Xijian River showed moderate enrichment. The high enrichment level of Cd may be attributed to anthropogenic activities, including industrial, road traffic, and agricultural runoff. The Cu levels at the Yuanjia River all exhibited moderate enrichment, which may be due to the agrochemicals commonly used

for disease control and discharge of industrial wastewaters along the river (Zahra et al. 2014). The Mo levels at 37.5% of the sites fell under minor enrichment, and the others exhibited no enrichment. The Pb levels at more than half of the sites exhibited minor enrichment, and the other 14 sites showed no enrichment.

3.3.2 Geoaccumulation Index

The I_{geo} values were always used to explain the sediment quality and the results are presented in Fig. 3. The calculated I_{geo} values in the sediments were -0.971 to 0.520 for Mo (mean: -0.097 ± 0.467), -0.875 to 1.464 for Cu (mean: 0.728 ± 0.418), -0.801 to -0.124 for Zn (mean: -0.425 ± 0.194), -0.997 to -0.217 for Ni

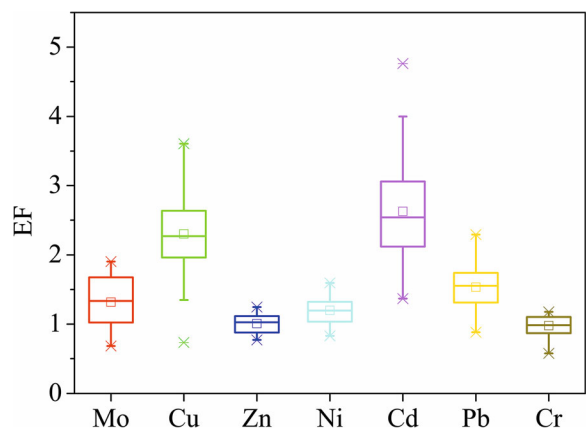


Fig. 2 Box-and-whisker plots for the enrichment factor (EF) of heavy metals in the sediments from Hai River and its tributaries

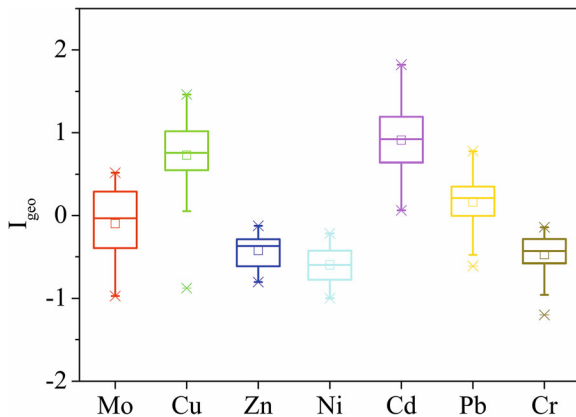


Fig. 3 Box-and-whisker plots for the Geoaccumulation index (I_{geo}) of heavy metals in the sediments from Hai River and its tributaries

(mean: -0.595 ± 0.228), 0.063 to 1.824 for Cd (mean: 0.910 ± 0.415), -0.609 to 0.776 for Pb (mean: 0.163 ± 0.312), and -1.199 to -0.142 for Cr (mean: -0.475 ± 0.242). The I_{geo} values for Zn, Ni, and Cr were below zero, and 16, 1, and 8 sites that had I_{geo} values were also below zero for Mo, Cu, and Pb, which can be viewed as an indication of no metal pollution. 50, 68.7, 56.2, and 75% of sites had values of 0–1 for Mo, Cu, Cd, and Pb, an indication of slight metal pollution. 9 and 14 sites had I_{geo} values of 1–2 for Cu and Cd, an indication of moderate metal pollution.

3.3.3 Pollution Load Index

The average CF values were ranked as follows: Cd (2.94) > Cu (2.57) > Pb (1.71) > Mo (1.47) > Ni (1.34) > Zn (1.13) > Cr (1.09), and the CF order agreed with the EF order (Fig. 4a). The highest CF values for heavy metals were found at sites L14 (Mo, 2.15), L3 (Cu, 4.14), L12 (Zn, 1.38), L18 (Ni, 1.72), L32 (Cd, 5.31), L7 (Pb, 2.22), and L16 (Cr, 1.36). All the CF values were more than 1, indicating moderate contamination. To further assess the integrative pollution of metals in this study area, the PLI was used to calculate pollution based on each metal content. PLI can provide understanding of the quality of the environment to its inhabitants and valuable information of the pollution status of the area to decision makers (Guo et al. 2015; Islam et al. 2015; Suresh et al. 2012). The PLI in this study ranged from 1.15 (L32) to 1.90 (L7), indicating that all 32 sites were contaminated with heavy metals (Fig. 4b). The high PLI values indicated that Cd and Cu were the major contributors to the sediment pollution.

The values of PLI in the Yuanjia River and Xijian River were higher than those in the other rivers, indicating that two rivers faced higher metal pollution risks which may be due to the colloidal materials in surface runoff, road traffic, and agricultural runoff.

3.3.4 Potential Ecological Index

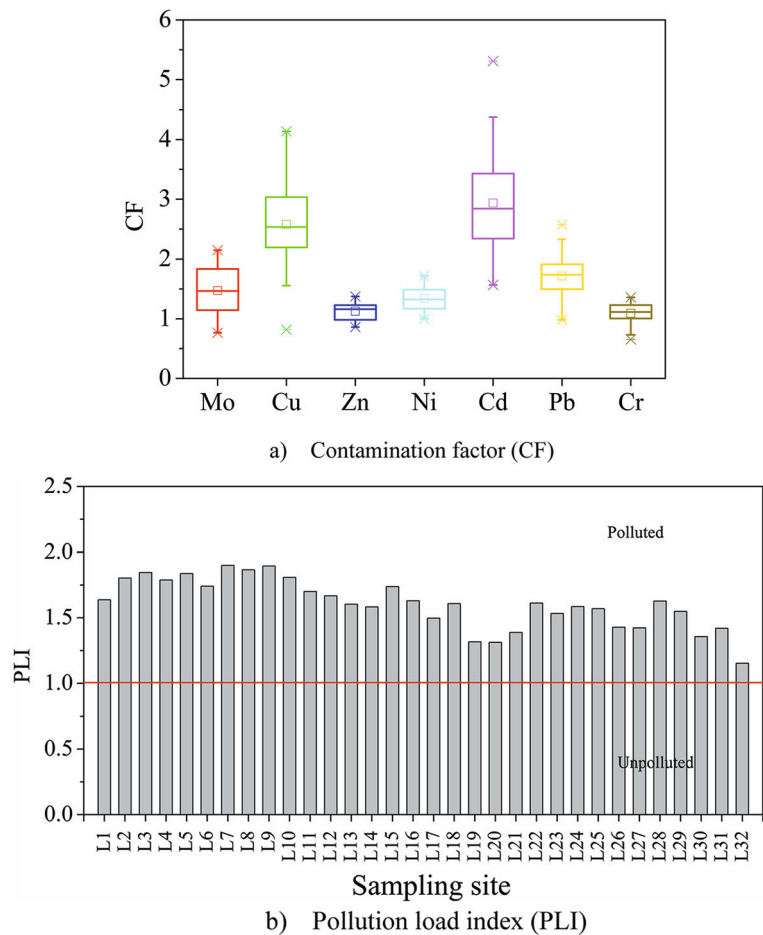
To determine the potential ecological risk of heavy metals in this study, the values of PERI were calculated; Table S3 presents both the PERI of individual elements and the comprehensive potential ecological index. The consequences of mean PERI degree was ranked as Cd (88.10) > Cu (12.89) > Pb (8.89) > Ni (2.68) > Cr (2.19) > Zn (1.13). The sampling sites with the highest degree of potential risk caused by each heavy metal were L3 for Cu, L11 for Zn, L18 for Ni, L32 for Cd, L31 for L31, and L20 for Cr. E_i for Cu, Zn, Ni, Pb, and Cr were less than 40, and they posed a low potential ecological risk. However, 18 sites suggested a considerable risk in view of Cd, and the rest 14 sites showed a moderate risk. Based on the PERI classification criterion, sites L6, L7, L8, L9, and L32 exhibited a moderate ecological risk, while the other sites exhibited a low ecological risk (Mao et al. 2017; Wu et al. 2018). The metals posed moderate risk in Xijian River and the Bohai Bay mainly due to the high Cd content in the sediment. As the dominant ecological risk factor, Cd contributed over 50% of the ecological risks at 32 sites, with contributions ranging from 61% (L18) to 92% (L32).

3.4 Multivariate Statistical Analysis

3.4.1 Cluster Analysis

Cluster analysis (CA) was used and applied to this study area sediment data set to group the similar sampling sites (Islam et al. 2018). Spatial CA rendered a dendrogram (Fig. 5a) where all thirty-two sampling sites were grouped into three statistically significant clusters. Sites of L6, L7, L8, L9, and L32 were categorized into cluster 3, indicating that they were heavily polluted with high potential risk, which receives contaminants from the industrial plant, agricultural runoff, domestic sewage, and traffic area. Cluster 2 contained four sites (L17, L18, L19, and L20) with the lowest metal content, low ecological risk, and low level of pollution. In addition, the main land-use types at these four sites are green land, bare farmland, and residential areas. Cluster 3 contained

Fig. 4 Box-and-whisker plots for the contamination factor (CF) of heavy metals and spatial variation in pollution load index (PLI) in the sediments from Hai River and its tributaries. **a** Contamination factor (CF); **b** Pollution load index (PLI)



23 sites that are mainly in the Heizhu River, Yuanjia River, Hongni River, Xingfu River, Oldhai River, Shuangqiao River, Machangjia River, and Hai River with a certain degree of pollution and ecological risk.

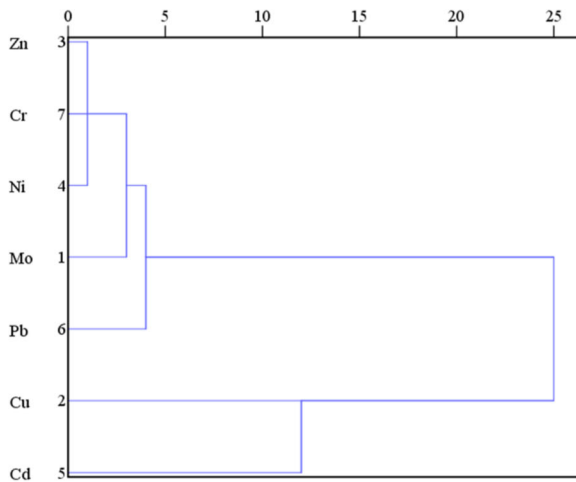
CA was also performed to group the analyzed parameters, and Fig. 5b showed all seven metal parameters were grouped into two statistically significant groups. Group 1 includes Cu and Cd, which were identified as contaminants derived from anthropogenic sources (agricultural surface runoff, discharge of municipal and industrial wastewater, and antifouling paints for ships). Group 2 contains Pb, Mo, Ni, Cr, and Zn, which were identified as contaminants derived from natural sources (rock weathering and soil erosion).

3.4.2 Principal Component Analysis

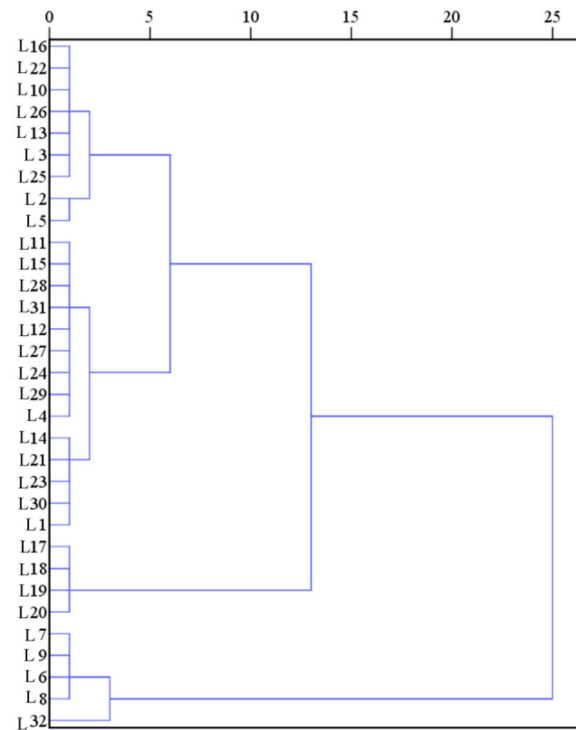
Principal component analysis (PCA) was primarily used to reduce the number of variables to a small set of latent factors and explore the similarity of distribution behavior

(Ke et al. 2017; Zahra et al. 2014). Table 6 shows the results of PCA, and three rotated principal components (PCs) were extracted with eigenvalues > 1 , accounting for 74.91% of the total variance. Each group of heavy metals possibly originates from similar sources. Many researches have used the association of elements with PCA to distinguish natural from anthropogenic sources (Nour et al. 2019; Zhang et al. 2016).

PC1 explained 34.03% of the total variance and was mainly related to Cu, Mo, and Zn, which all had strong positive loadings. The contents of Zn and Mo were closely to the background values. In addition, the results of EF, I_{geo} , and PLI indicated that this group of elements might originate from natural sources, such as mineral weathering and atmospheric precipitation (Ke et al. 2017). Though the Cu belonged to PC1, the content of Cu were higher than the background values, which was different from the result of CA. PC2 covered 23.87% and presented negative loading for Pb and positive loading for Cr and Ni. Moreover, the PC3 covered 17.02% and showed high positive



a) Sampling sites



b) Heavy metal elements

Fig. 5 Cluster diagram of sampling sites and heavy metal elements obtained using Ward's method and Euclidean distance matrix. **a** Sampling sites; **b** Heavy metal elements

loading for Cd. The spatial distribution characteristic of Cd are quite different from the other six heavy metals, with a relatively higher content, especially at the L2, L5, L6, L7,

Table 6 Loading of environmental variables on significant Varimax rotated principal components

Parameters	Component		
	PC1	PC2	PC3
Cu	<i>0.906</i>		
Zn	<i>0.780</i>		
Mo	<i>0.620</i>		
Cr		<i>0.850</i>	
Pb		<i>-0.705</i>	
Ni		<i>0.547</i>	
Cd			<i>0.900</i>
Eigenvalue	2.382	1.671	1.191
Total variance (%)	34.027	23.869	17.018
Cumulative variance (%)	34.027	57.896	74.914

Note: Italic values indicate strong loading

L8, L9, L13, L16, and L32, which could be ascribe to an anthropogenic factor. Contaminants from the pesticides and chemical fertilizers, road traffic and shipping might be responsible for the heavy Cd pollution at these sites (Ke et al. 2017; Wang et al. 2015c).

3.4.3 Correlation Analysis

The correlation coefficient matrix between the heavy metals and environmental parameters are listed in Table S4. Correlations between the elements may indicate that they originated from the same source and exhibited similar geochemical behaviors, and, if there was no correlation between the elements, the metals were not controlled by a single factor (Zhuang et al. 2018).

There were significantly positive correlations between TN, NH₄⁺-N, and TP and Mo, Zn, Cd, and Pb, indicating that the distributions of Mo, Zn, Cd, and Pb were controlled by the nutrient level in the overlying water. The results agreed with those found by Fu et al. (2014) and Zhang et al. (2007). Moreover, there were negative correlations between DO and (Mo, Cu, and Pb), indicating that DO facilitated the release of Mo, Cu, and Pb (Li et al. 2013). In addition, the contents of Cd were negatively correlated with pH, indicating that the pH may be also the factor affecting the distribution of Cd in the surface sediment of this study area. In contrast, no correlations occurred between COD and the seven heavy metals, suggesting that COD had no effect on the heavy metals contents. Positive correlations were found between several element pairs: Cu-Mo (0.517, *P* < 0.01), Cu-Zn (0.518, *P*

<0.01), Cu-Ni (0.472, $P < 0.01$), and Cr-Ni (0.467, $P < 0.01$), indicating that these elements had similar sources. There was a weak negative correlation between Pb and Cr (0.350, $P < 0.05$). There was no observed correlation between Cd and the other heavy metals, indicating that Cd pollution might originate from a separate source compared with the other heavy metals.

4 Conclusions

Thirty-two surface sediment and overlying water samples were collected from Hai River and its tributaries. The nutrient level in Xijian River was much higher than the other rivers and in Old Hai River was much lower. The mean total contents of Mo, Cu, Zn, Ni, Cd, Pb, and Cr were higher than the corresponding background values, particularly those of Cu and Cd. Compared with the TEC and PEC, Cu, Pb, and Cr were easily to impose adverse effects on the aquatic ecosystem. The mean EF and CF values followed the same order of $Cd > Cu > Pb > Mo > Ni > Zn > Cr$, and the Yuanjia River and Xijian River faced severer metal pollution risks. Cd contributed more than half of the ecological risk. The results of multivariate statistical analysis showed that Cd and Cu might be derived from anthropogenic source, such as agricultural surface runoff, discharge of municipal and industrial wastewater, and antifouling paints for ships. The distributions of Mo, Zn, Cd, and Pb were controlled by the nutrient level in the overlying water, but the COD had no effect on the heavy metals contents. In conclusion, heavy metal pollution in the Hai River and its tributaries is worthy of paying attention to, especially that of Cd.

Funding Information This work was supported by The Key Special Program on the Science and Technology for the Pollution Control and Treatment of Water Bodies of China (2014ZX07203-009).

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