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Distribution and risk assessment of trace metals in riverine surface sediments in gold mining area

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Abstract Recognizing the pollution characteristics and potential risks of trace metals in sediments are important to protect water ecosystem safety. In the present study, a systematic investigation was performed to assess the pollution and risk level of trace metals in river sediments located in the greatest gold production base in China. The geo-accumulation index was used to assess the contamination degree. The sediment quality guidelines and potential ecological risk index were employed to complete an ecological risk assessment. A non-carcinogenic health risk assessment was also carried out to evaluate potential adverse health risks. Correlations and principal component analyses were applied to check relationships among trace metals and ascertain potential pollution sources. The results suggested that the sediments in the river were most polluted by As, Cd, and Hg followed by Cu, Pb, and Zn. The assessment of potential human health risk revealed that there was no significant non-carcinogenic risk to the inhabitants. Gold mining and smelting activities and the long-term excessive application of fertilizers and agrochemicals were identified as the main anthropogenic releases. This study contributed an understanding that possible sources, contamination degree, and ecological risk level of trace metals in riverine surface sediments in a gold mining area.

Keywords Gold mining · Sediment · Trace metals · Assessment

Introduction

Trace metal contamination in aquatic system has attracted attention concerning their environmental endurance, biological accumulation, and potential adverse effects (Birch and Apostolatos 2013). In aquatic systems, trace metals quickly deposit into the sediment and then are combined with fine-grained components, iron and manganese oxides, organic matters, and sulfides (Tessier and Campbell 1987). Therefore, sediment was considered the main accumulation medium for trace metals (Pan and Wang 2012). However, metals combined in sediments may be released into the overlying water through the sediment-water interface, resulting in water quality deterioration and harmful effects on aquatic biota (Simpson and Batley 2007). Generally, anthropogenic metals have the characteristics of high mobility and toxicity to humans (Birch and Apostolatos 2013). Pan and Wang (2012) reported that a high metal content was observed in sediments along the coast resulting from industrial and domestic sewage discharges,

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mining, and smelting tailing, increasing the risk of metal exposure to biota. Previous study reported that a high freshwater content of Hg was dominantly produced by artisanal and small-scale gold mining (released to the environment at approximately 880 Mg/year, Obrist et al. 2018). Therefore, understanding the distribution pattern and their potential ecological risks of trace metals in the gold mining area is significant to sediment quality evaluation and aquatic environment protection.

The Jiehe River is located in the biggest gold mining and smelting industrial zone in China. The local city (Zhaoyuan City) has been called the gold capital of China because it is situated in the Zhao-Lai gold mineralization belt and has the largest gold repository. In recent decades, many artisanal gold mines employed the rudimentary amalgamation method in the gold extraction process. In the rainy season, some tailing (fine-sand) is transported to the Jiehe River, resulting in trace metal pollution in sediments (Cai et al. 2016, 2017). Furthermore, acid mine drainage (AMD, pH < 2) is another unavoidable byproduct during gold production; it also contains a high concentration of dissolved trace metals. The untreated AMD discharge had a detrimental effect on aquatic plant and fish life (Feng et al. 2000). Therefore, the river water and sediments in the Jiehe River were likely simultaneously polluted by tailing and the drainage of AMD.

Prior to carrying out trace metal pollution remediation, it is necessary to ascertain the pollution characteristics and environmental risks in the sediments in the gold mining area. However, very few studies have examined contamination degree, evaluated environmental risks, or identified sources for trace metals in gold mining areas (Esdaile and Chalker 2018; Taiwo and Awomeso 2017). Thus, the present study aimed to (i) synchronously investigate the contents and distributions of As, Cd, Cr, Cu, Pb, and Zn in surface sediments; (ii) ascertain the contamination condition and assess the ecological and health risk; and (iii) identify the potential origins of trace metals by correlation analysis and principal component analysis. These results can provide new knowledge for river ecosystem protection in gold mining area.

Material and methods

Study area

The Jiehe River (Fig. 1) is located in the northwestern Shandong Peninsula (E 120.08° to 120.38° and N 37.05° to 37.33°). The area of the entire watershed is ~ 585 km^2, and the width is 70–120 m. The sampling site was selected in the middle-lower reach with a dozen of gold mines and many gold smelting plants (e.g., the Jinling, Jinchiling, and Linglong gold mines) (Zhang et al. 2014). The continental climate of the study area is the continental monsoon type. The average annual temperature is 12.5 °C, and the mean annual rainfall is 669.2 mm.

Sample collection and analysis

The top 0–5 cm of undisturbed surface sediment was collected using a Van-Veen grab sampler from 38 sites (J1-J38) in the Jiehe River (Fig. 1). These sites were distributed uniformly (an interval of 100 m) across the middle-lower reaches (E 120.20° to 120.32° and N 37.21° to 37.30°). Because of the narrow river, two-points sediments (2–3 kg) were taken from each section and mixed them evenly to constitute the sediment sample of specific points. Samples were placed into polyethylene bags, stored in a cooler in the field, and stored at 4 °C in the laboratory before analysis.

The sediments were freeze-dried at − 50 °C and powdered with an agate mortar and pestle, and ~ 4 g of powder was pressed to obtain powder pellets (Ahmadi et al. 2019). The trace elements were analyzed by x-ray fluorescence (XRF) with the pressed power pellets, using an ARL AdvantXP automated X-ray spectrometer (Ruzickova et al. 2018). In this research, calibrations were performed with reference materials at each batch (30 samples determination), and matrix correction was obtained with the method of Lachance and Traill (1966) (Natali and Bianchini 2018). All analyses were carried out in duplicate. For trace elements at concentrations above 10 mg/kg in sediments, the errors were lower than 8% in the present study. To assure the reliability of analyses results, the intercalibration was covered in the applied XRF system on the sediment analysis that confirmed the precision and accuracy of the results (Vianello et al. 2014). Seven metals (Cd, Cr, Pb, Hg, As, Cu, and Zn) were determined for each sediment sample.

Contamination assessment methods

In this study, the geo-accumulation index (I_{geo}) was applied to certify the geochemical figures of the

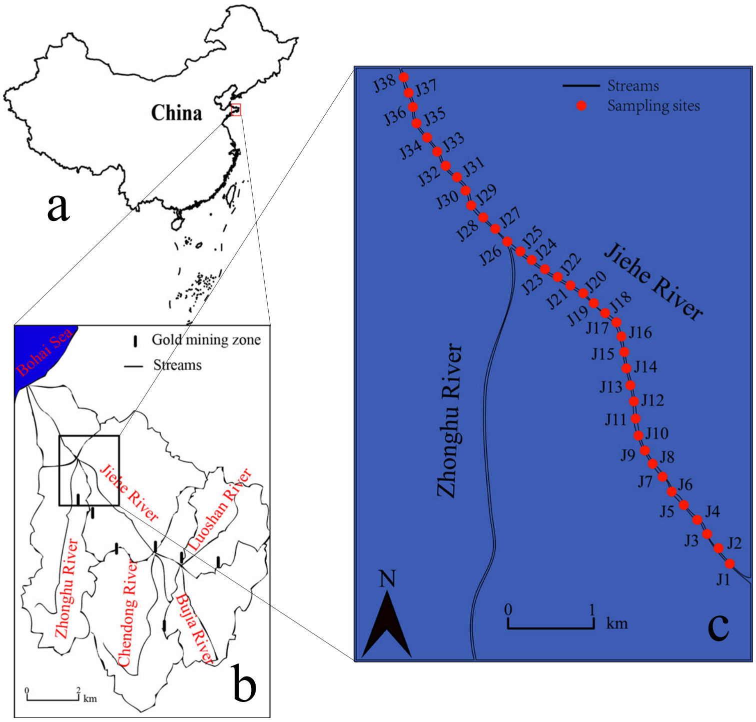

Fig. 1 a Geographical position of the Jiaodong Peninsula elucidates the sitting of Jiehe River aera (black box). **b** The showing of Jiehe River basin. **c** The distribution of sampling sits (red cycles)

sediment metals. According to Muller (1969), I_{geo} is used to identify metal accumulation in sediments and is calculated as defined below:

$$I_{\text{geo}} = log_2(C_n/1.5 \times B_n)$$

where C_n is the determined content of each trace metal (mg/kg), and B_n is defined as the geochemical background value of the corresponding trace metal (mg/kg). In the present study, the freshwater sediment background values in China were applied as the background value of trace metals in the studied area (Shi 2016). The coefficient of 1.5 was used to balance possible variations of the reference values resulting from the lithogenic effects. I_{geo} consists of seven classes as described in Table 1.

Ecological risk evaluation methods

Sediment quality guidelines (SQGs) compared the sediment trace metal concentration to the corresponding specific quality criteria to qualitatively assess the probable environmental risk (Varol 2011). The SQGs were commonly produced from the previous freshwater sediment quality guidelines, and the method created by MacDonald et al. (2000) was applied to evaluate the grade of potential risks with the high concentration metals in sediments. There were two standards among the methods, including the threshold effect concentration (TEC) and the probable effect concentration (PEC). If the determined metals concentrations are below TEC, the adverse effects generated from trace metals are not expected to occur, and if the values are above PEC, harmful effects are expected to occur frequently. In addition, the mean PEC quotients (mPEC-Q) have been described using the following equation to assess the potential biotoxic effect for many metals (Long and Macdonald 1998a, b):

$$\text{mPEC–Q} = \sum_{i=1}^{n} \frac{C_i}{\text{PEC}_i} / n$$

where C_i is the content of each metal in the research, PEC_i is the corresponding PEC of each trace metal, and n is the amount of determined metals in the research.

In addition, the potential ecological risk index (PERI), which indicates a toxic-response index for a particular metal, providing a definitive result for the potential risk with the pollution concentration

Table 1 Summary of I_{geo} classes, Er, and PERI risk levels

Contamination/risk grades					
$I_{geo} < 0$	Practically uncontaminated	$Er < 40$	Low risk	$PERI < 100$	Low risk
$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated	$40 \le Er < 80$	Moderate risk	$100 \le PERI < 200$	Moderate risk
$1 < I_{geo} < 2$	Moderately contaminated	$80 \le Er < 160$	Considerable risk	$200 \le PERI < 400$	Considerable risk
$2 < I_{geo} < 3$	Moderately to heavily contaminated	$160 \le Er < 320$	High risk	$PERI > 400$	Very high risk
$3 < I_{geo} < 4$	Heavily contaminated	$Er \ge 320$	Very high risk		
$4 < I_{geo} < 5$	Heavily to extremely contaminated				
$I_{geo} > 5$	Extremely contaminated				

of metals to the ecological system (Hakanson 1980). The PERI revealed by the following formula includes the concentration and toxic-response indexes of trace metals and it can be applied to quantitatively assess the potential risks to ecosystem.

$$\mathrm{PERI} = \sum \mathrm{Er}^i = \sum T_r^i C_f^i = \sum T_r^i \left(C_n^i / C_r^i \right)$$

where PERI is the total risk index for all metals in the research, Er is considered as the potential ecological risk value of a given metal, T_r is the toxic-response index for a given metal, C_f is considered as the pollution factor, C_n is the contents of trace metal in the study (mg/kg), and C_r is considered as the background value of a given metal (mg/kg). Consistent with Hakanson (1980), the consensus values T_r of Zn, Cr, Cu, Pb, As, Cd, and Hg are 1, 2, 5, 5, 10, 30, and 40, respectively. Therefore, the assessment standards for Er of each metal are given for the five grades shown in Table 1. Hakanson indicated that seven metals (Cr, As, Cd, Hg, Pb, Cu, and Zn) and one organic pollutant (polychlorinated biphenyls, PCBs) were involved, but the PCBs were not been examined in this study. Therefore, the modified assessment standard of PERI for all metals (Liu et al. 2018b) was adopted. The detail criterias were listed in Table 1.

Health risk analysis method

A human health risk evaluation method applied for sediments has been presented in many studies (Iqbal et al. 2013; Khalil et al. 2015; Kusin et al. 2018). Commonly, the three major pathways of trace metals' transformation in ecological systems that are generally involved in human health risk assessment include the following: ingestion, dermal contact, and respiration. This study considered the ingestion and dermal contact pathways of sediment metals transportation to evaluate human health risk, and the following equations are used to calculate the exposure values (USEPA 1989, 2004; Rovira et al. 2011; Wang et al. 2005).

$$\mathrm{Exp}_{\mathrm{ing}} = \frac{C_{\mathrm{sed}} \times \mathrm{IR} \times \mathrm{CF} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}}$$

where $\mathrm{Exp}_{\mathrm{ing}}$ is defined as the ingestion exposure risk from the sedimental metals (mg/kg/day); C_{sed} is the determined content in present sediment; IR is defined as the amount of ingestion each day (IR = 114 mg/day); CF is the measurement unit conversion factor ($\mathrm{CF} = 10^{-6}$ kg/mg); EF is defined as the exposure frequency on the sediment (EF = 350 days/year); ED is the exposure duration time (ED = 30 years); BW is defined as the adult weight (BW = 70 kg); AT is the number of days in 30 years (AT = 10,950 days) (Iqbal et al. 2013).

$$\mathrm{Exp}_{\mathrm{derm}} = \frac{C_{\mathrm{sed}} \times \mathrm{CF} \times \mathrm{SA} \times \mathrm{AF} \times \mathrm{ABS} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}}$$

where $\mathrm{Exp}_{\mathrm{derm}}$ is defined as the dermal uptake risk; SA is considered as the exposed skin area on the sediment ($\mathrm{SA} = 5700\ \mathrm{cm}^2$); AF is defined as the adhesion index of trace metal on unit skin area ($\mathrm{AF} = 0.07\ \mathrm{mg/cm}^2$); and ABS is considered as the dermal adsorption rate from sediment (ABS = 0.001) (Kusin et al. 2018), others were the same as above.

Hazardous quotients (HQs) were applied in evaluating the health risks of exposure to the trace metals of surface sediment in accordance with the USEPA (2004) health risk assessment guidelines (Wang et al. 2015). The HQs equation for the ingestion and dermal contact pathways are as follows:

$$\mathrm{HQ}_{\mathrm{ing/derm}} = \frac{\mathrm{Exp}_{\mathrm{ing/derm}}}{\mathrm{RfD}}$$

$$\mathrm{HI} = \sum_{i=1}^{n} \mathrm{HQ}_{\mathrm{ing/derm}}$$

where HQ is the hazardous quotients by one exposure pathway of ingestion or dermal contact under respective exposure concentration; RfD is the reference value for the adverse health effort resulting from metal contaminations. The reference value through dermal contact is commonly regarded to be same as through the ingestion pathway (Iqbal et al. 2013).

Statistical analysis

Correlation and multivariate statistical tools including principal component analyses were applied to determine the strong relationships for trace metals in the sediment samples and ascertain the potential origins of sediment trace metals of Jiehe River. PCA is used to ascertain the sources of the trace metals by calculating the eigenvectors and identifying the principal components. In the PCA, varimax normalized rotation is applied and the principal components (PCs) can be identified on account of cumulative variance higher than 70% and/or an Eigenvalue greater than 1.0 (Varol 2011). The correlation and multivariable statistical analysis is performed using IBM SPSS 21 statistics software. The data analysis is given by Origin 9 statistics software for Windows.

Results and discussion

Trace metals distribution in sediments

Table 2 listed the summary of trace metal concentrations. The contents ranges (mg/kg) of Cr 12.5–78.8, As 8.7–1674, Cd 0.1–394, Hg 5.2–51.0, Pb 18.3–426, Cu 8.1–1257, and Zn 53.6–1251. In order to estimate degree of contamination of trace metals in surface sediments, the sediment background values of freshwater lakes (SBVs) in China (Shi 2016), the average shale values of metals (ASVs) (Turekian 1961), and the Chinese environmental quality standard for soils (CEPA 1995) were applied. In Table 2, the average contents of As, Cd, Cu, Hg, Pb, and Zn in the sediments were higher than the corresponding SBVs (Hg, Cd, As, Cu, Zn, and Pb, which were 622.2, 329.8, 16.5, 10.3, 10.3, and 3.0 times the SBVs, respectively). Furthermore, the average content of each metal in the sediments exhibits metal distribution discrepancies compared to global the ASVs except for Cr. The results suggested that trace metals in sediments of the gold mining area were strongly affected by anthropogenic inputs (Ji et al. 2017).

In the CEPA (1995), the grade II level of quality standard for soils could be applied as the threshold values for protecting human health in China (Chen et al. 2016). Herein, approximately 100.0% of the samples for Hg, 86.8% for Cd, 78.9% for As, 63.1% for Cu, and 39.5% for Zn exceeded their corresponding thresholds by comparison with the grade II level of quality standard. Compared with a previous study on the Jiehe River, the average Cd and As content in the present study are higher than the previous results by 2.3 and 8.8 times, respectively (Zhang et al. 2014). The increase or accumulation of Cd and As was likely related to the AMD discharge in the adjacent gold mines and smelting plants, as well as agrochemical overuse.

Spatially, the metal contents in sediments of the Jiehe River significantly varied between sampling points, with the following CV values: 0.52 of Cr, 2.06 of As, 1.66 of Cd, 0.55 of Hg, 1.15 of Pb, 1.05 of Cu, and 0.83 of Zn. The spatial distribution of Cr, As, Cd, Hg, Pb, Cu, and Zn in sediments is shown in Fig. 2.

The Cr concentration showed fluctuation in the studied area (Fig. 2a). The contents of Cr in most sample sites (30 of 38) were lower than the corresponding background reference values. The spatial distribution of Cu showed the following characteristics in concentration: the highest concentration appeared in the J5 site, and high concentrations presented in the J26, J30, and J34 sites (Fig. 2b). The highest Cu concentration was 10.3 times higher than the reference value at the J5 site. The As and Zn concentrations in the surface sediment (Fig. 2b) were similar to Cu, with high values at the J5, J26, J30, and J34 sites. Cd, Hg, and Pb had generally common spatial concentration distribution (Fig. 2c). The highest content of Cd, Hg, and Pb at the J9 site were 394, 51.0, and 426 mg/Kg, respectively (Table 2). However, except for J9 site, the concentration showed a narrow range.

The Jiehe River is located in the biggest gold mining and smelting industrial zones in China, so the river sediment could be contaminated with trace metals

Table 2 Statistics of trace metals in sediment and various reference values (unit: mg/kg)

	Cr	As	Cd	Hg	Pb	Cu	Zn
Min	12.5	8.70	0.09	5.2	18.3	8.1	53.6
Mean	35.8	131.9	36.3	16.8	65.8	206.0	297.6
SD	18.7	272	60.1	9.2	75.9	217.2	247.9
Max	78.8	1674	394	51.0	426	1257	1251
CV	0.52	2.06	1.66	0.55	1.15	1.05	0.83
CEPA (grade II of soils)	300	25	0.6	0.5	300	100	250
SBVs	54	8	0.11	0.027	22	20	65
ASVs	90	13	0.3	0.4	20	45	95

produced by mine processing and smelting. A comparison of trace metals between the Jiehe River sediment and other rivers in gold mining areas and non-gold-mining areas was listed in Table 3.

The comparison revealed that the content levels of Cr, As, Cd, Hg, Pb, Cu, and Zn are consistent with those in the Villa River (Ecuador) and the Certej River (Romania). For the metals in sediment without gold mining effects, the levels in this study were greater than those in the Ganga (India), Sungai Buloh (Malaysia), Jialu, Yellow, and Yangtze (China) Rivers, with exception of Cr. The results indicated that the unavoidable byproducts in the mining industry may enhance the metal accumulation in riverine sediments.

Contamination assessment of metals in sediments

To identify the influence of human activities on trace metals' accumulation in surface sediment, the I_{geo} was calculated (Fig. 3). The median I_{geo} values for these

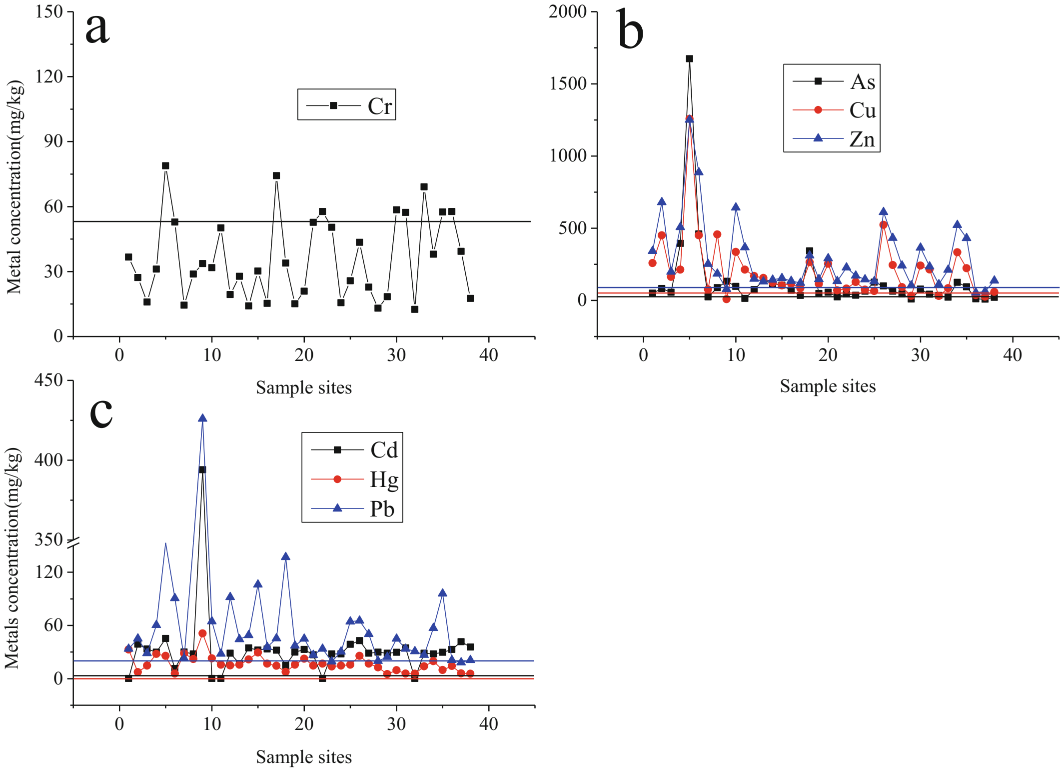

Fig. 2 Distribution of trace metals in sediments. (line: grade II level of the Chinese environmental quality standard for soils)

Table 3 Comparative levels of trace metals of sediment in the Jiehe River with those of other rivers around the world (unit: mg/kg)

	Site	Cr	As	Cd	Hg	Pb	Cu	Zn	Reference
Gold mining effort	Jiehe River, China	12.5–78.8	8.7–1674	0.1–394.0	5.2–51.0	18.3–426.0	8.1–1257	53.6–1251	Present study
	Villa River, Ecuador	34.0–80.0	180.0–482.0	–	1.0–3.0	–	367.0–821.0	–	(Sierra et al. 2017)
	Zhaosu River, China	–	22.7–232.0	–	0.05–0.256	15.3–110.0	20.0–27.9	60.2–120.0	(Gao 2018)
	Marahiq, Egypt	20.2–41.4	1.2–16.5	0.05–0.44	0.003–0.045	2.05–65.53	16.77–85.78	30.8–133.8	(Darwish 2017)
	Uraba Gulf, Colombia	109.61–212.45	–	–	0.001–0.136	0.17–6.93	25.08–102.94	75.15–161.53	(Vallejo Toro et al. 2016)
	Certej, Romania	30.7–274	314–3497	10.5–106	0.05–1.21	25.5–467	35.4–379	–	(Kim et al. 2016)
Non-gold-mining effort	Ganga, India	126.8–196.1	–	9.5–79.0	–	148.8–211.4	12.7–84.0	137.3–201.2	(Pandey et al. 2014)
	Tigis River, Turkey	28.4–163.4	2.0–18.0	0.7–4.9	–	62.3–566.7	11.2–5076	60.1–2396	(Varol 2011)
	Sungai Buloh, Malaysia	32.3–54.4	–	0.2–0.5	–	32.0–43.4	27.4–55.5	65.2–152.7	(Nemati et al. 2011)
	Jialu River, China	40.0–96.4	2.39–14.57	2.1–3.6	0.046–0.19	14.8–51.2	8.8–107.6	42.4–210.0	(Fu et al. 2014)
	Yellow River, China	61.3–139.5	–	0.1–0.3	–	15.5–24.6	14.1–30.3	39.9–74.6	(Ma et al. 2016)
	Yangtze River, China	51.81–165.7	3.45–35.17	0.12–0.45	0.01–0.13	18.24–144.4	8.51–72.34	115.9–351.2	(Liu et al. 2018c)

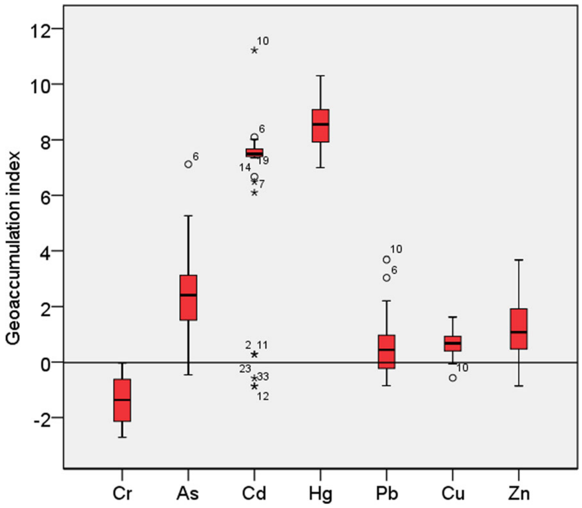

Fig. 3 Box-and-whisker plots for the I_{geo} of trace metals in sediments

metals were different (Hg > Cd > As > Zn > Cu > Pb > Cr). The median I_{geo} values for Cd and Hg were 7.49 and 8.56, respectively, presenting an extremely contaminated level. As and Zn led in moderately contaminated class, and Pb and Cu were the uncontaminated to moderately contaminated level. The highest mean I_{geo} value was shown in Cd (7.49) and Hg (8.56) which were above class 6 ($I_{geo} > 5$), indicating the river was heavily polluted by Cd and Hg. Previous studies revealed that the use of Hg in the amalgamation extraction process caused a large amount of AMD and waste effluents to be discharged to the Jiehe River from nearby gold mines or from large-scale mining and smelters/panning activities (Cai et al. 2017), resulting in the high accumulation of Hg, As, and Cd.

Ecological risks of trace metals in sediments

Based on the bioaccumulation and toxicity of trace metals on local biota, it is critical to evaluate the probable ecological risk of trace metals in sediment. Therefore, SQGs were applied to compare sediment contents of trace metals in contamination sediments with the corresponding standard values (Caeiro et al. 2005). The potential ecological risk index (PERI) of individual trace metal was evaluated to quantitatively assess their ecological risks.

Generally, SQGs can be widely applied to assess the sediment grade with contamination and contribute to understand sediment quality (Varol 2011). Table 4 listed the qualitative comparisons of trace metal concentrations

Table 4 Percentages of sediment samples below TEC, between TEC and PEC, and above PEC in the Jiehe River

SQGs	Cr	As	Cd	Hg	Pb	Cu	Zn
TEC	43.40	9.79	0.99	0.18	35.80	31.60	121.0
PEC	111.0	33.00	4.98	1.06	128.0	149.0	459.0
< TEC (%)	65.8	5.3	13.2	0.0	44.7	10.5	7.9
TEC-PEC (%)	34.2	15.8	0.0	0.0	44.7	39.5	73.7
> PEC (%)	0.0	78.9	86.8	100.0	10.6	50.0	18.4

in sediments with their consensus-based TEC and PEC values. The contents of Hg, Cd, As, and Cu were higher than their corresponding PEC with 100.0%, 86.8%, 78.9%, and 50.0%, respectively. These results indicated that all samples in the Jiehe River had Hg environmental risk and adverse effects on ecosystems. It also suggested that the majority of sites were affected by multiple trace metals (> 50%). Approximately 34.2% for Cr, 44.7% for Pb, 39.5% for Cu, and 73.7% for Zn were between the TEC and PEC values, indicating that Cr, Pb, and Zn may occasionally cause adverse effects on the environment, also implying Cr, Pb, and Zn have lower ecological risk than Hg, As, Cd, and Cu.

For the toxic risk, mPEC-Q was calculated and illustrated in Fig. 4. According to the results of this method, sediment sites are predicted to not have toxicity if mPEC-Q < 0.1; otherwise, sediment sites are considered to be toxic to ecological system (mPEC-Q > 1.0) (Long and Macdonald 1998a, b). In the present study, the calculated results of the mPEC-Q varied from 1.02 to 19.30 (Fig. 4). Therefore, all sediment samples were toxic to sediment-welling organisms (mPEC-Q of > 1.0). The result suggested that the combined trace metals' pollution is presented in Jiehe River sediments.

For ecological risk assessment, the PERI values of each sample sites ranged from 8380 to 183,276 with an average of 35,018 (Online Resource 1, Table S1). All sediment sample PERI values were much higher than 400, a high-risk criterion (Liu et al. 2018b), showing that a very high risk to the ecology was presented in Jiehe River sediments. The environmental risk of each metal in sediments was presented in Fig. 5. High concentrations or high toxic-response factor for single metals caused As, Cd, and Hg posed higher ecological risks than other metals. Particularly, the Er values for 100.0% of the Hg samples, 86.8% of Cd, and 15.8% of As presented above high risks ($160 \le Er < 320$). Approximately 34.2% As, and 15.8% Cu were at considerable risk ($80 \le Er < 160$). The highest Er values of As, Cd, and Hg presented at the J6 (576.25), J9 (107,455), and J9 site (75,556), respectively (Table S1). The high risk of As in the J6 site, in the vicinity of the agricultural land and rural areas, likely resulted from the abuse of

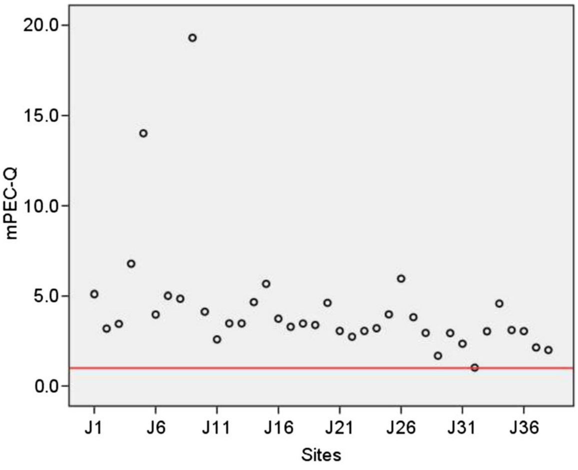

Fig. 4 The mPEC-Q of each sample site in Jiehe River (red line: mPEC-Q = 1)

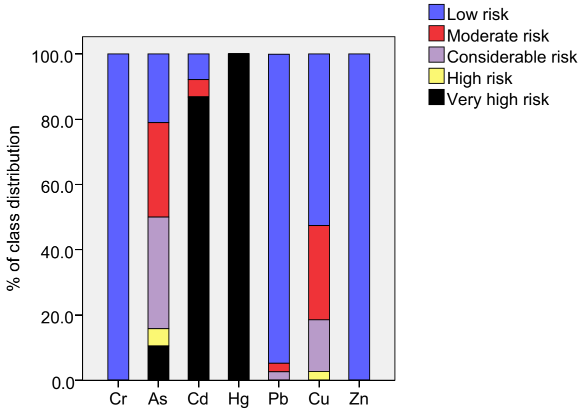

Fig. 5 Class distribution percentages for the ecological risk assessment of trace metals

fertilizer, metal-containing pesticides, and herbicides in agriculture. The Hg high environmental risk at the J9 site may be seriously influenced by the near-by gold mining industries. Therefore, the potential risk decreased in the following order: Hgs > Cd > As > Cu > Pb > Cr/Zn. The results were in accordance with previous research, indicating that the sediment pollution of trace metals in the river occurred downstream as far as the adjacent area of the Bohai Sea (Li et al. 2018; Zhang et al. 2014).

In summary, nearly identical results were obtained by different assessment methods. The same result showed all sites in the Jiehe River were heavily polluted by multi-metals, and the pollution degree and ecological risks of Hg, Cd, As, and Cu were much higher than those for Cr, Pb, and Zn.

Health risk evaluation of trace metals

The HQs and HI values higher than 1 suggest adverse health effects from trace metals occurring in sediment. In the present study, HQs and HI values in sediments were less than 1 (Table 5), suggesting non-carcinogenic health risk was present, and the risks through two pathways of ingestion or dermal contact of trace metal were low. In Table 4, the HI value for ingestion of sediment is 0.889. However, the HI value in the sediment is 3.11E-03 through the dermal contact pathway. Therefore, the non-carcinogenic health risk for ingestion was greater than for dermal contact, suggesting that the ingestion pathway contributed more to the health risks of trace-metal-contaminated sediment. Additionally, the sequence of the HQ values of ingestion is As > Hg > Cd > Pb > Cr > Cu > Zn. The results revealed the major contribution of health risks by As, Hg, and Cd through ingestion and dermal contact, while Cu and Zn were the minor components for the non-carcinogenic risks to humans. The main contributions of HI are from As, Hg, and Cd, and HQ values of As, Hg, and Cd are 0.69, 0.06, and 0.09, respectively. The HQ values remained contributed less to the HI value.

Source identification of trace metals in sediments

Correlation analysis

Correlations among trace metals in the studied area may represent the similar origin and transformation of these metals (Suresh et al. 2011). Metals revealing strong relationships may have common origins, similar migration behaviors with the changing physiochemical environment. If no relationship is found between two metals, the two metals will be not have many common factors (Kükrer et al. 2014). Positive correlations ($p < 0.01$) existed in the following metal pairs (Table 6): As-Pb (0.520), As-Cu (0.835), As-Zn (0.744), Cu-Zn (0.889), Cd-Hg (0.594), Cd-Pb (0.784), and Hg-Pb (0.607). Therefore, As, Cu, and Zn were found of a positive relationship among each other and might have common sources and transformation.

PCA results

PCA has been widely applied to further assist the source identification of trace metals in sediments (Jahan and Strezov 2018; Liu et al. 2018a; Xia et al. 2018). The meaning of Kaiser-Meyer-Olkin (KMO = 0.673) and Bartlett's sphericity tests ($p = 0$) was that trace metal

Table 5 Description of health risk evaluation for trace metals in the sediment

		Exposure assessment		Non-carcinogenic risk	
	RfD	Exp_{ing}	Exp_{derm}	HQ_{ing}	HQ_{derm}
Cr	3.00E-03	5.59E-05	1.96E-07	1.86E-02	6.52E-05
As	3.00E-04	2.06E-04	7.21E-07	6.87E-01	2.40E-03
Cd	1.00E-03	5.67E-05	1.98E-07	5.67E-02	1.98E-04
Hg	3.00E-04	2.62E-05	9.18E-08	8.75E-02	3.06E-04
Pb	3.50E-03	1.03E-04	3.60E-07	2.94E-02	1.03E-04
Cu	4.00E-02	3.22E-04	1.13E-06	8.04E-03	2.81E-05
Zn	3.00E-01	4.65E-04	1.63E-06	1.55E-03	5.42E-06
$HI_{ing/derm}$				8.89E-01	3.11E-03

Table 6 Pearson's correlation result of trace metals in the sediments

	Cr	As	Cd	Hg	Pb	Cu	Zn
Cr							
As	0.361*						
Cd	−0.019	0.037					
Hg	−0.049	0.173	0.594**				
Pb	0.167	0.520**	0.784**	0.607**			
Cu	0.366*	0.835**	−0.114	0.134	0.389**		
Zn	0.364*	0.744**	−0.142	0.081	0.273	0.889**	

* Significant at $p < 0.05$ levels. ** Significant at $p < 0.01$ levels

concentrations in surface sediments in Jiehe River were suitable for PCA analysis.

Table 7 listed the results of PCA using a varimax rotation process for trace metals and Fig. 6 illustrated the variation diagram in a rotated space. The initial dimensions of 38 in the data reduce to three PCs by PCA which explain 87.91% of the data variation. PC 1 was heavily loaded with Cu, Zn, and As which explained 45.82% of the total variance and showed an eigenvalue of 3.207. PC 2 explained 30.51% and had a strong correlation with Cd (0.921), Pb (0.886), and Hg (0.820). PC 3 explained 11.58% and was strongly relevant with Cr (0.954).

Sources identification

Three main sources could be certified by the previously mentioned correlation, PCA, and the spatial distribution analyses of trace metals in surface sediments, i.e., (1) As, Cu, and Zn mostly originated from agricultural sources; (2) Cd, Hg, and Pb directly originated from industrial and mining efforts; and (3) Cr mainly produced by natural sources.

Based on PC 1 analysis, As, Zn, and Cu exhibit a high CV indicating anthropogenic activities were the primary source because the mean concentrations were higher than their ASVs and SBVs. The correlation analysis showed strong relativity among the As, Cu, and Zn, with similar spatial distribution trends. Previous studies revealed that the trace metal was a threat to human life in agricultural areas due to the abuse of agricultural pesticides and chemical fertilizers (Kalaivanan and Ganeshamurthy 2016; Rai et al. 2016). The main human origin of Cu in agricultural soils was the application of Cu-based agrochemicals and phosphate fertilizers (Micó et al. 2006). Inorganic As compounds were widely applied in insecticides, herbicides, and pesticides to

Table 7 PCA analysis result of trace metals in the sediments of the Jiehe River

Metals	Rotated component matrix		
	PC 1	PC 2	PC 3
As	*0.883*	0.201	0.171
Cu	*0.961*	0.054	0.127
Zn	*0.928*	−0.024	0.130
Cd	−0.182	*0.929*	0.075
Hg	0.114	*0.813*	−0.168
Pb	0.334	*0.882*	0.132
Cr	0.252	−0.007	*0.954*
Initial eigenvalues	3.207	2.136	0.811
% of variance	45.82	30.51	11.58
Cumulative %	45.82	76.33	87.91

Italic data are the main contribution elements to factor

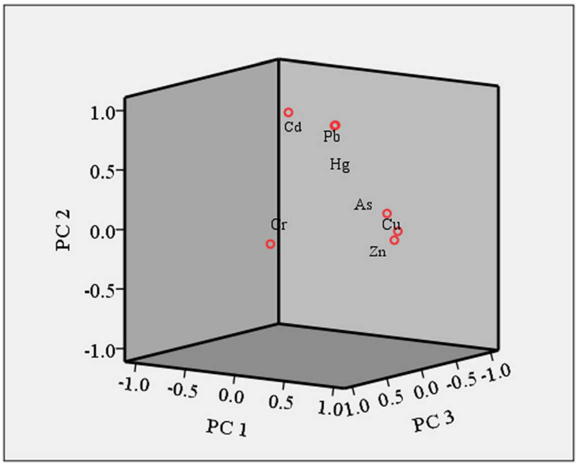

Fig. 6 Loading plot of the PCA of trace metals in the sediment of the Jiehe River

improve insecticidal effort (Cai et al. 2015). Chen et al. (2018) also reported that the average total input amount of Cu and Zn annually (mg/m^2/a) from the agricultural fertilizer were 13.313 and 2.376, respectively. There was a large scale wheat, maize, and vegetables in the study area, so the application of fertilizers and pesticides may be the primary source of Cu, Zn, and As. Thus, the first component can be defined as the agricultural component.

The PC2 consisted of Cd, Hg, and Pb, which can be considered as the industrial component. The highest concentration of Cd, Hg, and Pb at the J9 site, which was near the gold production industry of the Jinchiling gold mine, indicating their main source was from mining and smelting industries. The I_{geo} of Cd and Hg were above class 6 and were higher than their background values. High concentrations of Hg, Cd, and Pb were found in soils, sediments, and waters in the vicinity of mining activities (Marrugo-Negrete et al. 2017; Morton-Bermea et al. 2014; Strzebońska et al. 2017). Therefore, Cd, Hg, and Pb were possibly caused by anthropogenic inputs from upstream gold smelting industries in this study because small-scale gold mining often employs the immature amalgamation technique (Esdaile and Chalker 2018). Trace metals delivered by AMD, mining influent, and tailing were first transferred into water through sorption and precipitation processes, and then the metals were delivered to the sediments in the Jiehe River. Consequently, Cd, Hg, and Pb might mainly originate from mining and smelting activities.

For the PC 3, the Cr did not cause pollution. The concentration of Cr was slightly close to the ASVs. Furthermore, the $I_{geo,}$ SQGs, and Er results suggested that the contents of Cr revealed a low or zero potential ecological risk. These results indicated that Cr might produce from natural sources.

Conclusion

The river sediments were heavily contaminated with As, Cd, and Hg with the developing mining technology and agricultural activity in past decades. The contents of trace metals showed heterogeneity in the spatial distribution. By assessing trace metals in sediment, the potential ecological risks of Hg, Cd, As, and Cu in sediments were shown to be at high-risk levels and were harmful to sediment-dwelling organisms. The evaluation of possible human health risks suggested that low non-carcinogenic health risk existed for exposure to sediment via ingestion or dermal contact. Source identification revealed that trace metals in sediments mainly originated from gold mining discharges, industrial effluents, and agricultural activities.

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