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Research Article

Contamination and Ecological Risk Assessment of Heavy Metals in Surface Sediments of Huangshui River, Northwest China

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In the Xining area of Huangshui River, China, the concentrations of globally alarming toxic heavy metals such as chromium (Cr), arsenic (As), lead (Pb), cadmium (Cd), and zinc (Zn) in the surface sediments were measured to determine the ecological risks to the riverine ecosystem. Overall, the concentrations of heavy metals in the surface sediments were relatively high. The results indicated that the concentrations of Pb/Zn/Cr were lower than 120/250/200 $mg\cdot kg^{-1}$ which was the risk screening value of each heavy metal for soil contamination of agricultural land (GB15618-2018). The concentrations of As/Cd were higher than 120/3.0 $mg\cdot kg^{-1}$ which was the risk intervention value of As/Cd for soil contamination of agricultural land (GB15618-2018). Their values were arranged in the following decreasing order: As (151.23–818.55 $mg\cdot kg^{-1}$) > Cr (44.18–201.70 $mg\cdot kg^{-1}$) > Pb (29.10–121.95 $mg\cdot kg^{-1}$) > Zn (1.45–86.18 $mg\cdot kg^{-1}$) > Cd (4.36–6.21 $mg\cdot kg^{-1}$). The concentrations of As, Cr Pb, and Cd greatly exceeded the background contents of elements in Qinghai soils. While Zn was lower than background. The contamination factor (CF), the geoaccumulation index (I_{geo}), and the potential ecological risk index (RI) of As, Cr, Cd, and Pb followed the descending order of Cd > As > Pb > Cr > Zn. The order of the enrichment factor (EF) was as follows: As > Cd > Pb > Cr > Zn. The contamination level of heavy metals implied that the condition is frightening and probably severely affecting the aquatic ecology. Cd and As were the main contributing elements to the ecological risk of the sediments in the Xining area of the Huangshui River, which should be mainly studied and prevented.

1. Introduction

River serves a set of economic, cultural, and ecological functions such as transportation, ecotourism, aquaculture, agriculture, ecological habitat, and ecological defense impacts. However, human activities have a significant negative impact on the river shore regions and aquatic resources. The input of many bioaccumulative and persistent pollutants from anthropogenic activities might cause serious ecosystem issues [1–3]. Many rivers have been continuously threatened by various contaminants [4, 5]. In a consequence of their nonbiodegradation, biomagnification, and toxicity, heavy metals are considered as one of the world's most hazardous contaminants in the riverine aquatic environment [2, 6, 7]. In fact, different studies were performed on heavy metal accumulation in subsurface sediment and in many biochemical cycles [8–10].

Huangshui River is one of the most important rivers in the northeastern part of Qinghai Province. The water quality and quantity of Huangshui River is the research focus of many scholars. The research on the Huangshui River water body mostly focuses on the water quality of the river and the spatial and temporal distribution of pollutants [11–14]. Li et al. studied the impact of Huangshui River water quality on benthic fauna during the process of urbanization and analyzed the impact of water quality on the ecological environment from the perspective of biological habitats [15, 16].

There are few studies on the Huangshui River sediments. Chen and Huang studied the macroelement geochemical characteristics of the Huangshui River sediments from Huangyuan to Ledu and analyzed the relationship between chemical weathering index and regional natural climatic conditions [17, 18]. Zeng studied the overall situation of

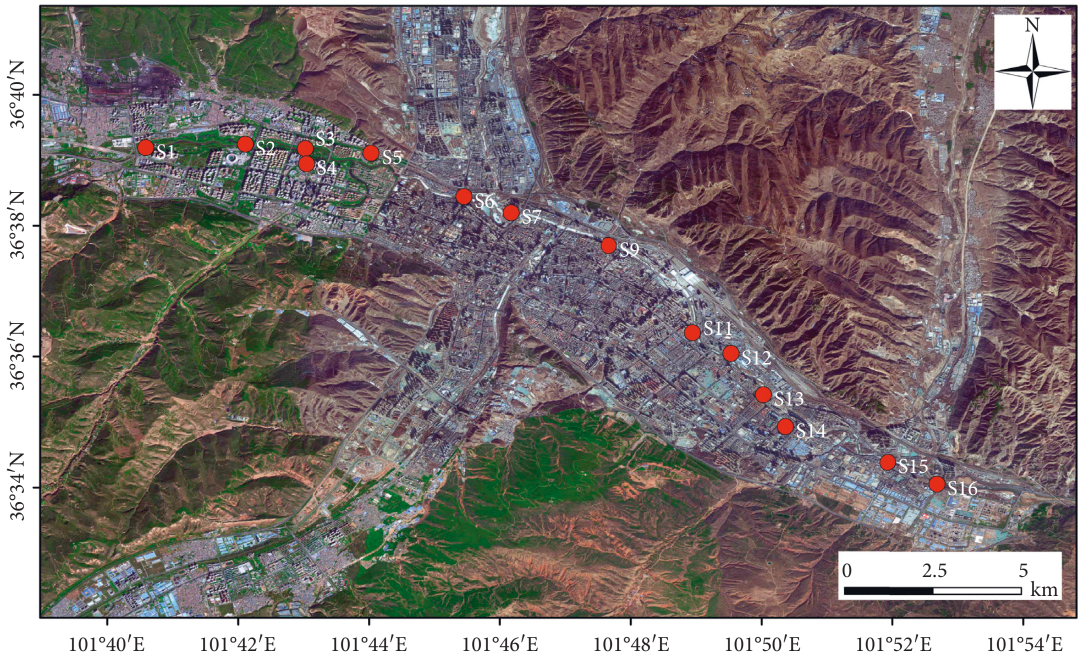

Figure 1: Sampling sites of Huangshui River.

heavy metal pollution along the Huangshui River by measuring the heavy metal content in the surface sediments and river water and the surface soil of the Huangshui River in Xining [19]. Few relevant studies have been conducted in the region; the studies that have been conducted have focused on a few areas. These indicated that the research on heavy metals in river sediments is not well studied.

Unlike some organic pollutants that can be partly degraded, many of the heavy metals accumulated in sediments for a long period pose severe toxicity risks. In addition, when water environmental conditions change, they will be released into water again, causing secondary pollution of water [20]. River sediment is the source and sink of heavy metals and other pollutants in the water environment. It is complex and essential for the ecosystem health, which deserves more investigations. The study fully considered the occurrence, spatial distribution, pollution status, and ecological risk of heavy metals in river sediments. It could reveal the migration and transformation of heavy metals between river water and sediments [21], help people better understand the change of the characteristics of heavy metals in the water environment, and provide a basic understanding of heavy metal pollution control in rivers.

2. Materials and Methods

2.1. Study Sites and Samples. Huangshui River is a tributary of the upper reaches of the Yellow River. It originates from Baohutu Mountain in Haiyan County, Qinghai Province, northwest of China. It has a wide valley and pleasant climate, giving birth to the plateau civilization for thousands of years. The narrow Huangshui River valley is home to nearly 60% of the population, 52% of the cultivated land, and more than 70% of the industrial and mining enterprises in Qinghai Province. Therefore, Huangshui River is called the "Mother River" of Qinghai Province. It is one of the main sources of the Yellow River. Some areas are 2000–4000 m above the sea level. The climate of the Huangshui River basin has the continental characteristics of plateau drought and semi-drought, and the average annual temperature is 2.8–7.9°C, the precipitation is 360–540 mm, and evaporation is 1100–1800 mm. The precipitation from May to September accounts for 81–88% of the annual precipitation.

Based on the characters of land form and intersection of the main stream and tributaries, Xining area of Huangshui River basin was investigated. To collect the inshore sediment samples, 16 sampling points were selected using the global positioning system (GPS) at 1.4 km interval going upstream to downstream (Figure 1) in 2018. The name of sampling stations was marked S1–S16 (Table 1).

Due to the actual terrain conditions, sampling point S8 was too deep to get the sample. Sampling point S10 was in the underground river of the Xining railway station area. No samples were collected. So, a total of 14 sediment samples were collected.

About 1 kg of surface sediments (at a depth of 0–10 cm) from the Huangshui River were collected at each sampling point with plastic spade, which were stored in clean and sterile polyethylene bags and then carried to the laboratory.

2.2. Sample Pretreatment and Instrumental Analysis. After removing foreign objects (leaves, rocks, snails or shells, and plant roots), sediment samples were dried naturally in the laboratory at room temperature and then were processed for grain size analysis. The sediment sample were passed through a 100-mesh sieve for analysis.

1 g of each sample was digested in 25 mL Teflon crucibles on the electric heating plate in mixed solution of HCl-

Table 1: Description of sampling points in the Huangshui River.

Sample number	Latitude	Longitude	Sampling position
S1	36°39′12″ N	101°40′35″ E	Xining Special Steel Park
S2	36°39′15″ N	101°42′6 E	Haihu Wetland Park
S3	36°39′11″ N	101°43′1″ E	Western Suburb Park
S4	36°38′57″ N	101°43′2″ E	Haihu Middle School
S5	36°39′7″ N	101°44′2″ E	Culture Park
S6	36°38′27″ N	101°45′27″ E	People's Park
S7	36°38′12″ N	101°46′10″ E	Local Police Station of Qilian road
S9	36°′42″ N	101°47′40″ E	Morning Market of Wuyi road
S11	36°36′22″ N	101°48′57″ E	Lianhe Village Mosque
S12	36°36′3″ N	101°49′32″ E	Huangzhong Road
S13	36°35′25″ N	101°50′2″ E	Bridge of Minhe Road
S14	36°34′56″ N	101°50′22″ E	Jingxifeng Wetland Park
S15	36°34′23″ N	101°51′56″ E	Tuanjieqiao Market
S16	36°34′3″ N	101°52′41″ E	Ninghu Wetland Park

HNO_3-HF-$HClO_4$, according to the National Standards of People's Republic of China (HJ 832–2017). The concentrations of As, Cr, Zn, Pb, and Cd in sediments were determined by the atomic absorption spectrophotometer (AAS, TAS-990, Beijing General Analysis).

Three parallel samples were used for all samples to control the relative error of each sediment sample which was less than 10%. Moreover, statistical analysis was performed by SPSS 2019. Origin 2019 was used for data visualization.

2.3. Pollution and Ecological Risk Assessment. The contamination factor (CF), enrichment factor (EF), and geo-accumulation index (I_{geo}) are used to assess the pollution and enrichment levels of heavy metal. Potential ecological risk index (RI) was used as pollution indices to assess ecological risks of heavy metals.

2.3.1. Contamination Factor (CF). The contamination factor (CF) is the ratio of the concentration of heavy metals and the background value in the soil. It was introduced by Hakanson and used to describe the contamination level of a substance [22].

$$CF_i = \frac{C_i}{B_i}, \tag{1}$$

where CF_i is the contamination factor for pollutant, C_i is the concentration of the heavy metal in the sediment sample (mg·kg^{-1}), and B_i is the background concentration for this heavy metal (background contents of elements in soils of Qinghai Province, Table 2) (mg·kg^{-1}).

There are four grades of CF: low degree ($CF_i < 1$), moderate degree ($1 < CF_i < 3$), substantial degree ($3 < CF_i < 6$), and very high degree ($CF_i > 6$) [23].

2.3.2. Enrichment Factor (EF). The enrichment factor is considered as a normalized method to indicate differential variability of heavy metals in sediments from the anthropogenic and natural metal sources [24]. This involves the standardization of heavy metals in sediment with reference elements such as aluminum (Al), iron (Fe), manganese (Mn), titanium (Ti), selenium (Se), lithium (Li), and cesium (Cs) [25–27]. In this study, Li was been chosen to normalize metal concentration because it basically comes from natural sources. The following equation is used to define the normalized EF of heavy metals:

Table 2: The background concentrations of heavy metals in Qinghai Province.

Heavy metals	Cr	As	Pb	Cd	Zn
Background concentrations (mg·kg^{-1})	70.1	14	20.9	0.137	80.3

$$EF_i = \frac{(C_i/[Li])_{sample}}{(B_i/[Li])_{background}}, \tag{2}$$

where C_i is the concentration of the heavy metal in the sediment sample (mg·kg^{-1}), and B_i is the background concentration for this heavy metal (mg·kg^{-1}). Background contents of elements in soils of Qinghai Province were used to calculate. There are five categories of contamination recognized: moderate enrichment ($2 < EF < 5$), moderately severe enrichment ($5 < EF < 10$), severe enrichment ($10 < EF < 25$), very severe enrichment ($25 < EF < 50$), and extremely high enrichment ($EF > 50$) [28].

2.3.3. Geoaccumulation Index (I_{geo}). The geoaccumulation index was suggested by Muller [29]. It is a geochemical approach for estimating the enrichment of metal concentrations above background or baseline concentrations. Studies have shown that it is an efficient tool for characterizing the sediment pollution levels.

The geoaccumulation index (I_{geo}) indicates the pollution by heavy metals. It is calculated as follows:

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n}, \tag{3}$$

where C_n and B_n are the heavy metal concentrations in sample (mg·kg^{-1}) and its geochemical baseline concentration (mg·kg^{-1}), respectively. The constant factor 1.5 is introduced to minimize the effect of possible variations in the

Table 3: The concentrations of heavy metals in the sediments of Huangshui River (mg·kg^{-1}).

Site	Cr		As		Pb		Cd		Zn	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
S1	63.55	0.40	414.93	0.07	80.05	0.07	6.21	0.11	27.70	0.26
S2	44.18	0.45	151.23	0.14	42.75	0.23	5.74	0.03	6.95	0.07
S3	82.68	0.40	425.83	0.25	91.30	0.15	4.53	0.22	35.78	0.09
S4	77.35	0.42	464.20	0.23	29.10	0.09	4.39	0.13	86.18	0.08
S5	86.03	0.12	498.55	0.22	85.80	0.11	4.50	0.13	17.95	0.03
S6	139.85	0.22	499.38	0.41	89.20	0.14	4.36	0.11	34.23	0.08
S7	198.13	0.56	671.05	0.16	106.25	0.15	4.68	0.23	5.90	0.23
S9	190.90	0.29	788.35	0.54	115.60	0.51	4.71	0.33	5.13	0.11
S11	138.75	0.28	473.48	0.33	94.35	0.77	4.80	0.08	2.78	0.08
S12	200.20	0.22	818.55	0.32	116.00	0.08	4.82	0.12	3.50	0.11
S13	201.70	0.45	718.98	0.15	121.95	0.06	5.10	0.08	5.60	0.25
S14	186.25	0.35	532.78	0.14	88.95	0.38	5.09	0.06	3.00	0.11
S15	157.95	0.02	293.90	0.24	54.50	0.44	4.91	0.07	1.60	0.09
S16	161.25	0.21	362.58	0.28	57.00	0.22	5.15	0.04	1.45	0.10

geochemical background values, which may be attributed to mineralogical variations in the sediments [30]. The geochemical baseline concentrations of heavy metals in study area were referred to background contents of elements in soils of Qinghai Province [31]. Degrees of contamination are typically divided into six classifications based on I_{geo} values [32]. Classification I ($I_{geo} < 0$) represents unpolluted, classification II ($0 \leq I_{geo} < 1$) represents unpolluted to moderated polluted, classification III ($1 \leq I_{geo} < 2$) represents moderated polluted, classification IV ($2 \leq I_{geo} < 3$) represents moderate to heavily polluted, classification V ($3 \leq I_{geo} < 4$) represents heavily polluted, classification VI ($4 \leq I_{geo} < 5$) represents heavily to extremely polluted, and classification VII ($I_{geo} \geq 5$) represents extremely polluted.

2.3.4. Potential Ecological Risk Index (RI). Ecological risk index (RI) is a sedimentological approach for ecological assessment using a diagnostic tool developed by Hakanson [22]. This method not only pays attention to the amount of heavy metals but also combines the ecological effect with the toxicology. Therefore, it can intuitively show the toxicity of heavy metals and its harm to biology. The calculation of RI is on the basis of the assumption that the sensitivity of the aquatic system depends on its productivity. It can be determined through the following formula:

$$C_f^i = \frac{C^i}{C_n^i},$$
$$E_r^i = T_r^i \times C_f^i, \quad (4)$$
$$\mathrm{RI} = \sum E_r^i,$$

where C_f^i represents the contamination factor, C^i is the concentration of the heavy metal (mg·kg^{-1}), and $C_n{}^i$ is background values (mg·kg^{-1}). If $E_r{}^i < 45$, $RI < 150$, it is ranked as low risk; if $45 \leq E_r{}^i < 90$, $150 < RI < 300$, it is moderate potential ecological risk; if $90 \leq E_r{}^i < 180$, $300 < \mathrm{RI} < 600$, it is considerable potential ecological risk; if $180 \leq E_r{}^i < 360$, it is ranked high potential ecological risk; if $E_r{}^i \geq 360$, $RI > 600$, it may cause a very high risk for environment. $T_r{}^i$ is the toxic response factors (Cd: 30; Cr: 2; Pb: 5; Zn: 1; As: 10) [33].

3. Results and Discussion

3.1. Concentrations and Spatial Distribution of Heavy Metals. Table 3 provides the concentrations of 5 heavy metals in 14 surface sediments from Xining area of Huangshui River. Among the sampling sites, a broad range of heavy metal concentrations was observed. The spatial distribution of As, Cr, and Pb exhibited the similar trend (Figure 2).

The variation of As concentration was 151.23–818.55 mg·kg^{-1}, with an average of 508.13 mg·kg^{-1}. The concentration of As in all sampling points of sediment was higher than the risk intervention values for soil contamination of agricultural land (GB15618-2018) [34] seriously and generally increased first and then decreased, with a sharp decline at sampling points S2 and S11 (Figure 2(a)). However, the concentration of As was still in a high range, and the pollution of As in the sediments of Huangshui River was very serious.

Cr concentrations varied in the range of 44.18–201.70 mg·kg^{-1}, which were lower than the risk screening values for soil contamination of agricultural land. In the Xining area of Huangshui River, the concentration of Cr in sediment gradually increased. From sampling site S6, it increased significantly and maintained a high concentration level within a certain distance, while at sampling site S11, it decreased significantly (Figure 2(b)). The concentration of Pb varied in the range of 29.10–121.95 mg·kg^{-1}, which was lower than the risk screening values for soil contamination of agricultural land. Its variation trend was basically the same as that of As and Cr. The concentration at sampling site S11 decreased significantly. During sampling site investigation, it was found that there were construction projects in the middle reaches, which may be the cause of lead pollution.

The concentration of Zn was lower than the background value of soil content in Qinghai Province and the risk screening values for soil contamination of agricultural land.

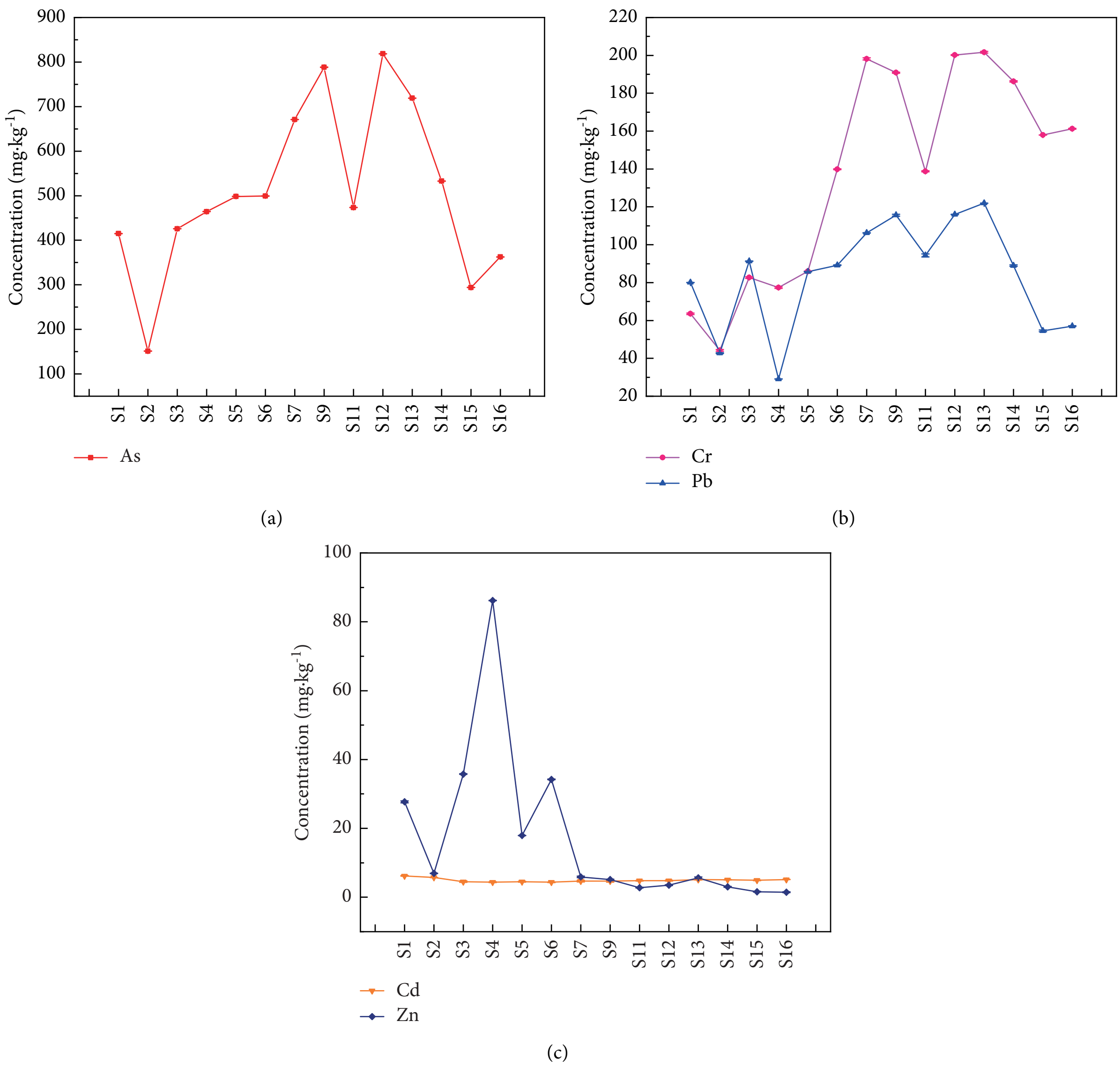

FIGURE 2: Variation of heavy metals concentrations in the sediments. (a) As; (b) Cr, Pb; (c) Cd, Zn.

Zn exhibited a nonfluctuating pattern with lower values (Figure 2(c)). Therefore, it can be preliminarily judged that there is no Zn pollution in the sediments of Huangshui River. Cd concentration varied from 4.36 $mg·kg^{-1}$ to 6.21 $mg·kg^{-1}$ with the maximum value near S1 which exceeded *t*, the risk intervention values for soil contamination of agricultural land seriously. It indicated that Cd released from Xining Special Steel Co., Ltd. affected the concentration of heavy metals in sediments of Huangshui River.

The concentrations of Cr, Pb, As, and Cd were higher than the corresponding values of soil elements in layer A of Qinghai Province. The order of the heavy metals concentration was as follows: As > Cr > Pb > Zn > Cd.

The concentration and variation trends of Pb and Cd were similar to those of previous studies [14, 18, 19]. But as for As and Cr were quite different. Most of the concentrations of five heavy metals were clearly greater than previous studies. Different sampling sites may be the reasons for such differences. Moreover, the reason for exceeding the standard and background values of heavy metals in sediment is that Xining Special Steel Co., Ltd. in the upstream area expands production scale year by year and the increase of new construction sites along the Huangshui River. The rapid urbanization process and development of transportation result in the accumulation of heavy metals in river sediments [35, 36].

3.2. *Assessment of Heavy Metals Pollution in Sediment.*

The mean contamination factor (CF) values of Cr, As, Pb, Cd, and Zn were 1.97, 36.29, 4.01, 35.97, and 0.02, respectively (Figure 3). The contamination factor value for Zn was low (CF < 1). In contrast, As and Cd showed very high levels of contamination at all locations. Cr showed moderate levels of contamination (except at S1 and S2 which was low

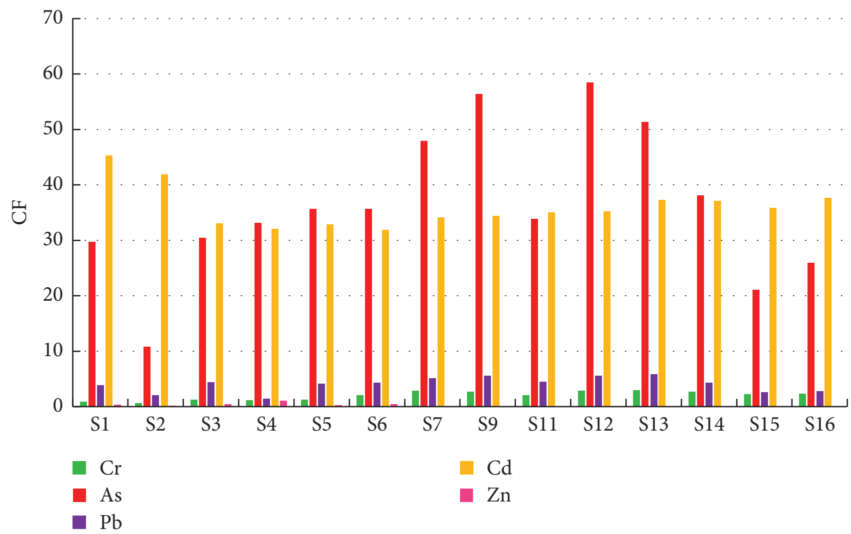

FIGURE 3: The column chart of the concentration factor (CF) of heavy metals in sediments.

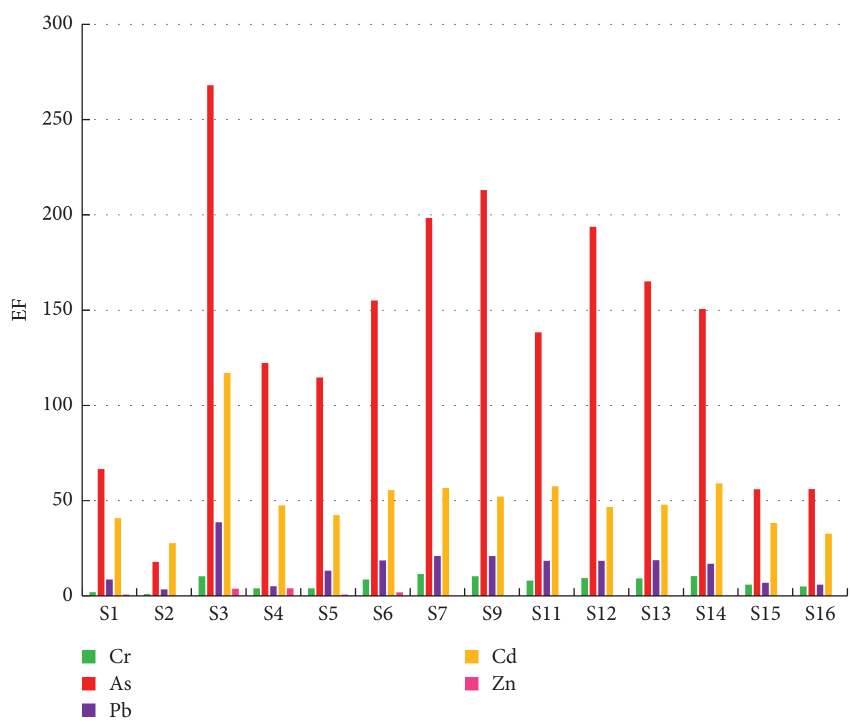

FIGURE 4: The column chart of the enrichment factor (EF) of heavy metals in sediments.

degree). Overall, the descending order of Cd > As > Pb > Cr > Zn for CF was found as heavy metals in the sediment of Huangshui River.

Figure 4 shows the EF values of heavy metals studied in this work. As and Cd recorded extremely high enrichment (average EF = 136.88 and 51.60, respectively). Cr indicated moderate to moderately severe enrichment (1.04 < EF < 11.66 with the average of 7.15). Pb recorded severe enrichment (average EF = 15.39). Zn showed no enrichment (EF < 1 except S3, S4, and S6). Since EF values represented the difference between anthropogenic and natural sources of heavy metals, the results suggested that emissions of As, Cd, Cr, and Pb from human activities had an impact on the river environment. Researchers have found similar results in other water environments [37–39].

Thus, with respect to the background concentration values, the surface river sediments are observed to be highly polluted with As and Cd. The order of the EF values was as follows: As > Cd > Pb > Cr > Zn.

The potential ecological hazard index E_r^i and comprehensive potential ecological hazard index (RI) of Cr, As, Pb, Cd, and Zn are shown in Figure 5. The E_r^i values of Cr, Pb, and Zn were less than 45, indicating low ecological risk. E_r^i for As were higher than 180 which indicated high risk

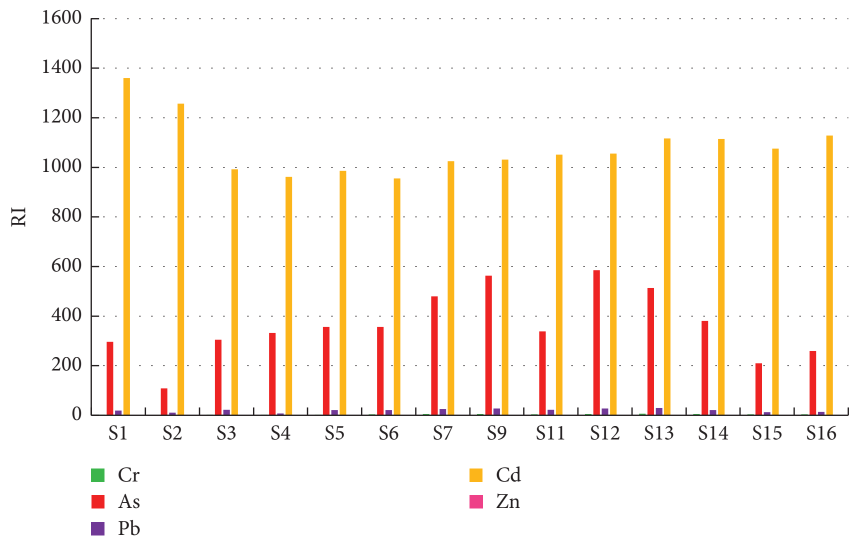

FIGURE 5: The column chart of the potential ecological risk index (RI) of heavy metals in sediments.

TABLE 4: Geoaccumulation index and pollution classification of heavy metals in sediments.

Site	Cr		As		Pb		Cd		Zn	
	I_{geo}	Classification	I_{geo}	Classification	I_{geo}	Classification	I_{geo}	Classification	I_{geo}	Classification
S1	−0.73	0	4.30	5	1.35	2	4.92	5	−2.12	0
S2	−1.25	0	2.85	3	0.45	1	4.80	5	−4.12	0
S3	−0.35	0	4.34	5	1.54	2	4.46	5	−1.75	0
S4	−0.44	0	4.47	5	−0.11	0	4.42	5	−0.48	0
S5	−0.29	0	4.57	5	1.45	2	4.45	5	−2.75	0
S6	0.41	1	4.57	5	1.51	2	4.41	5	−1.82	0
S7	0.91	1	5.00	5	1.76	2	4.51	5	−4.35	0
S9	0.86	1	5.23	6	1.88	2	4.52	5	−4.55	0
S11	0.40	1	4.49	5	1.59	2	4.55	5	−5.44	0
S12	0.93	1	5.28	6	1.89	2	4.55	5	−5.10	0
S13	0.94	1	5.10	6	1.96	2	4.63	5	−4.43	0
S14	0.82	1	4.67	5	1.50	2	4.63	5	−5.33	0
S15	0.59	1	3.81	4	0.80	1	4.58	5	−6.23	0
S16	0.62	1	4.11	5	0.86	1	4.65	5	−6.38	0

(except considerable risk for site S2). Cd has extremely serious ecological hazard risk. Considering the ecological risk index (RI) all stations was at extremely high risk, mainly due to the high content of Cd in the sediments. The order of the RI values was as follows: Cd > As > Pb > Cr > Zn. High ecological risk induced by these five heavy metals demonstrates that human activities have greatly affected the river environment. At the same time, rivers can release these pollutants again, causing ecological risks [40, 41].

Based on Table 2, the geoaccumulation index (I_{geo}) and comprehensive pollution classification of Cr, As, Pb, Cd, and Zn are given in Table 4. The I_{geo} values indicated that no sampling site was observably polluted by Zn. The upstream part was not polluted by Cr, while the middle and downstream part was mildly to moderately polluted. Two-thirds of the sampling sites were mildly to moderately polluted by Cr. All sampling sites (except S4) were moderately polluted by Pb. Both As and Cd were highly polluted and extremely polluted. The order of the I_{geo} values was as follows: Cd > As > Pb > Cr > Zn. Sediments always reflect the contamination history of water bodies [42]. It can be inferred that the heavy metals in sediments in Xining area of Huangshui River have existed for a period. This is also confirmed by previous studies [11, 16, 17, 19].

In general, there is no difference between the results of CF, I_{geo}, and RI. The only difference lies in the EF risk order of Cd and As. For the studied sediments, the four methods show medium to extreme risk.

This implies that although the total concentrations of Pb and Cr are relatively low, the high toxicity and mobility of them in sediments can lead to high risk to the Huangshui River area. The concentration of Zn in the sampling area is lower than the background concentration. Relatively small range of metal distribution indicates that these metals are mainly from natural sources [43].

4. Conclusion

Analyses of heavy metals concentrations in 14 surface sediments from Xining area of the Huangshui River led to the following order of heavy metal concentrations: As > Cr > Pb > Zn > Cd.

The concentrations of Pb, Zn, and Cr are low, which are below the risk screening values for soil contamination of agricultural land. As and Cd pollution are very serious. Their concentrations exceed the risk intervention values for soil contamination of agricultural land. The distribution of heavy metals within the studied section revealed that a fluctuating pattern, but there were some individual samples containing high proportion of certain metals. Furthermore, based on 4 different pollution indices, the order of the ecological risk is as follows: Cd > As > Pb > Cr > Zn. Cd and As are the main contributing elements to ecological risk in Xining area of Huangshui River.

The results of this study give valuable information about heavy metal distribution in surface sediments from Huangshui River. Moreover, the study suggests initiating a long-term monitoring program to improve the understanding of the behavior of such metals and the temporal changes of the environment.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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