



# **Evaluation of Heavy Metal Pollutants From Plateau Mines in Wetland Surface Deposits**

Li Yu<sup>1,2</sup>, Shi Kaiyi<sup>1,2</sup>\*, Yuan Jie<sup>1,2</sup> and Kuang Qiyu<sup>3</sup>

<sup>1</sup>School of Chemistry and Materials Engineering, Liupanshui Normal University, Liupanshui, China, <sup>2</sup>Guizhou Key Laboratory of Coal Clean Utilization, Liupanshui Normal University, Liupanshui, China, <sup>3</sup>Scientific Research Office, Liupanshui Normal University, Liupanshui, China

The Liupanshui Minghu Wetland is a typical artificial urban wetland in a plateau mining region. It is important to identify the sources and potential ecological risks of heavy metal contaminants in its surface sediments to monitor the wetland and the downstream water guality and prevent pollution. In this study, we measured the concentrations of six toxic heavy metals (Pb, Zn, Cr, Cu, Ni, and Cd) in the surface sediments collected from the Liupanshui Minghu Wetland. Further, the geological accumulation indices of heavy metals and their potential ecological risk indices, pollution levels, and associated ecological hazards were evaluated. The average levels of Pb, Zn, Cr, Cu, Ni, and Cd in the superficial sediments were 197, 222, 79.0, 59.1, 68.6, 4.67 mg/kg, respectively. With the exception of Cr, the concentrations of the remaining metals were greater than the background levels in the region. The Statistical analysis indicated a strong correlation between Pb, Zn, Cr, and Cu (p < 0.01). The pollution in the wetland by these elements can be attributed to human activities such as transportation, industrial activity, and agricultural production. Ni and Cd pollution can be attributed to human activities, such as coal mining, and natural phenomena, such as the weathering of mountains and rocks. The geological accumulation indices of Zn, Ni, and Cu indicated low levels of accumulation and minimal contamination. Cd and Pb were moderately enriched, and the levels of Cd and Pb contamination ranged from moderate to high. The potential ecological risk to the Shiyuan region (S) was the highest among the three regions in the wetland park. It was followed by the Longtoutan (L) region, and the potential ecological risk was the lowest in the Erdaoba (E) region. Among the six heavy metals, Cd was the main contributor to pollution in the Minghu Wetland. This study also strives to provide theoretical basis and data support for the prevention and control of heavy metal pollution in artificial wetlands in Alpine mining areas.

Keywords: pollution sources, heavy metals, constructed wetlands, mining region, superficial sediments

# INTRODUCTION

Coal mining and processing are sources of pollution in mining regions and nearby cities. This causes various problems, including the pollution of the wetland environments and the disruption of ecological functions (Chen et al., 2000). Heavy metal pollutants are the most ubiquitous and difficult to control because they undergo morphological changes, accumulate readily, and persist in the

## OPEN ACCESS

#### Edited by:

Ravi Naidu, University of Newcastle, Australia

#### Reviewed by:

Clare Alexandra Wilson, University of Stirling, United Kingdom Mahimairaja Santiago, Tamil Nadu Agricultural University, India

> \*Correspondence: Shi Kaiyi andrewshikai@126.com

#### Specialty section:

This article was submitted to Toxicology, Pollution and the Environment, a section of the journal Frontiers in Environmental Science

Received: 06 May 2020 Accepted: 23 December 2020 Published: 29 January 2021

#### Citation:

Yu L, Kaiyi S, Jie Y and Qiyu K (2021) Evaluation of Heavy Metal Pollutants From Plateau Mines in Wetland Surface Deposits. Front. Environ. Sci. 8:557302. doi: 10.3389/fenvs.2020.557302

1

environment. They are also highly toxic and can be ecologically hazardous for long time periods. The development of wetlands is one of the most commonly used methods to control the environmental pollution in mining regions. These wetlands provide an ecological value and have important roles in urban climate regulation, throttling, and flood discharge. They can be used to protect regional biodiversity and maintain ecological balance (Xu and Tang, 2009; Lei et al., 2013), and they can also promote local tourism and economic development.

The heavy metals in the constructed wetlands in mining regions originate from natural phenomena and human activity. They are introduced into wetland water bodies by falling dust, rock weathering, soil erosion, rain-induced leachates, and direct wastewater discharge. They accumulate in wetland sediments because of the decomposition of particulate matter, adsorption, complexation, and precipitation. Finally, they remain in the wetland for a long time as forms of sediments. Thus, the sediments in wetland systems become sinks for heavy metals, causing permanent potential harm. The heavy metals in wetland sediments can also be resuspended because of fluctuations in the water-soil environment, such as the pH, Eh, water level, and temperature. The metals can then migrate into water bodies; resuspension has become the primary source of secondary heavy metal pollution in wetland water (Akcay et al., 2003; Hiller et al., 2010). The secondary heavy metals can be further transformed into metal organic compounds with strong toxicity under certain conditions, harming the aquatic, animal, and plant ecosystems and threatening human health through food chain (Fan et al., 2002).

Sediments provide a record of the changes in the urban wetland environment. They are rich sources of geochemical information and reflect the impacts of urban activities on the wetland ecosystems (Forstner and Wittamnn, 1979; Rognerud and Fjeld, 2001). Therefore, it is important to study the characteristics of the heavy metal pollutants in urban wetland sediments and evaluate their ecological risks, in order to plan for mitigating heavy metal pollution and restoring the affected ecosystems.

Recently, scholars around the world have conducted a great deal of research on heavy metal pollution in urban sediments. However, majority of these studies have focused on large, natural wetlands and economically developed regions (Lei et al., 2013; Li, B. et al., 2019; Ye et al., 2019), and plateaus, mining regions, and economically underdeveloped areas have received little attention. Only few reports have investigated the heavy metal pollution in the sediments of the constructed wetlands in small cities.

Minghu Wetland is located in Liupanshui City in west Guizhou Province. It is a constructed wetland surrounded by small and medium mining areas with typical plateau karst landforms (Chen et al., 2013; Qin et al., 2013; Hao et al., 2019).

The surface sediments from the Minghu Wetland were investigated in this study. Based on the wetland topography and the distribution characteristics of production and living activities, the study area was divided into three parts: Longtengtan, Erdaoba, and the artificial lake of Shiyuan. Through GPS positioning, 14 sampling sites were set up to collect (0–10 cm thickness) sediment samples. Subsequently, the sources and concentrations of Pb, Zn, Cr, Cu, Ni, and Cd in the samples were characterized. We used the geological accumulation index ( $I_{geo}$ ) and the potential ecological risk index (ERI) of each heavy metal in the surface sediments to quantitatively assess the potential ecological risk. We aimed to provide data and a scientific basis for water monitoring and controlling the heavy metal pollution in the Minghu Wetland. We also sought to provide a reference to prevent and control the heavy metal pollution in similar constructed urban wetlands.

## MATERIALS AND METHODS

### **Overview of the Study Region**

The Minghu Wetland is located in the western district of Liupanshui City, which is located in the Wumeng Mountain region of the Guizhou Province (25°19'44"-26°55'33", N104°18′20″-105°42′50″E). This region is the coal capital toward the south of the Yangtze River and has an average altitude of 1,800 m. The subtropical monsoon climate is mild with no summer heat extremes or severely cold temperatures in winter. Thus, the local plateau has a unique climate. The 197.7-ha wetland region contains mostly artificial ponds and a few permanent rivers. Geologically, it is located in a double transition zone between the eastern Yunnan plateau, the hills of central Guizhou, the northwestern plateau of Guizhou, and the hills of the Guangxi Provence. The elevation of the terrain is high in the northwest and low in the southeast, forming a slope from the northwest to the southeast. The majority of the water in the wetland originates from natural precipitation, and the area receives an average annual rainfall of 1,420.8 mm. The water in the territory flows from west to east into the Xiangshui River, which is a tributary of the Sancha River in the Wujiang River system (Chen et al., 2013).

## **Sample Collection and Pretreatment**

The Minghu Wetland comprises three regions, i.e., Longtengtan (L1–L6), Erdaoba (E1–E4), and Shiyuan (S1–S4). The GPS coordinates of each region were determined in November 2019. The 14 sampling sites are presented in **Figure 1**. At random locations within each 5 m  $\times$  5 m site, a mussel grab was used to collect three or four surface sediment samples from depths of 0–10 cm. The organic residues and large pieces of gravel were removed. The samples were mixed thoroughly, bagged, marked, and brought to the laboratory. They were allowed to air-dry, ground in an agate mortar, and then sieved using a 100-mesh nylon sieve. The 14 samples were then bagged and sealed.

# Sample Digestion and Determination of Heavy Metal Concentrations

The samples were treated with  $HNO_3$ , HCl, HF, and  $HClO_4$  through a wet digestion process (Dauvalter and Rognerud, 2001; Zhao et al., 2019). An AA-6300 atomic absorption spectrophotometer (Shimadzu, Japan) was used to determine the Pb, Cd, Zn, Cu, Cr, and Ni concentrations in the digests according to the standard method NY/T 1613-2008. The pH of

**TABLE 1** | The system for evaluating the degree of heavy metal pollution based on  $I_{\text{oeo}}$ .

I <sub>geo</sub>	<0	0–1	1–2	2–3	3–4	4–5	≥5
Level Pollution degree	0 No pollution	l Mild	II Moderate	III Moderate	IV Strong	V Serious	VI Very serious

each sample was measured according to the standard method NY/T 1377-2007. Blank samples, 10% samples, and reference materials (GBW-07314) were used as controls and analyzed in parallel to ensure the accuracy of the experimentally determined concentrations. The relative standard deviation of the experimental values was controlled to within 5%, and the recovery error was within 10% to satisfy the industry quality control criteria of the Environmental Protection Agency.

# **Evaluation of Heavy Metal Pollution**

### Geoaccumulation Index (I<sub>geo</sub>)

The geoaccumulation index ( $I_{geo}$ ) (Müller, 1969) proposed by the German scientist Gilles Müller in 1967 is a widely accepted indicator used for the quantitative evaluation of the heavy metal pollution in sediments.  $I_{geo}$  can be calculated as follows:

$$I_{\text{geo}} = \log_2 \left( \frac{c_{\text{s}}^{\text{i}}}{1.5 \times B_i} \right) \tag{1}$$

$$I_{\text{tut}} = \sum_{n}^{i=1} I_{\text{geo}} = \sum_{n}^{i=1} \log_2 \left( \frac{c_s^i}{1.5 \times B_i} \right)$$
(2)

where  $c_s^i$  is the concentration of heavy metal *i* in the sample (mg/kg) and  $B_i$  is the background concentration of *i* in the surrounding environment. The geochemical heavy metal concentrations in the Guizhou surface sediment were used as the background reference values (He, 1998). Seven criteria were used to evaluate the degree of heavy metal contamination based on the magnitude of  $I_{\text{geo}}$  (Table 1).

#### 2.4.2 Potential ERI

The potential risk of each heavy metal to the Minghu Wetland ecosystem was dependent on its concentration (mg/kg) in the sediment and its toxicity. The Håkanson (1980) potential ERI has been commonly reported. The ERI (**Equation 2**) was used to more fully assess the potential ecological risk of each heavy metal (Håkanson, 1980).

$$RI = \sum_{i=1}^{n} E_{r}^{i} = \sum_{i=1}^{n} T_{r}^{i} \times \frac{c_{s}^{i}}{c_{g}^{i}},$$
(3)

where RI is the potential ERI,  $E_r^i$  is the potential ecological risk coefficient of heavy metal *i*, and  $T_r^i$  is the biological toxicity coefficient of the metal. The  $T_r^i$  values of Pb, Zn, Cr, Cu, Ni, and Cd are 5, 1, 2, 5, 5, and 30, respectively (Xu et al., 2008).  $C_s^i$  is the measured concentration of heavy metal *i* in the superficial sediment (mg/kg), and  $C_g^i$  is the reference value for the metal in the superficial sediment. Our evaluation differed from the classical Håkanson method because we analyzed six heavy metals. TABLE 2 | Criteria for evaluating the degree of ecological risk.

E <sub>r</sub> <sup>i</sup>	RI	Degree of risk
-30	<60	Slight
30–60	60 < 120	Moderate
60–120	120 < 240	Higher
120-240	≥240	Very strong
+240	_	Extremely serious

#### **TABLE 3** | pH and heavy metal content in superficial sediments.

pН	w <sub>(Pb)</sub> <sup>a</sup>	W <sub>(Zn)</sub>	W <sub>(Cr)</sub>	W <sub>(Cu)</sub>	W <sub>(Ni)</sub>	W <sub>(Cd)</sub>
6.85	118	95.2	20.5	17.1	27.3	0.751
8.14	453	535	196	180	169	16.7
7.53	197	222	79.0	59.1	68.6	4.67
0.335	84.8	108	44.1	51.2	43.3	3.81
4.44	43.1	48.8	55.9	86.7	63.0	81.5
-	29.4	89.9	79.4	29.4	32.8	0.310
-	6.69	2.46	0.994	2.01	2.09	15.06
	6.85 8.14 7.53 0.335	6.85     118       8.14     453       7.53     197       0.335     84.8       4.44     43.1       -     29.4	6.85         118         95.2           8.14         453         535           7.53         197         222           0.335         84.8         108           4.44         43.1         48.8           -         29.4         89.9	6.85       118       95.2       20.5         8.14       453       535       196         7.53       197       222       79.0         0.335       84.8       108       44.1         4.44       43.1       48.8       55.9         -       29.4       89.9       79.4	6.85         118         95.2         20.5         17.1           8.14         453         535         196         180           7.53         197         222         79.0         59.1           0.335         84.8         108         44.1         51.2           4.44         43.1         48.8         55.9         86.7           -         29.4         89.9         79.4         29.4	6.85       118       95.2       20.5       17.1       27.3         8.14       453       535       196       180       169         7.53       197       222       79.0       59.1       68.6         0.335       84.8       108       44.1       51.2       43.3         4.44       43.1       48.8       55.9       86.7       63.0         -       29.4       89.9       79.4       29.4       32.8

<sup>a</sup>Unit of heavy metal content is mg/kg.

Thus, the potential ERI evaluation criteria had to be adjusted according to the types and quantities of the heavy metals (Hou et al., 2011; Li et al., 2013; Li, F. et al., 2019), as listed in **Table 2**.

### **Data Processing**

The SPSS 23.0 software package was used to identify the correlations between the heavy metals in the study region and perform principal component analysis. Graphics were generated using the Origin 2017 software package.

## RESULTS

# Heavy Metals in the Minghu Wetland Surface Sediments

The pH of the Minghu Wetland sediments and the concentration of each heavy metal  $(w_i)$  in the samples are presented in **Table 3**. The average concentrations of the heavy metals in superficial sediments ranged from 4.67 to 222 mg/kg and exhibited the trend of w(Zn) > w(Pb) > w(Cr) > w(Ni) > w(Cu) > w(Cd). At each sampling point, w(Pb) was 4.01–15.4 times greater than the background value. w(Zn) and w(Cd) were 1.06-5.95 and 0.258-2.47 times greater than the background level, respectively. Further, when compared with the background level, w(Cu) was 0.582-6.14 times greater and w(Ni) and w(Cd) were 0.830–5.14 and 2.42–53.9 times greater, respectively. The background values were 2.46, 6.69, 0.994, 2.09, 2.01, and 15.1%. w(Cr) exceeded the standard value in superficial sediments obtained from only some of the sites, and the average w(Cr) was lower than the background concentration. w(Cr) and w(Ni) exceeded the standard values by 71.4 and 92.9%, respectively. w(Pb), w(Zn), and w(Cd) exceeded the standard

**TABLE 4** | Correlation analysis of the pH and heavy metals in superficial sediments.

Index	pН	Pb	Zn	Cr	Cu	Ni	Cd
pН	1.00	0.244	0.421	0.459	0.211	0.099	0.494
Pb	0.244	1.00	0.921 <sup>a</sup>	0.719 <sup>a</sup>	0.750 <sup>a</sup>	-0.139	0.013
Zn	0.421	0.921 <sup>a</sup>	1.00	0.695 <sup>a</sup>	0.771 <sup>a</sup>	-0.133	0.247
Cr	0.495	0.719 <sup>a</sup>	0.695 <sup>a</sup>	1.00	0.648 <sup>a</sup>	0.148	-0.033
Cu	0.211	0.750 <sup>a</sup>	0.771 <sup>a</sup>	0.648 <sup>a</sup>	1.00	0.176	0.032
Ni	0.099	-0.139	-0.133	0.148	0.176	1.00	-0.102
Cd	0.494	0.013	0.247	-0.033	0.032	-0.102	1

<sup>a</sup>Indicates a very significant positive correlation at the 1% (two-sided) level.

values by 100%. These results indicated that the surface sediments in the Minghu Wetland were heavily contaminated with all the heavy metals with the exception of Cr and that the accumulation of heavy metals was extensive. W(Cd) exceeded the standard value to the greatest extent. Thus, Cd was the main contributor to pollution.

The coefficient of variation (CV) was calculated for each of the six heavy metals and analyzed to determine the spatial distributions of the metals in the Minghu Wetland surface sediments (**Table 3**). The CVs ranged from 43.1 to 86.7. The CV of w(Cu) was the largest among the metals, indicating the possibility of point-source pollution. The remaining coefficients followed the order of w(Cd) > w(Ni) > w(Cr) > w(Zn). w(Pb) had the smallest CV, although it still exceeded 43.0%. The difference between the maximum and minimum values was large, suggesting that the wetland environment was frequently disrupted by human activity, and point-source and surface-source pollution coexisted. The spatial distributions of the heavy metals in the sediments were uneven and highly variable.

# Sources of Heavy Metal Contaminants in the Surface Sediments

The correlation between different heavy metals can be clarified based on the correlation analysis of the heavy metals in sediments. If the correlation coefficient is close to 1, it can be preliminarily judged that there are common sources or multielement compound pollution among different heavy metal elements. In addition, the influence of pH and heavy metals was analyzed via Pearson correlation analysis of the measured values. The results are summarized in Table 4. The pH of the sediments had the most influence over the distributions of heavy metals (Ona et al., 2006). The spatial distribution of pH had a CV of 4.44% in the study region, indicating little variability. There was no significant correlation between pH and any of the heavy metals. This may have been because the pH of the Minghu Lake surface sediments was neutral. The [H<sup>+</sup>] and [OH<sup>-</sup>] values in the surface sediments were equal. Therefore, the number of positive charges was equal to the number of negative charges and had little effect on the adsorption of positively charged metal species (Tessier et al., 1979; Yang et al., 2006). A strong positive correlation between Pb, Zn, Cr, and Cu (p < 0.01) indicated that the four heavy metals originated from the same source and exhibited similar deposition mechanisms in superficial sediments. However, this may have occurred because of compound pollution. There was no correlation between Ni and Cd or between Ni and Cd and the remaining four heavy metals. Thus, Ni and Cd may have had unique sources and geochemical deposition mechanisms.

To further reveal the pollution sources of heavy metals in the surface sediments of the Minghu Wetland, principal component analysis (PCA) was conducted by considering the heavy metal contents (Cr, Cd, Cu, Zn, Ni, and Pb) as variables to identify the primary sources of pollution in the Minghu Wetland surface sediments. The greater the absolute value of a factor, the closer will be the relation between the factor and its CVs (Gulgundi and Shetty, 2016), as shown in **Table 5**. The six heavy metals could be resolved into two principal components containing majority of the information. The metals had a cumulative contribution of 74.7, 54.5% of which was accounted for in principal component 1. The loadings of Pb (0.94), Zn (0.95), Cu (0.84), and Cr (0.88) were high. These results differed considerably from those obtained via correlation analysis of the four heavy metals, although strong positive correlations could be observed.

## Heavy Metal Levels in Superficial Sediments and Potential Ecological Risk Assessment *I*<sub>geo</sub> Evaluation

We calculated the individual heavy metal  $I_{geo}$  values (Eq. 1) and the heavy metal composite pollution index  $I_{tut}$  (Eq. 2) at each sampling point to better understand the individual heavy metal pollution levels and the composite heavy metal concentration in the wetland surface sediments. The results are presented in Figures 1 and 2, respectively.

The  $I_{\text{geo}}$  values of the heavy metals ranged from -2.54 to 5.17 (**Figure 2**), and the average values followed the order of Cd > Pb > Zn > Ni > Cu > Cr. The  $I_{\text{geo}}$  values at 12 of the 14 sites evaluated in the study region were lower than zero. The exceptions were the Cr  $I_{\text{geo}}$  values at the S2 and E3 sites, which were between 0 and 1, indicating low levels of Cr pollution. Among the pollution detected in the entire study area, 85.7% involved no Cr, although the average geological accumulation index ( $\bar{I}_{geo}$ ) of -0.590 was less than zero. The  $\bar{I}_{geo}$  values of Zn, Ni, and Cu were 0.721, 0.483, and 0.420, respectively. Thus, Zn, Ni, and Cu could be classified as Grade I pollutants, and the degree of contamination by these metals was low. Cd and Pb were responsible for the most serious contamination in the wetland

**TABLE 5** | Principal component load analysis of heavy metals in the surface sediments of the Minghu Wetland.

PC <sub>1</sub>	PC <sub>2</sub>
0.94	0.04
0.95	-0.21
0.84	0.15
0.83	0.26
0.15	0.78
0.09	0.77
54.45	20.23
54.45	74.68
	0.94 0.95 0.84 0.83 0.15 0.09 54.45



surface sediments.  $I_{\text{geo}}$  of that was between 0.690 and 5.17, and  $I_{\text{geo}}$  was 3.33 and 2.16. The Cd and Pb concentrations in the 14 samples were greater than the background values. Cd and Pb accumulated at 100% of the sites, and the concentrations at each site exceeded the background values. The geological accumulation index of Cd was the largest when compared with those of the remaining individual heavy metals in the wetland, and its  $I_{\text{geo}}$  was 5.17 at the Longtoutan (L2) site. The extent of Cd contamination (Grade VI) was severe. The largest  $I_{\text{geo}}$  of Pb (3.36) in the wetlands could be observed in the Shiyuan region (S2), indicating that Pb was a serious Grade IV pollutant. The accumulation of Cd and Pb in the Minghu Wetland surface sediments was in the middle range, and the Cd and Pd contamination levels were above Grade VI.

The horizontal distributions of the heavy metal pollution indices  $(I_{tut})$  at the 14 sampling sites are presented in **Figure 3**. The  $\bar{I}_{tut}$  of the wetland surface sediments was 6.51, and Cd and Pb contributed 84.3% as the predominant heavy metal pollutants.

#### Assessment of Potential Ecological Hazards

The changes in the individual potential ecological risk index  $(E_r^i)$  distribution and the integrated potential ERI of each heavy metal in the wetland surface sediments are shown in **Figures 4** and **5**, respectively. The  $E_r^i$  of Cd (**Figure 4**) ranged from 72.6 to 1,619, which was considerably greater than those of the remaining five metals. The  $E_r^i$  of Pb was greater than 30 only at a few sites, whereas the  $E_r^i$  values of Zn, Ni, Cu, and Cr were in single digits.







The average values followed the order of Cd (540) > Pb (33.5) > Ni (10.5) > Cu (10.0) > Zn (2.46) > Cr (1.99). Based on the grading standard (**Table 2**), the Ni, Cu, Zn, and Cr in the sediments appeared to be minor ecological hazards, whereas Pb was a moderate hazard. However, the potential ERI of Cd was >240. This indicated that Cd contamination was considerably severe and that the level of ecological risk because of Cd



contamination was extremely high. This was likely related to the extensive accumulation of Cd in the sediments and its high biological toxicity  $T_r^i$  (30).

The comprehensive potential ecological hazard RIs of the heavy metals in the sediments were between 147 and 1,730 (**Figure 5**), and the average RI was 540. The maximum RI (1,730) could be observed at the L2 site downstream from the Small Three Gorges scenic region in Longshan, indicating the most serious Cd contamination in the study region. Therefore, there was a direct and irrefutable relation between coal mining and an extremely high potential ecological risk in the Longshan region. The RI values of the E4 (120), L5 (147–179), and L6 (240) sites were similar, indicating a moderate risk.

# DISCUSSION

Zhang et al. (2019) studied the heavy metals in surface sediments obtained from the Zhangze Reservoir and observed that Zn and Cu primarily originated from agricultural production, construction dust, anticorrosion coatings, metallurgy, slag accumulation, residential sources, and discharged industrial sewage. Singh et al. (2017) observed that coal mining, crude oil combustion, and motor vehicle exhaust were the dominant sources of Pb. Cr mainly originated from fertilizers, agricultural pesticide residues, and wastewater from coal mines (Facchinelli et al., 2001; Wen et al., 2020). Based on the analysis of the sampling site and the surrounding environment of the Minghu Wetland, it is speculated that the main components of heavy metals (Cu, Zn, Pb, and Cr) may originate from these three sources:

1) Liupanshui city is a heavy industrial city with coal mines and nonferrous metal minerals as the pillar of industrial activities in this region. More than 45 types of minerals (including lead-zinc ore, bauxite, nickel, cadmium, germanium, gallium, indium, selenium and silver, uranium, nickel, and pyrite) have been discovered. In the early 1980s, majority of the mining mines around the wetland mainly used artificial coarse open mining. The local residents earned money by using the original method of coking, zinc smelting, lead smelting, lime making, and manufacturing brick kilns and tiles. The mineral residues left after production lacked were not treated; these residues piled up everywhere and were exposed because of the imperfect environmental protection system and people's weak awareness regarding environmental protection at that time. Through sunshine, rain, and weathering, the waste residue containing a large amount of metal ions (Pb, Zn, Cu, Cr, etc.) was imported into the Minghu Wetland to accumulate in the sediments via surface runoff and atmospheric sedimentation (Mico et al., 2006).

Chemical fertilizers and pesticides (generally containing high concentrations of Zn, Cu, and Cr) were utilized during the processes of greening and vegetation maintenance after the construction of the Minghu Wetland because there were many farmlands, vegetable plots, and village fish ponds at the original site of Minghu Wetland before construction. Recently, the development of real estate around the wetland, the reconstruction of school buildings, the random disposal of residues and waste, and the discharge of construction wastewater have increased the accumulation of Zn, Cu, and other metal elements in the sediments of the water body (Chen et al., 2005).

The fine particles of the coal-burning dry ash and the exhaust emissions of transportation are important sources of Pb (Sia and Abdullah, 2012). The wetland is located in the west of the city adjacent to the main road west of the urban area. A dense traffic flow can be observed in this region (especially heavy coal trucks and engineering vehicles), resulting in a large amount of exhaust gas and tire wear residues and considerably contributing to the coke production of the city. The coal ash dust generated via thermal power generation contains a large amount of Pb; it can directly enter the wetland through winds, dust, rain leaching, and washing or indirectly and accumulate in the surface sediments. Therefore, the pollution of the four heavy metals (Pb, Zn, Cu, and Cr) dominated by principal component 1 can be primarily attributed to the combined effects of industrial processing, agricultural production, transportation, infrastructure, and life.

Ni and Cd exhibited high positive charges with respect to principal component 2 and accounted for 20.2% of the variance. Ni and Cd pollution can be mainly attributed to coal mining as well as metal smelting and processing. Longshan (Wen et al., 2020), which is located adjacent to the southwest of the wetland, contains abundant coal resources, and the coal seam is shallow and easy to mine. Additionally, Liupanshui is a typical limestone karst hilly landform, and the mountain caves and underground rivers are highly interconnected. The wastewater and rainwater during coal mine production can be leached and soaked in coal gangue. Streams and other sources of water enter the wetland. Furthermore, Cd is an element of the Zn family and often coexists in raw zinc ore as sulfides in nature. Therefore, Cd pollution is responsible for the subsequent effects of the slag residue obtained via smelting and zinc smelting around the wetlands in the previous century (Yiu et al., 2016). Ni can originate from the exhaust gas and dust deposition from coal combustion (Lu et al., 1995). Liupanshui exhibited a large amount of dust floating in the air during coal production, metal smelting, building material processing, thermal power generation, and other activities. In addition, the local subtropical climate, abundant rainfall, and large temperature difference between morning and evening, suspended particulate matter in the atmosphere (including Ni, Cd, and other metal elements), with the help of wind, it enters the wetland by means of condensation, gravity sedimentation, rainfall, etc., and is adsorbed on the surface of the sediment after landing. Thus, the Cd and Ni in principal component 2 can be attributed to a combination of human activity and natural processes.

According to **Figure 3**, The highest value of  $I_{tut}$  (11.3) can be observed at S2 in the Shiyuan region, indicating a very serious composite heavy metal pollution. This is because S2 is located in the southeast low-lying corner of the wetland, the water flow is gentle, and the water exchange period is long. A large number of gravels, silt, and suspended particles (containing a large amount of Cd and Pb) are carried by the water flow from the west and north. They settle in the sediment by gravity sliding, resulting in the abnormal high value of the point. The  $I_{tut}$  values between 0 and 1 were the lowest in the region. The  $I_{tut}$  of Erdaoba (1.89) was Grade II, indicating a moderate degree of contamination by a combination of heavy metals. The  $I_{tut}$  of Longtoutan (4.87) indicated severe Grade V pollution, whereas that of the Shiyuan region (8.77) indicated the accumulation of all six heavy metals and a very serious pollution level (Grade VI). Thus, the pollution in the surface sediments of the Minghu Wetland region evolved from individual heavy metal contaminants to more serious composite pollution.

The average comprehensive potential ecological hazard risk index (147 < RI < 1730) of the sediment heavy metals in **Figure 5** is 540; the maximum value (1730) can be observed at L2 downstream of the Small Three Gorges Scenic region in L2, indicating the most serious Cd pollution in the regional study point. Therefore, there is a direct and inevitable relation between the extremely high potential ecological hazards and the large amount of coal powder and slag (containing Cd, Pb, Ni, Cu, Zn, and Cr) flowing into the site by mountain runoff because of the waste obtained via mining and smelting by applying the local method in the Longshan Coal Mine.

The potential ecological risks at the remaining sites were extremely high because the RI values exceeded 240. The percentages of the total potential ecological risk in the three wetland regions were 36.0% (Longtoutan), 22.8% (Erdaoba), and

41.3% (Shiyuan), which were consistent with their  $I_{tut}$  values. Cd accounted for 83.7% of the RI, and the remaining five species made a cumulative contribution of only 16.3%. The results confirmed that the Cd in the surface sediments was predominantly responsible for the high potential ecological risk to the wetland.

## CONCLUSION

In this paper, heavy metal pollution in Alpine mining area, artificial wetland in the west of Guizhou Province, was studied and evaluated; the source and development trend of heavy metal pollution were analyzed afterward. The results show that industrial and agricultural production and transportation are the main sources of Pb, Zn, Cr, and Cu contamination, while mineral exploitation and metal smelting are the main sources of Cd and Ni pollution. In addition, Zn, Ni, and Cu have low concentrations and cause less contamination. Cd and Pb show moderate accumulation and their contamination levels are moderate to severe. Among these, Cd is the main controlling element for the extremely high ecological risk of wetland surface sediments because of its high ecological toxicity. Although the coal mines and traditional smelting around the wetland have been shut down for several years, the impact on the Minghu lake and the surrounding environment may still exist for a long time. Therefore, further treatment of heavy metal pollution in artificial wetland environment and prevention of primary and secondary hazards of pollution sources can better protect the fragile ecological environment of Alpine mining areas, reconstruct the sustainable development environment with clear water and green mountains, and reduce or even eliminate the adverse impact of wetland rivers on the downstream ecological environment. This study also strives to provide theoretical basis

## REFERENCES

- Akcay, H., Oguz, A., and Karapire, C. (2003). Study of heavy metal pollution and speciation in Buyak Menderes and Gediz River sediments. *Water Res.* 37 (4), 813–822. doi:10.1016/s0043-1354(02)00392-5
- Chen, C. Y., Stemberger, R. S., Klaue, B., Blum, J. D., Pickhardt, P. C., and Folt, C. L. (2000). Accumulation of heavy metals in food web components across a gradient of lakes. *Limnol. Oceanogr.* 45 (7), 1525–1536.
- Chen, H., Li, S., and Xiong, R. (2013). An investigation of vertebrate resources in Minghu National Wetland Park of Liupanshui, Guizhou Province. *J. Liupanshui Normal Univ.* 25 (6), 1–20 [in Chinese]. doi:10.1016/j. physleta.2020.126538
- Chen, T. B., Zheng, Y. M., Le, M., Huang, Z. C., Wua, H. T., Chen, H., et al. (2005). Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China. *Chemosphere* 60 (4), 542–551. doi:10.1016/j.chemosphere. 2004.12.072
- Dauvalter, V., and Rognerud, S. (2001). Heavy metal pollution in sediments of the Pasvik River drainage. *Chemosphere* 42 (1), 9–18. doi:10.1016/s0045-6535(00)00094-1
- Facchinelli, A., Sacchi, E., and Mallen, L. (2001). Multivariate statistical and GISbased approach to identify heavy metal sources in soils. *Environ. Pollut.* 114 (3), 313–324. doi:10.1016/s0269-7491(00)00243-8
- Fan, W. H., Chen, J. S., and Hong, S. (2002). Recent development in biotoxicological assessment of heavy metal in aquatic sediments. *Env. Sci. Tech.* 25 (1), 36–48. doi:10.19672/j.cnki.1003-6504.2002.01.015

and data support for the prevention and control of heavy metal pollution in artificial wetlands in Alpine mining areas.

## DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

## **AUTHOR CONTRIBUTIONS**

LY mainly contributed to experimental design and data processing. SK contributed to data analysis and processing and writing the article. YJ and KQ contributed to sample collection, data analysis, etc.

### FUNDING

This research was financially supported by the Alliance fund of Guizhou Provincial Department of science and Technology (qkhlhz (2015) No. 7616), National Natural Science Foundation of China (No. 51504134), Key Supported Discipline of Guizhou Provence (Qian Xuewei He Zi ZDXK(2016)24), and 2011 Collaborative Innovation Center of Guizhou Province (QianJiaohexietongchuangxinzi (2016) 02).

## ACKNOWLEDGMENTS

The authors would like to thank Professor LY of the experimental center for his help in sample testing.

- Forstner, U., and Wittamnn, G. T. W. (1979). Metal pollution in the aquatic environment. Berlin: Springer-Verlag, 399-472.
- Gulgundi, M. S., and Shetty, A. (2016). Identification and apportionment of pollution sources to groundwater quality. *Env. Proc.* 3 (2), 451–461. doi:10. 1007/s40710-016-0160-4
- Håkanson, L. (1980). An ecological risk index for aquatic pollution control- a sedimentological approach. *Water Res.* 14 (8), 975–1001.
- Hao, S., Wang, C., and Lin, H. (2019). Design and assessment of biodiversity in urban wetland parks: take Liupanshui Minghu National Wetland Park as an example. Acta Ecol. Sin. 39 (16), 5967–5977. doi:10.5846/stxb201812052666
- He, S. (1998). Geochemical background of supergene sediments in Guiz. Guizhou Geol. 15 (2), 149–156 [in Chinese]. doi:10.1016/s0269-7491(00) 00243-8
- Hiller, E., Jurkovic, L., and Sutriepka, M. (2010). Metals in the surface sediments of selected water reservoirs, Slovakia. *Bull. Environ. Contam. Toxicol.* 84 (5), 635–640. doi:10.1007/s00128-010-0008-y
- Hou, Q., Ma, J., and Wang, X. (2011). Bioavailability and potential ecological risk of soil heavy metals in kindergartens, Kaifeng City. *Environ. Sci.* 32 (6), 1764–1771 [in Chinese].
- Lei, Y. R., Li, C. H., He, C. Q., Chen, X. P., Liang, X., Cui, X. H., et al. (2013). Comparative evaluation of sediment characteristics of Shanghai Dalian Lake wetland and Jiangwan wetland. *J. Shanghai Univ. (Soc. Sci. Ed.)* 19 (4), 380–392 [in Chinese]. doi:10.21275/v5i2.nov161605
- Li, B., Yu, Q., and Wei, F. (2019). Distributions and ecological risks of heavy metals in surface sediments from Jianhu Lake, Northwestern Yunnan Plateau. *China Environ. Poll. Control.* 41 (04), 468–473 [in Chinese].

- Li, F., Liu, Y., and Guo, D. (2019). Distribution and potential ecological risk assessment of heavy metals in the sediment of the songjiang wetland in Harbin City. *Res. Environ. Sci.* 32 (11), 1869–1878. doi:10.1063/1.5034306
- Li, R., Xu, J., and Jiang, Y. (2013). Fraction distribution and ecological risk assessment of soil heavy metals in the riparian zone of Huixi stream in Tongling City. *Res. Environ. Sci.* 26 (1), 88–96. doi:10.1080/10807039.2017. 1288562
- Lu, X. H., Zeng, H. C., and Ouyang, Z. H. (1995). The distribution and enrichment of trace elements in particles released from coal combustion. *Env. Chem.* 14 (6), 489–493.
- Mico, C., Recatala, L., Peris, M., and Sánchez, J. (2006). Assessing heavy metalsources in agricultural soils of an European Mediterranean area by multivariate analysis. *Chemosphere* 65 (5), 863–872. doi:10.1016/j. chemosphere.2006.03.016
- Müller, G. (1969). Index of geoaccumulation in sediments of the Rhine river. *Geojournal* 2 (3), 108–118.
- Ona, L. F., Alberto, A., and Prudente, J. A. (2006). Levels of lead in urban soils from selected cities in a central region of the Philippines. *Environ. Sci. Pollut. Res. Int.* 13 (3), 177–183. doi:10.1065/espr2005.08.275
- Rognerud, S., and Fjeld, E. (2001). Trace element contamination of Norwegian Lake sediments. Ambio 30 (1), 11–19. doi:10.1579/0044-7447-30.1.11
- Qi, S., Sigua, Q., Dai, W., and Liu, X. (2013). Health assessment on artificial wetland of city ecosystem in wumeng mountain area—Case of minghu national wetland park in Liupanshui City. J. Hydroecol. 34 (5), 43–46. doi:10.4211/hs. 17600892c08447fd9c4df3a5c85b31b7
- Sia, S. G., and Abdullah, W. H. (2012). Enrichment of arsenic, lead, and antimony in Balingian coal from Sarawak, Malaysia: modes of occurrence, origin, and partitioning behaviour during coal combustio. *Int. J. Coal Geol.* 101, 1–15. doi:10.1016/j.coal.2012.07.005
- Singh, H., Pandey, R., and Singh, S. K. (2017). Assessment of heavy metal contamination in the sediment of the River Ghaghara, a major tributary of the River Ganga in Northern India. *Appl. Water Sci.* 7, 4133–4149. doi:10.1007/ s13201-017-0572-y
- Stoffella, H., Zang, S., and Zhang, L. (2019). Distribution and potential ecological risk assessment of heavy metals in sediments of Zhalong Wetland. *Huanjing Kexue* 34 (04), 1333–1339. doi:10.1063/1.5034306

- Tessier, A., Campbell, P. G. C., and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51 (7), 844–851.
- Wen, Q., Zhao, Y., and Cao, W. (2020). Distribution characteristics, sources and potential ecological risks of heavy metal pollution in the middle reaches of Chaobai River. *Res. Environ. Sci.* 33, 599–607 [in Chinese]. doi:10.1016/j. envpol.2011.06.011
- Xu, Y., and Tang, Q. (2009). Land use optimization at small watershed scale on the Loess Plateau. J. Geogr. Sci. 19 (10), 577–586. doi:10.1007/s11442-009-0577-z
- Xu, Z., Ni, S., and Tuo, X. (2008). Calculation of heavy metals'toxicity coefficient in the evaluation of potential ecological risk index. *Environ. Sci. Technol.* 31 (2), 112–115 [in Chinese]. doi:10.1016/j.marpolbul.2020.111288
- Yang, J. Y., Yang, X. E., and He, Z. L. (2006). Effects of pH, organic acids, and inorganic ions on lead desorption from soils. *Environ. Pollut.* 143 (1), 9–15. doi:10.1016/j.envpol.2005.11.010
- Yiu, Y. N., Zhu, S. F., Wei, X. F., Miao, J., Zhou, M., and Guan, F. J. (2016). Characteristics and evaluation of heavy metal pollution in different functional areas of Luoyang City, Henan Province. *Env. Sci.* 37 (6), 2322–2328. doi:10. 13227/j.hjkx.2016.06.041
- Zhang, Q., Feng, M., and Hao, X. (2019). Pollution characteristics and ecological risk assessment of heavy metals in the sediments of Zhangze Reservoir. *Environ. Eng.* 37 (1), 11–17 [in Chinese]. doi:10. 21203/rs.3.rs-51877/v2
- Zhao, B., Zhu, S., and Yang, X. (2019). Pollution status and ecological risk assessment of heavy metals in sediments of Caohai Lake. *Res. Environ. Sci.* 32 (2), 235–245. doi:10.21203/rs.3.rs-51877/v2

**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Copyright © 2021 Yu, Kaiyi, Jie and Qiyu. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.