Environmental Earth Sciences (2018) 77:569
https://doi.org/10.1007/s12665-018-7750-6

ORIGINAL ARTICLE

Distribution, ecological risk, and source analysis of heavy metals in sediments of Taizihe River, China

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Received: 26 January 2018 / Accepted: 9 August 2018 / Published online: 14 August 2018
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Abstract

Heavy metal contaminants can enter the water system through the hydrological cycle, after a period of flocculation and sedimentation, and finally accumulate in the sediments of the receiving water body. Sediment samples were collected along the Taizihe River, the concentration and ecological risks of Zn, Cu, Pb, Cr, As, and Cd were detected and evaluated, and the pollution sources was analyzed through principal components analyses. The results indicated that As, Pb, and Cd were the main heavy metal contaminants in the sediment from Taizihe River, and all the monitored sites in the wet and dry season exceed PEC value. In addition to Zn, the average concentrations of the rest of the heavy metals in the dry season were higher than that in the wet season, and most of the heavy metals showed a certain accumulation tendency from upstream to downstream. The level order of potential ecological risk was Cd > As > Pb > Zn > Cu > Cr, and the risk in dry season was higher than that in wet season. Among them, As, Cd, and Pb had the highest single potential ecological risk coefficient (E_r^i), which occupied the dominate position of total risk. The potential ecological risk of most heavy metals in the dry season was higher than that in the wet season. The sources of heavy metal pollution in the sediments of the Taizihe River in different periods were the same, mainly from industrial pollution, especially from the petrochemical, electroplating industries, and mining. The heavy metal pollution in the Taizihe River was located in the middle and lower reaches of the cities, and has a certain relationship with the factories in the lower reaches of nearby city. During the dry season, the contribution rate of industrial pollution sources to heavy metals was more significant.

Keywords Taizihe River · Sediment · Heavy metal · Ecological risk · Source analysis

Introduction

As the wide range of sources, difficult to degrade, easy to accumulate in the environment, and toxic to organisms and human, heavy metals are considered one of the most important pollutants in the environment. Heavy metal pollutants can enter the water system through the hydrological cycle, after a period of flocculation and sedimentation, and accumulate in the sediments of the receiving water body finally. The concentration of heavy metals in sediments is generally several orders of magnitude higher than that in water body (Jia et al. 2000), and heavy metals does not degrade and migrate during in the natural degradation processes. Instead, heavy metal can be accumulated and stored in the sediment for a long-term. After a series of physical, chemical, biological effects, and the food chain delivery processes, heavy metals can continue to endanger the ecological environment of water and human health ultimately (Kaushik et al. 2009; Shang et al. 2012). Therefore, the study of heavy metal concentration, distribution, and risk assessment in the sediments is an effective means to understand the status of heavy metal pollution in water, which can reflect the degree of pollution of human activities (Niu et al. 2014; Song et al. 2014). The evaluation of heavy metal pollution in river sediments has become a hot issue in current research on water environment.

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Ecological risk is the risk that ecosystems and their components can bear, and it refers to the possible effects of uncertainties or disasters on ecosystems and their components in a given area (De Lange et al. 2010). The results of these effects may lead to damage to ecosystems structure and function, thereby endangering the safety and health of ecosystems (Liu et al. 2017; Effendi et al. 2016). At present, the ecological risk assessment has been used widely in the United States, the United Kingdom, the Netherlands, and other countries. However, risk assessment work started in China lately; the research on theoretical and technical is still relative weak, which lead to difficult to applied to risk management and environmental impact assessment systematically (Zeng et al. 2017; Zhang and Liu 2010; Power and McCarty 2002). Hakanson index, a widely used method for ecological risk assessment, is to eliminate regional differences and heterogeneous pollution effects through comparing with the regional background values, and considering the toxicity, migration law and the sensitivity of the region to heavy metal (Hakanson 1980; Yang et al. 2017). In recent years, there were more researches on the pollution level and ecological risk of heavy metals in river sediments were reported, but the diagnosis of pollution sources has just attracted attention (He et al. 2015; Bing et al. 2016; Li et al. 2013). Some scholars have analyzed the sedimentary behavior, ecological risk, and pollution sources of heavy metals in some reservoirs (Zhang et al. 2016; Zhu et al. 2017), rivers, lakes, and estuary in China (Wang et al. 2014, 2015; Chen et al. 2016; Han et al. 2016). Li et al. (2017) report the spatial distribution, ecological risk, and pollution source of heavy metals in the Mining Area in Henan province of China, also Ke et al. (2017) analyzed the ecological risk and main sources of heavy metals of Liaohe river of China. However, as the late start of related research in China, the basic data and pollution status of rivers in the heavy industry area is insufficient or unknown, further relevant research is urgently needed.

As the main tributary of the Liaohe River of China, Taizihe River is the living water sources of Benxi, Liaoyang, Anshan, and other heavy industrial cities. With the development of industries such as steel, smelting, and electroplating, a large amount of heavy metal-containing waste water is discharged into the river, causing pollution of the Taizihe River water (Fan et al. 2015). Previous studies pay more attention to water pollution of Liaohe or estuaries (He et al. 2015), which lack to heavy metal of Taizihe river (Wan et al. 2013; Song et al. 2010). Shao and Zhao (2012) analyzed and detected the level of heavy metals in Taizihe River and evaluated their potential ecological risks. However, there are few reports on the distribution characteristics of different water season, and the sources of pollution are not clear and available. Up until now, no systematic or integrated research has focused on the ecological risk assessment of heavy metal contamination in the Taizihe River. In this study, the sediment samples of the Taizihe River were collected in different water season; the pollution level and potential ecological risk were evaluated by analyzing the contents of heavy metals, and we tried to analyze the pollution sources through applying the principal component analysis of SPSS software. The results will provide a scientific basis for water resource protection and governance management.

Materials and methods

Study area and sampling

Taizihe River flows from east to west through Benxi, Liaoyang, and Anshan cities with a total length of 464 km, which is one of the important river systems in the Liaohe River Basin. The basin area is 4000 km^2 with an average annual runoff of 26.86×10^8 m^3. The rapid urbanization and industrialization along the Taizihe River basin have further compounded the pressure on the sewerage system, and ultimately domestic sewage and industrial effluents are discharged in the river. Water consumption of Taizihe River accounted for 70% of the total water consumption in Liaoning Province, which has formed the most serious water shortage area in Liaoning province. Furthermore, large number of forested area have been deforested because of mining activities for coal production and mineral exploration in the upper part of Taizihe River Basin. Due to these activities, the river basin can be associated with toxic metals, ionized substances and biodegradable municipal wastes. At present, as the dramatic impact of human activities on the land, Taizihe River Basin has been to the most serious water pollution and ecosystem damage areas in Liaohe River Basin. In dry season and wet season, 24 water samples (Fig. 1) were collected along the Taizihe River and its main tributary. The distribution of the sampling sites is shown in Fig. 1. The sampling sites were selected based on the importance of tributary for contributing to the river flow. They are Guanyinge reservoir (site 1), Xiaoshi (site 2), Taizihe bridge (site 3), Yangshuquan (site 4), Fatai bridge (site 5), wucenglazi (site 6), Sanjiazi bridge upstream (site 7), Sanjiazi bridge tributary (site 8), Sanjiazi bridge downstream (site 9), Benxi Electrical and Mechanical Engineering School (site 10), Benxi vocational and technical schools (site 11), Beitai bridge (site 12), Lanhe bridge (site 13), Shenwo reservoir (site 14), Meihualing (site 15), Xishuangmiaoling (site 16), Taizihe River Park (site 17), Xiaolinzi (site 18), Tangmazhai (site 19), Shijiawopeng (site 20), Xiaojiemiao (site 21), Jiaxinzi (site 22), Sanchahe (site 23), and Guchengzi (site 24).

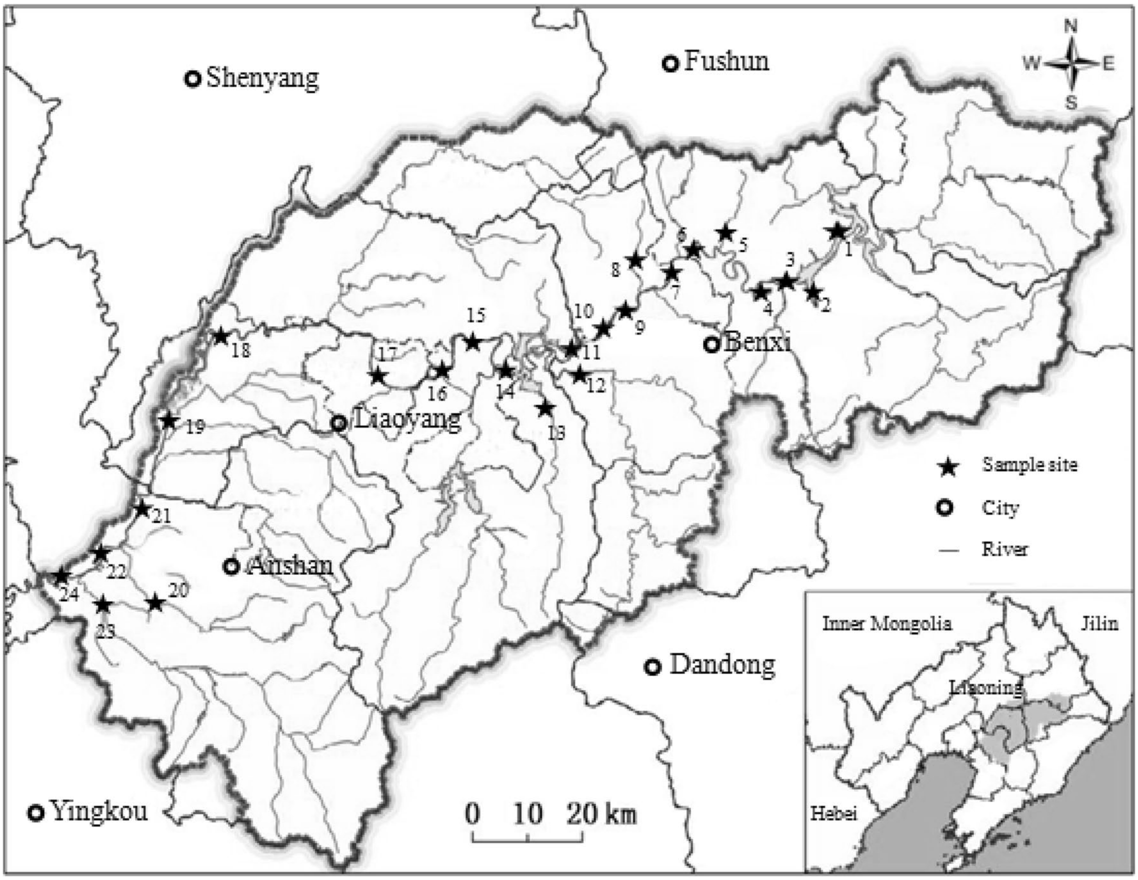

Fig. 1 Location of sample sites from Taizihe River

Chemical analysis

The 0–5 cm surface sediment of the river was collected by using the grab-type mud collection device and taken back to the laboratory after sealing with polyethylene self-sealing bag. After air-drying, debris such as stones and leaves were removed, and then the sample was divided into 2–3 parts for grinding, sieving, and finally several grinding samples were mixed and saved. After digesting, the samples were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). First, weigh the pretreated sample 0.100 g in the polytetrafluoroethylene digestion tank and add 10 mL water, then add 1 mL $HClO_4$ and 2 mL HF. And then, take the assemble digestion tank into a microwave digestion (set at 120 °C, 150 °C and 180 °C for 15 min and 900 W in both time and power). Second, take the digestion solution onto the temperature control board (130 °C) steam for 60 min, after that, volume to 25 mL volumetric flask with deionized water. All samples were analyzed in duplicate and the metal concentration in several blanks was determined. The results of the duplicate analyses revealed an excellent reproducibility of the equipment. The recovery percentage of the external standard ranged between 90 and 120% for all the elements. The limits of detection were Pb 10 μg/L, Cd 0.3 μg/L, Cu 2 μg/L, Cr 1 μg/L, Zn 1 μg/L and As 1 μg/L; the relative standard error of each group of samples is not more than 10%. To ensure the validity of data and the accuracy and precision of analysis methods, the reference materials were adopted [As: GBW(E)080390; Cr: GBW(E)080403; Cd: GBW(E)080401; Pb: GBW(E)080399; Cu: GBW(E)080396; Zn: GBW(E)080400]. All chemical analytical results of this study were performed by quality control system, which includes reagent blanks, replicate samples and certified international reference materials.

Potential ecological risk assessment

The sediment quality guidelines (SQGs) provided a simple, comparative mean for assessing the risk of contamination in an aquatic ecosystem (Macdonald et al. 2000). In this study, two types of limit values were applied to evaluate the potential risk of the ecosystem, based on the concentration of pollutants, threshold effect concentration (TEC) and probable effect concentration (PEC) (Feng et al. 2011). The concentrations below the TEC represent a minimal-effect range, which is intended to estimate the conditions where biological effects are rarely observed (Suresh et al. 2015). The concentrations equal to or greater than the TEC, but less than the PEC represent a range where biological effects occasionally occur. The concentrations above the PEC represent a probable effect range where adverse biological effects frequently occur (Zhang et al. 2013).

Investigations of heavy metal concentrations in surface sediments reveal a degree of pollution over freshwater ecosystems. The effect and degree of the heavy metal pollution over river sediments were characterized by the Hakanson index (Hakanson 1980). The methodology was developed by Hakanson to assess eco-risks for aquatic pollution control, which is based on the assumption that the sensitivity of the aquatic system depends on its productivity. The ecological factor (E_{r}^{i}) and potential eco-risk index (RI) of heavy metals were calculated by this method. The potential eco-risk of a given contaminant is calculated as the follow formula:

$$E_{\mathrm{r}}^{i} = T_{\mathrm{r}}^{i} \times C_{\mathrm{f}}^{i}; \quad C_{\mathrm{f}}^{i} = C_{\mathrm{D}}^{i}/C_{\mathrm{R}}^{i};$$

$$C_{\mathrm{d}} = \sum_{i-1}^{m} C_{\mathrm{f}}^{i}; \quad \mathrm{RI} = \sum_{i=1}^{m} E_{\mathrm{r}}^{i},$$

where E_{r}^{i} is the toxic-response factor for a given substance; C_{f}^{i} is the contamination factor (a ration between reference records and present concentrations values in sediments); Cd is contamination degree of multiple metals; C_{D}^{i} is measured concentrations of samples; and C_{R}^{i} is the reference records. The toxic-response factor T_{r}^{i}, which accounts for the toxic requirement and the sensitivity requirement, is described as Cd (30) > As (10) > Cu = Pb (5) > Cr (2) > Zn (1) after a series statistic and standardization considering the pollution characteristics. RI is the sum of the individual potential risks is the potential risk for the sediment. The soil background of concentration in sediments (Ke et al. 2017) for As, Zn, Cu, Pb, Cr and Cd, were 8.8 mg/kg, 63.5 mg/kg, 19.8 mg/kg, 21.4 mg/kg, 57.9 mg/kg, and 0.11 mg/kg, respectively. Ecological risk assessment criteria for heavy metal are listed in Table 1.

Table 1 Indices and corresponding degree of potential ecological risk assessment (Hakanson 1980)

E_{r}^{i}	Grade of ecological risk of single metal	RI	Grade of ecological risk of the environment
$E_{\mathrm{r}}^{i} < 40$	Low	$\mathrm{RI} < 150$	Low
$40 \le E_{\mathrm{r}}^{i} < 80$	Moderate	$150 \le \mathrm{RI} \le 300$	Moderate
$80 \le E_{\mathrm{r}}^{i} < 160$	Considerable	$300 \le \mathrm{RI} \le 600$	Considerable
$160 \le E_{\mathrm{r}}^{i} < 320$	High	$\mathrm{RI} \ge 600$	Very high
$E_{\mathrm{r}}^{i} \ge 320$	Very high		

Low, most underwater organisms can tolerate; moderate, sediment can be contaminated, benthic organisms can be effected; high, interfere and damage the activities of benthic organisms significantly; very high, affect the health of benthic communities seriously

Statistical analysis

Data were analyzed by using SPSS 20.0 software. Correlation and principal components analyses (PCA), the most common multivariate statistical methods, were used to check for significant relationships among heavy metals in the sediment samples. The various statistical methods were performed with a 95% confidence interval (significance $p < 0.05$).

Results and discussion

Distribution and pollution level

The distribution characteristics of heavy metals in the sediment of the Taizihe River are shown in Fig. 2. In the wet season, the concentration scale of As in Taizihe River was 404.3–1470.3 mg/kg, with the average concentrations as high as 673.8 mg/kg. It can be noted that the highest value appeared in the Shenwo reservoir, the lowest value appeared in the Tazihe River Bridge. According to the comparison with the consensus-based sediment quality guideline values (Table 2), As concentration at all sites exceeded the PEC value (33 mg/kg), and the highest value was more than 44 times. The concentration scale of Zn in Taizihe River was 113.0–5630.0 mg/kg, with the average concentrations as high as 2293.2 mg/kg. It can be noted that the highest value appeared in the Jiaxinzi; the lowest value appeared in Guchengzi. Zn concentration at 54.2% sites exceeded the PEC value (459 mg/kg), and the highest value was greater than 12 times. The concentration scale of Cu in Taizihe River was 46.5–298.5 mg/kg, with the average concentrations as high as 86.3 mg/kg. It can be noted that the highest value appeared in the Shenwo reservoir, the lowest value appeared in Meihualing. Except Xiaoshi and Shenwo reservoir, the contents of Cu at the rest sites were no more than the PEC

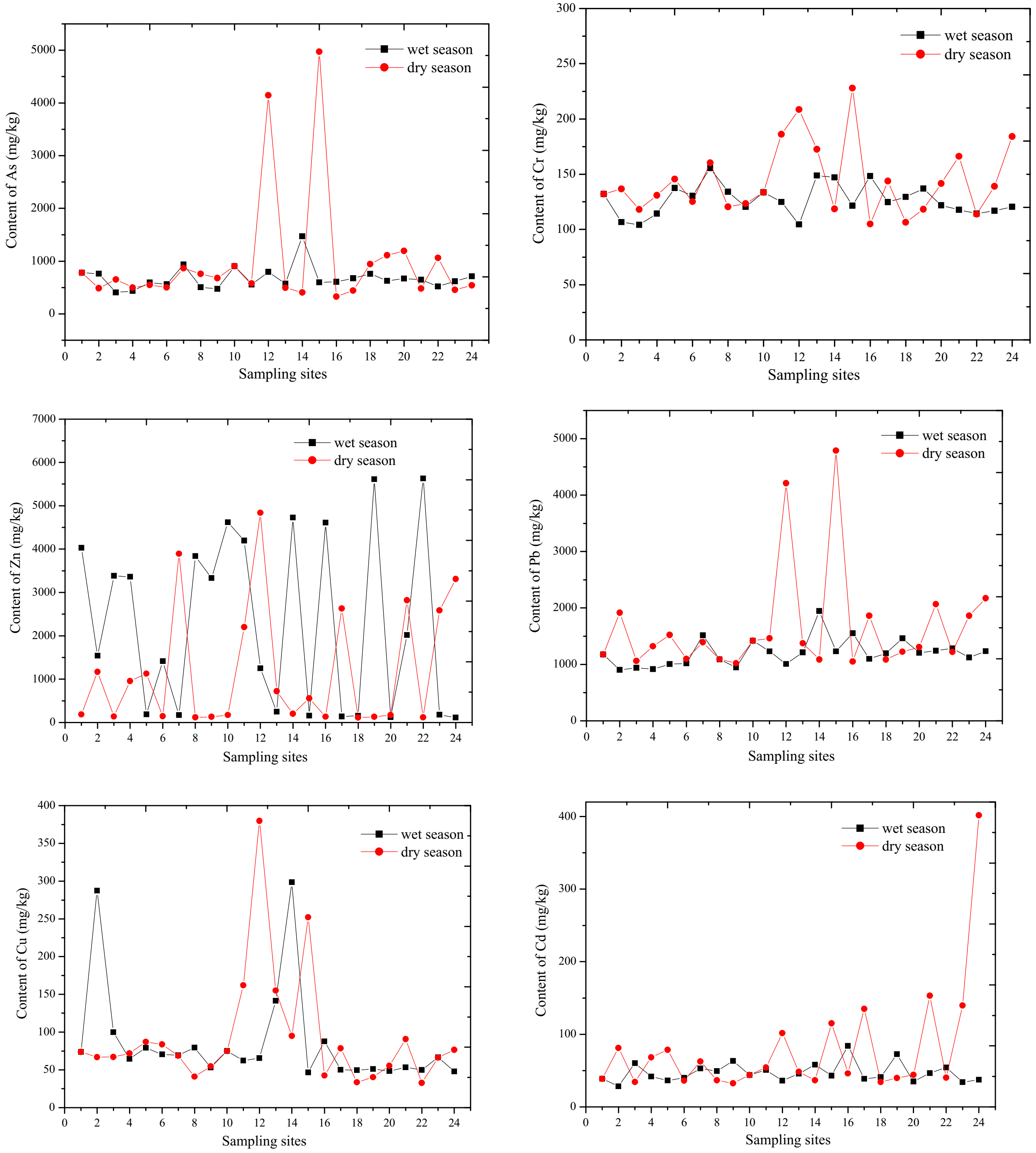

Fig. 2 Content and distribution of heavy metals in sediment

value (149 mg/kg). Cu in the sediment showed a decreased tendency from upstream to downstream. The concentration scale of Pb in Taizihe River was 903.5–1944.9 mg/kg, with the average concentrations as high as 1206.4 mg/kg. It can be noted that the highest value appeared in the Shenwo reservoir, and the lowest value appeared in Xiaoshi. Pb concentration at the all sites exceeded the PEC value (128 mg/kg), and the highest value was greater than 15 times. Pb in the sediments showed an increased tendency from upstream to downstream. The concentration scale of Cr in Taizihe

Table 2 Consensus-based sediment quality guideline values and content range of heavy metals from Taizihe River (mg/kg)

	As	Zn	Cu	Pb	Cr	Cd
TEC	9.79	121	31.6	35.8	43.4	0.99
PEC	33	459	149	128	111	4.98
Wet						
Range	404.3–1470.3	113.0–5630.0	46.5–298.5	903.5–1944.9	104.2–155.5	28.4–84.0
Average	673.8	2293.2	86.3	1206.4	127.0	47.2
Dry						
Range	325.3–4970.0	115.1–4837.5	32.7–379.8	1021.8–4787.5	104.9–227.9	32.7–401.8
Average	977.3	1181.5	98.9	1662.1	146.6	78.6
Wet						
> PEC	100%	54.2%	8.3%	100%	87.5%	100%
Dry						
> PEC	100%	50%	16.7%	100%	95.8%	100%

River was 104.2–155.5 mg/kg, with the average concentrations as high as 127.0 mg/kg. It can be noted that the highest value appeared in the Sanjaizi Bridge, the lowest value appeared in Taizihe Bridge. Cr concentration at 87.5% sites exceeded the PEC value (111 mg/kg), and the highest value was more than 1.4 times. The concentration scale of Cd in Taizihe River was 28.4–84.0 mg/kg, with the average concentrations as high as 47.2 mg/kg. It can be noted that the highest value appeared in the Xishungmiao, the lowest value appeared in Xiaoshi. Cd concentration at all sites exceeded the PEC value (4.98 mg/kg), and the highest value was more than 16 times.

In the dry season, the concentration scale of As in Taizihe River was 325.3–4970.0 mg/kg, with the average concentrations as high as 977.3 mg/kg. It can be noted that the highest value appeared in the Meihualing, the lowest value appeared in the Xishuangmiao. According to the comparison with Table 2, As concentration at all sites exceeded the PEC value (33 mg/kg), and the highest value was greater than 150 times. The concentration scale of Zn in Taizihe River was 115.1–4837.5 mg/kg, with the average concentrations as high as 1181.5 mg/kg. It can be noted that the highest value appeared in the Beitai Bridge, the lowest value appeared in Xiaolinzi. Zn concentration at 50% sites exceeded the PEC value (459 mg/kg), and the highest value was more than 10 times. The concentration scale of Cu in Taizihe River was 32.7–379.8 mg/kg, with the average concentrations as high as 98.9 mg/kg. It can be noted that the highest value appeared in the Beitai Bridge, the lowest value appeared in Jiaxinzi. Cu concentration at 16.7% sites exceeded the PEC value (149 mg/kg). The concentration scale of Pb in Taizihe River was 1021.8–4787.5 mg/kg, with the average concentrations as high as 1662.1 mg/kg. It can be noted that the highest value appeared in the Meihualing, the lowest value appeared in Sanjiazi Bridge. Pb concentration at the all sites exceeded the PEC value (128 mg/kg), and the highest value was more than 37 times. The concentration scale of Cr in Taizihe River was 104.9–227.9 mg/kg, with the average concentrations as high as 146.6 mg/kg. It can be noted that the highest value appeared in the Meihualing, the lowest value appeared in Xishuangmiao. Except Xishuangmiao and Xiaolinzi, Cr concentrations at the rest sites all exceed the PEC value (111 mg/kg), and the highest value was more than two times. The concentration scale of Cd in Taizihe River was 32.7–401.8 mg/kg, with the average concentrations as high as 78.6 mg/kg. It can be noted that the highest value appeared in the Guchengzi, the lowest value appeared in Sanjiazi Bridge. Cd concentration at all sites exceeded the PEC value (4.98 mg/kg), and the highest value was more than 80 times.

In general, the main heavy metal contaminants in the Taizihe River sediment were As, Pb and Cd, and all the monitoring sites in the wet and dry season exceeded the PEC value. Followed by was Cr, and 84–92% sites exceeded the PEC value. Shao and Zhao (2012) noted that the main heavy metal pollutants in the Taizihe River were Cd and Zn. Except Shenwo reservoir and Xiaoshi in the wet season, Cu contents did not exceed the PEC value at other sites. The content of Cu, Pb, and Cr at middle stream showed higher than upper and lower downstream. The content of Cd showed a gradual increased trend from upstream to downstream. The range of Zn content varied greatly, the lowest value was 113.0 mg/kg and the highest value was 5630.0 mg/kg. In addition to Zn, the highest values of other heavy metals were appeared in the upstream in the wet season, such as Xiaoshi and Taizihe Bridge. Except Cr, the highest values of other heavy metals were appeared in the middle and lower reaches in the dry season, such as Shenwo reservoir, Xishuangmiao and Jiaxinzi. In the dry season, the minimum and maximum values of all monitored heavy metals all occurred in the middle and lower reaches. Perhaps, there was a certain accumulation tendency of the heavy metals from upstream to downstream, or downstream industrial enterprises pollutants input to the river. In addition to Zn, the average concentration of other heavy metals in the dry season was higher than that in the wet season, which may be explained by the decrease of the amount of water and self-purification reduced in the dry season. According to compare with some other rivers (Table 3), it was noted that the contents of As, Pb, and Zn in Taizihe River were relatively high. Among them, the content of Cd was less than that of the Haihe River Basin, and higher than some other rivers. The content of Cr was less than that of the Yuexi reservoir and Moshui Lake, and was slightly higher than other rivers. The content of Cu was the same as some other rivers. In general, the content of heavy metals in the rivers from China was higher than that of foreign rivers. As the heavy industrial cities, Taizihe River accepts petrochemical, pharmaceutical companies, metal smelting, and other industrial sewage, which lead to a higher heavy metal content than other rivers.

Ecological risk level of heavy metals in sediment

Using the Hakanson potential risk index method, single potential ecological risk coefficient (E_r^i) and the potential ecological risk index (RI) were calculated. The risk index and the risk distribution are presented in Table 4 and Fig. 3, respectively. From Table 4 and Fig. 3, the heavy metals in the sediments showed a high ecological risk at all sites monitored, among which the highest values appeared in the Jiaxinzi (site 22), followed by the Guchengzi (site 24) and Xiaolinzi (site 18) with the comprehensive risk value (RI) more than 40,000. As and Cd were in a very high-risk level ($E_r^i > 320$) in both wet and dry season. Zn and Cu showed the low, moderate or considerable risk level at all the sites in the wet season and dry season. Pb showed the high or very high-risk level ($160 < E_r^i < 320$ or $E_r^i > 320$) at all the sites in the wet or dry season. Cr was in a slight risk level ($E_r^i < 40$) at most sites. Therefore, the potential ecological risks in the sediments of the Taizihe River were very high risk for As and Cd, high risk for Pb, moderate or low risk for Cu and Zn, light risk for Cr, and the RI values of the six kinds of heavy metals were all more than 600. The level order of potential ecological risk was Cd > As > Pb > Zn > Cu > Cr, and the risk in the dry season was higher than that in the wet season.

Pollution source analysis of heavy metals

Based on the statistical analysis of the heavy metal content in the Taizihe River, the correlation among the heavy metal was analyzed and the Pearson correlation coefficient was calculated. The results are presented in Table 5. In the regression matrix, the correlation of As–Cu and As–Pb was strong, and the correlation coefficients were 0.576 and 0.795, respectively, which reached the extremely significant level ($p < 0.01$). The correlation between Cr–As and Cr–Cd was also significantly correlated ($p < 0.05$). It was noted that the change of concentration between them was

Table 3 The highest concentration of heavy metals in different rivers

Indicators no.	Concentration value (mg/kg)						References
	As	Pb	Cd	Cr	Cu	Zn	
1	24.80	30.00	0.90	83.00	35.00	112.00	Liu et al. (2014)
2	42.4	176.8	2.2	28.8	32.5	–	Xing et al. (2008)
3	3.905	–	–	56.80	44.09	–	Cai et al. (2007)
4	–	473.05	4.55	330.47	612.53	1460.63	Ning et al. (2009)
5	24.8	157.82	195765.83	152.73	178.61	1076.25	Liu et al. (2014)
6	–	220	–	1779	1249	1337	Liu et al. (2008)
7	29.9	98	3.4	205	129.9	1142	Yang et al. (2009)
8	–	113	0.33	73.7	54.6	83.1	Zhang and Shan (2008)
9	–	62	3.84	–	6495	439	Dauvalter and Rognerud (2001)
10	–	3600	25,320	–	–	–	Arnason and Fletcher (2003)
11	–	75.3	8.38	19.13	35.03	101.7	Singh et al. (2005)
12	–	85		–	280	221	Tang et al. (2008)
13	–	98.5	2.1	–	90.1	305	Farkas et al. (2007)
14	–	189	4.3	23.4	420.8	708.8	Olivares-Rieumont et al. (2005)
15	–	68.4	1.13	–	48.2	245.2	Martin (2004)
16	1470.3	1944.9	84	155.5	298.5	5630	This study
17	4970	4787.5	401.8	227.9	379.8	4837.5	This study

1 is Baiyangdian lake, China; 2 is Human reservoir, China; 3 is Yanghe reservoir, China; 4 is Guangdong reservoir, China; 5 is Haihe River Basin, China; 6 is Moshui lake, 7 is Yangtza river, China; 8 is Huaihe river, China; 9 is Pasvik River, Northern Fennoscandia; 10 is Patroom Reservoir, USA; 11 is Gomti River, India; 12 is Victoria Harbour, Hong Kong; 13 is Po River, Italy; 14 is Almendares River, Cuba; 15 is Lahn River, German; 16 and 17 are this study

Table 4 Individual risk coefficient (E_r^i) and comprehensive risk index (RI) of heavy metals

Sites	Season	Single risk coefficient (E_r^i)						RI
		As	Zn	Cu	Pb	Cr	Cd	
1	Wet	886.9	63.5	18.6	274.6	4.6	10,561.4	11,809.6
	Dry	886.9	2.9	18.6	274.6	4.6	11,617.5	12,805.2
2	Wet	864.5	24.2	72.5	211.1	3.7	7731.8	8907.8
	Dry	550.0	18.4	16.9	447.3	4.7	24,390.0	25,427.3
3	Wet	459.4	53.3	25.2	219.6	3.6	16,397.7	17,158.8
	Dry	741.2	2.2	16.9	248.2	4.1	10,305.0	11,317.6
4	Wet	493.2	53.0	16.3	214.3	3.9	11,427.3	12,208.0
	Dry	565.6	15.0	18.1	308.5	4.5	20,445.0	21,356.8
5	Wet	673.9	3.0	20.0	235.2	4.8	9900.0	10,836.9
	Dry	620.7	17.7	22.0	355.5	5.0	23,632.5	24,653.5
6	Wet	636.6	22.2	17.8	237.7	4.5	10,868.2	11,787.0
	Dry	569.0	2.3	21.1	256.5	4.3	10,830.0	11,683.3
7	Wet	1061.4	2.7	17.5	354.1	5.4	14,427.3	15,868.4
	Dry	983.0	61.3	17.3	324.9	5.5	18,810.0	20,202.1
8	Wet	574.7	60.4	20.1	254.3	4.6	13,459.1	14,373.2
	Dry	863.1	1.8	10.4	254.8	4.2	10,965.0	12,099.3
9	Wet	535.2	52.4	13.4	220.9	4.2	17,290.9	18,117.0
	Dry	768.5	2.0	13.8	238.7	4.3	9795.0	10,822.3
10	Wet	1027.6	72.8	18.9	331.5	4.6	11,986.4	13,441.8
	Dry	1027.6	2.8	18.9	331.5	4.6	13,185.0	14,570.4
11	Wet	631.3	66.1	15.7	287.4	4.3	13,847.7	14,852.5
	Dry	712.8	15.3	55.9	413.2	7.1	18,712.5	19,916.8
12	Wet	904.0	19.7	16.5	235.3	3.6	9859.1	11,038.2
	Dry	654.3	34.7	40.9	342.2	6.4	16,297.5	17,375.9
13	Wet	649.7	3.9	35.7	283.3	5.1	12,422.7	13,400.4
	Dry	4707.4	76.2	95.9	983.6	7.2	30,450.0	36,320.3
14	Wet	1670.7	74.5	75.4	454.4	5.1	15,872.7	18,152.8
	Dry	562.8	11.4	39.2	320.8	6.0	14,542.5	15,482.5
15	Wet	678.1	2.5	11.7	287.6	4.2	11,747.7	12,731.8
	Dry	458.8	3.1	24.0	253.4	4.1	10,950.0	11,693.4
16	Wet	691.5	72.6	22.1	362.7	5.1	22,909.1	24,063.1
	Dry	5647.7	8.7	63.7	1118.6	7.9	34,522.5	41,369.1
17	Wet	765.1	2.2	12.7	256.9	4.3	10,561.4	11,602.6
	Dry	369.6	2.1	10.7	245.6	3.6	13,845.0	14,476.7
18	Wet	863.4	2.4	12.5	279.7	4.5	11,222.7	12,385.2
	Dry	502.0	41.4	19.8	434.8	5.0	40,560.0	41,563.0
19	Wet	711.6	88.4	12.9	342.1	4.7	19,793.2	20,952.9
	Dry	1072.2	1.8	8.5	253.4	3.7	10,290.0	11,629.6
20	Wet	760.5	1.9	12.2	281.6	4.2	9552.3	10,612.7
	Dry	1262.8	2.1	10.1	286.3	4.1	11,880.0	13,445.4
21	Wet	736.9	31.8	13.5	290.5	4.1	12,675.0	13,751.8
	Dry	1357.1	2.7	14.0	304.8	4.9	13,267.5	14,951.0
22	Wet	591.5	88.7	12.6	299.8	3.9	14,802.3	15,798.8
	Dry	543.8	44.4	22.9	482.9	5.7	45,892.5	46,992.2
23	Wet	701.4	2.8	16.8	262.0	4.0	9300.0	10,287.0
	Dry	1206.8	1.9	8.3	285.5	3.9	12,037.5	13,543.8
24	Wet	807.7	1.8	12.1	288.1	4.2	10,193.2	11,307.1
	Dry	518.8	40.7	16.7	435.2	4.8	41,872.5	42,888.7
Sum	–	45529.1	1279.8	1127.3	15965.7	225.4	777,904.2	–

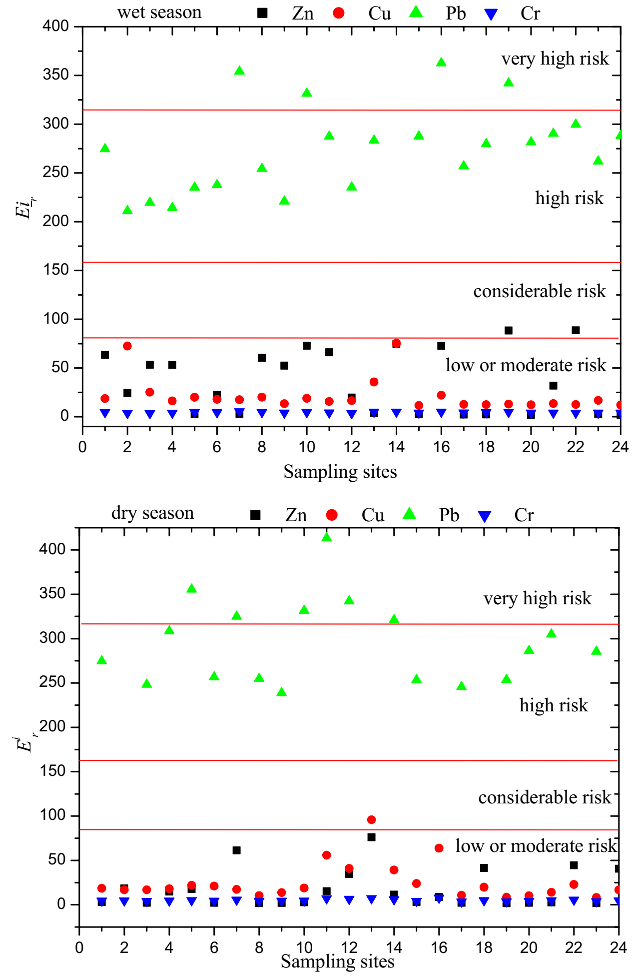

Fig. 3 Ecological risk of Zn, Cu, Pb, and Cr in wet and dry season

very similar, and there was significant correlation between heavy metal elements, indicating that As, Cu, and Pb elements might be complex pollution relationship or homology (Sun et al. 2010). In the dry season, in addition to Cd, the correlation between the other five heavy metals was strong, which reached a significant level ($p < 0.01$). The correlation of Cd–Cr and Cd–Zn was strong, and the correlation coefficients were 0.430 ($p < 0.05$) and 0.627 ($p < 0.01$), respectively. However, Cd was not related to other heavy metals except Cr and Zn. The strong association of Cr and Cd indicates that they are derived from industrial waste especially from mining, metal smelting and electroplating industry (Wuana and Okieimen 2011).

For the composition analysis, the PCA of heavy metal concentration was carried out by using the maximum variance rotation method. It is useful to reduce the dimensions of multivariate data and its problem (Petersen et al. 2001). It also provides information about important parameters present in the whole data set which is advantageous to reduce insignificant parameters from monitoring stations (Shreshtha and Kazama 2007). The loading factors extracted by PCA analysis at different periods are presented in Table 6. Considering the total contribution rate of should be more than 80%, the three and two principal components were extracted in wet and dry season, respectively.

In the wet season, three principle components (PCs) were obtained to explain 81.161% of the total variance of the system where 46.635% of variance explained by PC1 followed by 22.149% by PC2 and 16.377% by PC3, respectively (Table 6). For this study, the loadings of PCs above 0.8 are considered for explanation. The loadings of the PCs for first three components explained 86.732% of variance which has been used in Fig. 4. It is useful to evaluate compositional relationship and grouping pattern between variables. It is

Table 5 Correlative analysis of the heavy metals in the wet and dry season in sediment

	Zn	As	Cu	Pb	Cr	Cd
Wet season						
Zn	1.000					
As	−0.102	1.000				
Cu	−0.061	0.576**	1.000			
Pb	−0.016	0.795**	0.663**	1.000		
Cr	−0.019	0.403*	0.118	0.334	1.000	
Cd	0.086	−0.049	−0.035	0.203	0.396*	1.000
Dry season						
Zn	1.000					
As	0.694**	1.000				
Cu	0.618**	0.698**	1.000			
Pb	0.918**	0.884**	0.787**	1.000		
Cr	0.674**	0.593**	0.552**	0.786**	1.000	
Cd	0.627**	0.055	0.103	0.389	0.430*	1.000

*Indicates $p < 0.05$, **indicates $p < 0.01$

Table 6 The load factors of PCA extracted of heavy metals in sediments

Components	Wet season			Dry season	
	PC1	PC2	PC3	PC1	PC2
Zn	−0.093	0.312	**0.934**	**0.922**	0.237
As	**0.890**	−0.190	0.004	**0.841**	−0.409
Cu	**0.760**	−0.346	0.167	**0.794**	−0.376
Pb	**0.921**	−0.040	0.117	**0.991**	−0.081
Cr	0.539	**0.600**	−0.244	**0.826**	0.121
Cd	0.206	**0.845**	−0.096	0.471	**0.860**
Variation contribution/%	42.635	22.149	16.377	67.916	18.754
Cumulative variance contribution/%	42.635	64.784	81.161	67.916	86.670
Sources	Petrochemical	Electroplating	Mining	Petrochemical	Electroplating

The bold values are greater than 0.5, which meant that provide a significant contribution relatively

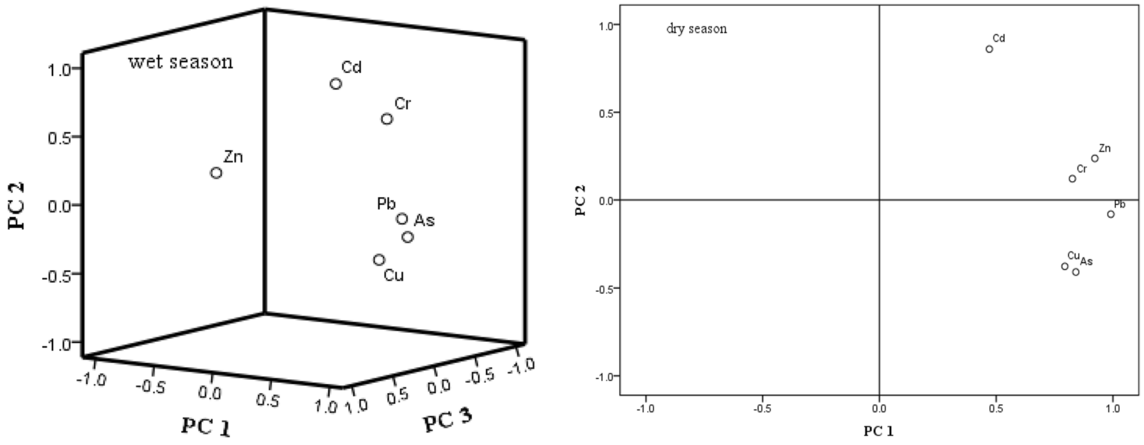

Fig. 4 The load map of the principal components in wet and dry season

generally believed that Cu, Cd, Zn, Cr, and Pb in soil and sediment mainly come from anthropogenic sources (Simeonov et al. 2000; Thuong et al. 2013). Studies showed (Li et al. 2009; Zhao et al. 2010) that heavy metals such as As, Cu and Pb are produced in the use of metal smelting, petrochemicals industry and traffic source. The load of As, Cu and Pb in PC1 is relatively high, and investigations have found that there are more petrochemical near the Taizihe River or near the tributaries (Fig. 5). The heavy metals such as arsenic, copper, and lead in PC1 are mainly derived from petrochemicals and metal smelting. As the sewage disposal, rain washed away, solid wastes dumping, and the deposition process of the atmosphere, the heavy metals can be discharged into the river body and accumulated in sediment after migration, adsorption, and sedimentation. Therefore, PC1 is mainly derived from petrochemical pollution sources. Cd is mainly used for batteries, metal surface treatment, pigment and stabilization agent in plastics and in alloys (Lindström 2001; Ke et al. 2017), while PC2 has higher loading of Cr and Cd, so PC2 represents the source of electroplating industrial pollution. Depending on surveys, Zn resources are abundant in the Benxi area. The mining process and the erosion of water flow will lead to the accumulation of Zn in the surrounding environment. Therefore, PC3 represents the mining source. Therefore, the main source of heavy metal pollution in the Taizihe River in the wet season was the industrial pollution, especially the petrochemical pollution, electroplating industry pollution, and mining source.

In the dry season, a total of two principal components were extracted, to explain the 67.916 and 18.754% of the variation information, respectively. The loadings of the PCs for first three components explained 86.670% of variance which has been employed. The loads of Zn, As, Cu, Pb, and Cr in PC1 were higher, which related to industrial pollution source, especially for the petrochemical pollution and metal smelting sources as the representative of As and Pb. The loads of Cd in PC2 were higher, which may be mainly related to the electroplating industry.

Whether in the wet or dry season, the high concentration of heavy metal occurred at the downstream section

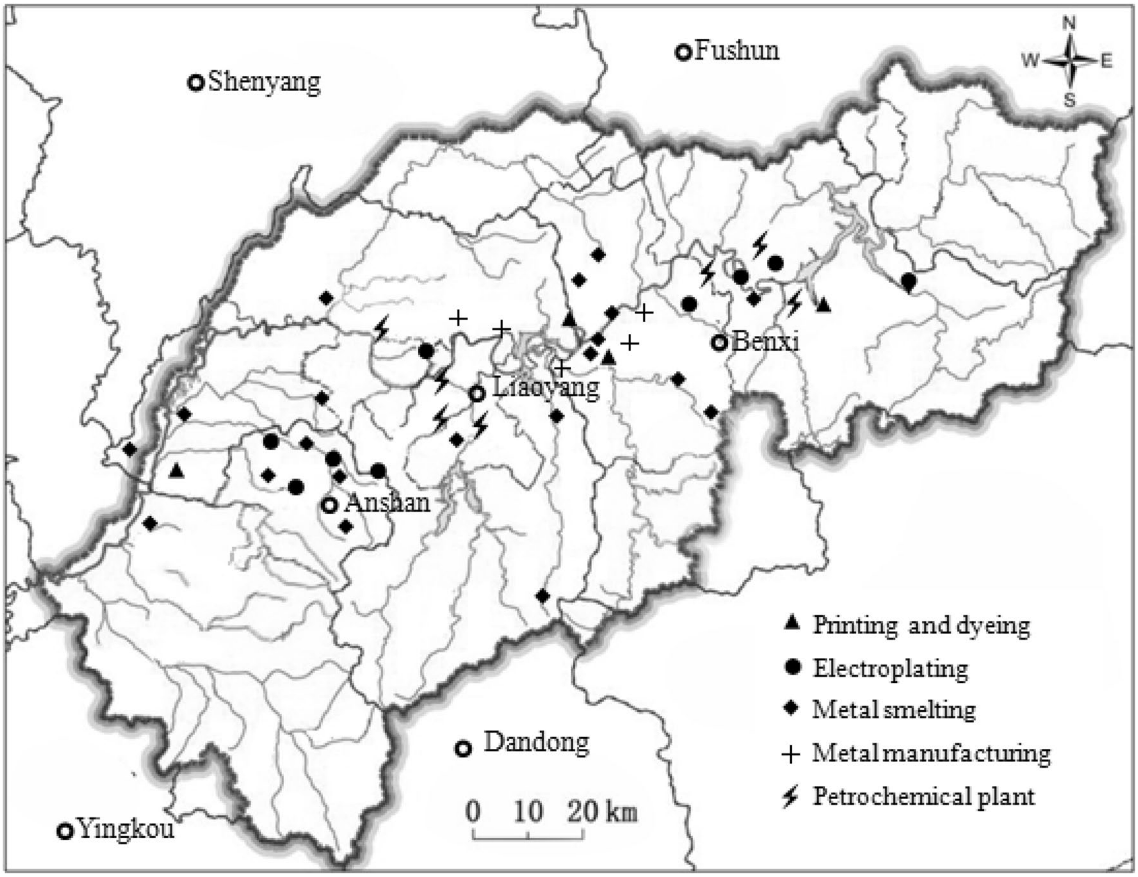

Fig. 5 The industrial layout map in the Taizihe River Basin

of the Benxi city and Liaoyang city, which may be relate to the petrochemical and metal smelting industries of downstream of the cities (Xia et al. 2011). Figure 5 shows the location of the factories near the Taizihe River Basin, where the point source pollution industries such as metal manufacturing, petrochemicals and printing are distributed. The metal manufacturing industry would develop a large amount of wastewater, waste gas, and solid waste in metallurgy and parts manufacturing. Wastewater discharge would result in the increase of heavy metals in water bodies and sediments, and the waste gas would also carry a large number of heavy metal elements and enter the soil and water bodies through atmospheric deposition process (Chen et al. 2016). Heavy metals in solid waste will also get into the water body as rainwater rushes. Printing and electroplating can also produce large amounts of waste water containing heavy metals. In addition to the heavy use of pesticides in agricultural production, heavy metal elements can enter the water through surface runoff and subsurface infiltration. In addition, there is zinc ore, metallurgical plants, electroplating factories, pharmaceutical factories and paper mills along the Taizihe River in Benxi City. Also, there are metal smelters, petrochemical plants, printing plants, and metal parts manufacturers along the rivers in Liaoyang City and Anshan City. Most of the factories are located on the shoreline of the Taizihe River and nearby areas, and a few are located in the tributaries of the Taizihe River. In fact, some mining sites or an industry releasing the particular metal are just at the vicinity of the river, which may be the reason for increasing heavy metals in sediment. As a result, the mainly pollution source of heavy metals in Taizihe River was industry, especially mining, metal smelting, and electroplating industry. During the wet season, with the water flow increases, rainwater scours, and removes surface sediment, which causes migration and release of heavy metal elements from the sediment to the water. In the dry season, with the reduction of water flow rate, heavy metal in the water will be absorbed and accumulated in the sediment. Due to the difference of flow runoff in the different seasons, the river dilution capacity in the wet season is higher than that in the dry season, so the pollution of the industrial source in the dry season is obvious.

Conclusions

According to analyzing the concentration and assessed the ecological risk of six heavy metals of sediment from Taizihe River Basin, the conclusions were listed as follows:

1. As, Pb, and Cd were the main heavy metal contaminants in the Taizihe River sediment. In addition to Zn, the average concentrations of the rest of the heavy metals in the dry season were higher than that in the wet season, and most of the heavy metal showed a certain accumulation tendency from upstream to downstream. Compared with some other rivers, the content of As, Pb, and Zn in Taizihe River was relatively high.
2. The level order of potential ecological risk was Cd > As > Pb > Zn > Cu > Cr, and the risk in the dry season was higher than that in the wet season. Among them, As, Cd, and Pb had the highest single potential ecological risk coefficient (E_r^i), which occupied the dominate position of total risk. The potential ecological risk of most heavy metals in the dry season was higher than that in the wet season.
3. The sources of heavy metal pollution in the sediments of the Taizihe River in different periods were the same, mainly from industrial pollution, especially from the petrochemical, metal smelting, and electroplating industries. The heavy metal pollution in the Taizihe River was located in the middle and lower reaches of the cities, and has a certain relationship with the factories in the lower reaches of each city. During the dry season, the contribution rate of industrial pollution sources to heavy metal was more significant.

Acknowledgements This work was financially supported by the National Natural Science Foundation of China (41301573), the Doctor Scientific Research Foundation (054-55440109010), and the outstanding scholar plan (054-91400114007) and Ecological Environment Research Center Director Fund (EERC-T-201501) of Shenyang Normal University.

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