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Bioaccumulation and Risk Assessment of Potentially Toxic Elements in Soil-Rice System in Karst Area, Southwest China

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The accumulation of potentially toxic elements (PTE) in a soil–rice system poses a significant issue of concern in agricultural soils, particularly in the polluted or high PTE geological background regions, such as karst areas. The source identification, bioaccumulation factors of PTE, and its health risk were investigated by correlation analysis, principal components analysis, and single/comprehensive assessments in a soil-rice system in Mashan County, Guangxi Province. The results showed that the mean contents of PTE in rice rhizosphere soil samples were higher than Guangxi surface soil, but lower than Mashan background. Of the samples, 84.21% have Cd content exceeding the soil environmental quality -- risk control standard for soil contamination of agricultural land in China (GB 15618-2018) risk screening value. The Nemerow comprehensive pollution index indicated that 21.05 and 26.32% of the soil samples were moderately and heavily polluted. The contents of pH-related exchangeable Ca, exchangeable Mg, and redox-related available Fe and available Mn in soil affected the bioaccumulation of PTE in rice. In all the rice samples, 55.26% of Cd and 31.58% of Pb exceed the maximum allowable value of contaminants in rice recommended by the national food safety standard for maximum levels of contaminants in foods in China (GB 2762-2017). The average targeted hazard quotient values (THQ) of PTE decreased in an order of As > Cd > Cr > Cu > Zn > Pb > Hg, and the degree of health risk it posed to the population was Children > Female > Male. The hazard index (HI) of all samples was greater than one due to all THQ_{As} and the THQ_{Cd} of more than half samples were above 1, which implied that the residents were exposed to non-carcinogenic risk by rice ingestion. Therefore, the PTE in the karst area with a high geological background can be absorbed and migrated by crops, leading to a greater health risk to humans, which should be paid attention to in future research and agricultural management.

Keywords: bioaccumulation, risk assessment, potentially toxic elements, soil-rice, karst

INTRODUCTION

With population growth and economic development, the natural process of slow release of heavy metals is accelerated, resulting in heavy metal pollution of soil, water, and the atmosphere (Bing et al., 2021; Savignan et al., 2021; Egbueri et al., 2022a). Heavy metals can accumulate in soil and dissolve into groundwater during leaching, resulting in groundwater and surface contamination of water (Ayejoto et al., 2022; Egbueri et al., 2022b). Heavy metal pollution in cropland soils is a global environmental issue of concern owing to its toxicological effects on soil-plant systems and humans (Bashir et al., 2018; Hou D. et al., 2020; Kukusamude et al., 2021). Cobalt (Co), copper (Cu), nickel (Ni), iron (Fe), manganese (Mn), zinc (Zn), molybdenum (Mo), and selenium (Se) are essential elements of the human body; still, they would cause health problems after years of insufficient intake or excessive intake of food exceeding the safety limit (Giri et al., 2020), while arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), and lead (Pb) are nonessential to the human body, and these can cause health problems even at low contents (Giri et al., 2019; Jalili et al., 2020). Human exposure to heavy metals is through inhalation, oral ingestion, and skin absorption (Sanaei et al., 2021; Ayejoto et al., 2022; Egbueri et al., 2022b). Rice is the most widely consumed grain on the planet, with global rice production exceeding 740 million tons in 2014, with Asian countries such as China, Thailand, Japan, and Indonesia leading the way in global rice production (Hu et al., 2016). Rice is one of the most essential staple foods in China, particularly in southern areas. The average consumption of rice is 219 g/person/day, which is nearly 50% higher than the global average (Hu et al., 2016). Dietary intake of rice grown in soils with a high content of potentially toxic elements (PTE) exceeding the maximum allowable contaminant concentration could be a serious threat to human health (Chen et al., 2018; Mu et al., 2020). Previous studies revealed that the content of PTE in rice grains is mainly determined by soil physicochemical properties, element availability, and rice varieties (Li et al., 2019).

The content of PTE in rice grains is correlated with its corresponding soil (Baruah et al., 2021). Approximately 19.4% of farmland in China has been reported contaminated by PTE in 2014 (Qu et al., 2016), with higher contents of Cd and Pb distributed in northwest, south, and southwest China than elsewhere (Bing et al., 2021). Weathering of parent materials is a natural source of heavy metals in soils. High geological background characteristics of soil heavy metals have been found in karst areas such as Southwest China (Wen et al., 2020b; Tang et al., 2021; Yang et al., 2021b), the Indo-China Peninsula (Mallongi et al., 2022), and Europe (Savignan et al., 2021). The soil in the karst valley densely populated and concentrated in rural towns is strongly affected by anthropic activities. Soil heavy metals can be affected by wet and dry deposition of fossil fuel combustion, fertilizer and pesticide application, sewage irrigation, and improper disposal of waste (Egbueri et al., 2020; Egbueri et al., 2021b; Savignan et al., 2021). In addition, the combination of a high geological background of heavy metals and human activities makes crops in karst areas vulnerable to heavy metal pollution, which will affect future environmental sustainability and human health (Zhang et al., 2019; Zhang et al., 2021; Mallongi et al., 2022).

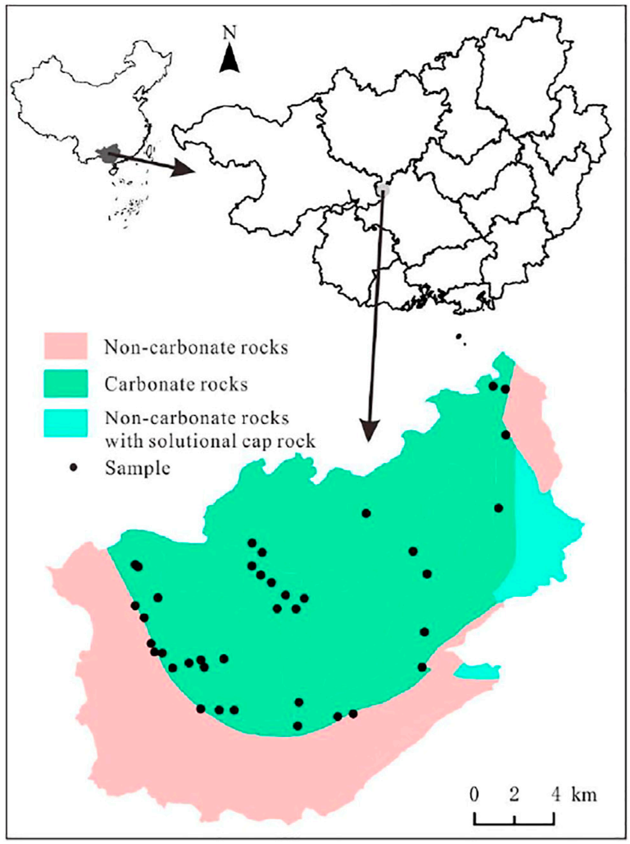

FIGURE 1 | Map of sampling sites and geological background.

Due to the enrichment of heavy metal elements in the carbonate weathering process and soil genesis, the resulting soil has significantly high contents of PTE (Wen et al., 2020b; Yang et al., 2021b). The first national pollutant survey reflected that the average contents of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in the surface soils of Guangxi where karst is widely distributed were 2.0, 4.5, 1.6, 1.1, 2.6, 1.3, 1.4, and 1.4 times higher than that of China, respectively. Due to the limited arable land per capita, part of farmlands with a high heavy metal geological background in the karst area in Southwest China is still used to grow crops (Zhang et al., 2019).

Limestone soil developed from weathering of carbonate rocks may affect the accumulation of trace elements in the edible parts of crop plants (Wen et al., 2020a; Li et al., 2021; Tang et al., 2021; Zhang et al., 2021). Yang et al. (2021a) studied the excess rate and influencing factors of Cd in the soil-rice system in karst areas and proposed a new safety standard based on pH and soil Cd content. Soil carbonate in the karst area increased soil pH, and the adsorption of Cd by Fe/Mn oxide/hydroxide significantly reduced the bioavailability of soil Cd, and the excess rate of rice in the karst area was much lower than that in the non-karst area (Li et al., 2021). The limestone soil in the karst area is calcium-rich and alkaline. Unfortunately, to the best of our knowledge, the effect of exchangeable Ca and Mg on the immobilization of heavy metals in the soil-rice system has not been reported yet. Therefore, the purposes of this study were to (1) evaluate the contents of 7 PTE (As, Cd, Cr, Cu, Hg, Pb, and Zn) in rice grains and rhizosphere soils of the karst area, identifying the source of heavy metals and understanding the influence of soil physicochemical properties related to pH and redox on the accumulation of PTE in the soil-rice system; and (2) assess the potential health (non-carcinogenic) risk of these PTE to children and adult through rice consumption.

MATERIALS AND METHODS

Study Area

The studied area is located west of Mashan County, Guangxi Province, China (**Figure 1**). This area is characterized by a mean annual rainfall of 1722.5 mm, with an annual average temperature of 21.8°C. The central part of the study area is characterized by thick limestone layers with dolomitic limestone intercalations. Soils are dominated by brown rendzina. The land use types are mainly shrubs in mountainous areas and abandoned farmland in depressions. Non-carbonate rocks, comprising sandstones and mudstones, are distributed to the west, south, and east of the study area. The land uses in this area mainly include secondary forests and reservoirs. The valley consists of Holocene clay and loamy sand sediments, distributed among the mountains, and the land uses include paddy fields, drylands, and villages. Agricultural activities are the source of income for residents in the study area. Cultivated land includes two-season rice, water and vegetable rotation, corn and orchards, etc. Excessive use of chemical fertilizers and pesticides to pursue higher yields may bring heavy metal pollution to the cultivated soil.

Samples

Thirty-eight groups of rice and rhizosphere soil samples were collected in early November 2017 (**Figure 1**). Field sampling was conducted according to a standardized sampling method (MLRPRC Ministry of Land and Resources of the People's Republic of China, 2016). At each sampling point, rice and rhizosphere soil were collected from four sub-spots within 20 m of the surrounding area and combined into a compositional sample, sealed, and transported with a plastic bag. After removing the debris and roots, the fresh soil sample was passed through a 2-mm nylon sieve to improve uniformity. Air-dried soil samples and polished rice were ground to a particle size of not more than 74 um for trace element analysis.

Laboratory Analysis

Contents of Cd, Cr, Cu, Pb, and Zn measuring were performed on inductively coupled plasma (ICP)-mass spectrometry (PerkinElmer Inc., United States, NexION 300) after digesting the soil samples with <0.074-mm particle size by $HCl—HF—HClO_4—HNO_3$ mixture, and rice sample digested by $HNO_3–H_2O_2$. After digesting by aqua regia, and reducting by potassium borohydride, As and Hg were determined by atomic fluorescence spectroscopy. Soil pH was determined at a 1:2.5 (w/v) soil/water ratio by a precision pH meter (PHS-3C) in the lab. The soil organic carbon (Corg) was determined through titration using the potassium dichromate oxidation–ferrous ammonium sulfate method. Exchangeable calcium (E_{Ca}) and magnesium (E_{Mg}) were leached with 1 mol/L ammonium acetate (pH = 7.0), and measured by ICP-emission spectrometry (PerkinElmer Inc., United States, OPTIMA 8300). The availably iron (A_{Fe}), copper (A_{Cu}), zinc (A_{Zn}), and manganese (A_{Mn}) were leached with leaching solution (0.1 mol/L hydrochloric acids for acid soil, and DTPA for calcareous soil). The leaching solution was determined by ICP-emission spectrometry. The available silicon (A_{Si}) was leached with 0.025 mol/L citric acid at 30°C for 5 h equilibrating, and the filtrate was taken for colorimetric comparison with silicon molybdenum blue. Standard materials of soil (GBW07417 for effective state analysis of soil elements, GBW07427 for total concentration analysis of soil elements) and rice (GSB-1 and GSB-23, both for total concentration analysis of rice elements) covered all studied elements and were tested among every ninth sample, revealing that the average analytical errors were about 5%.

PTE Contamination Assessment

Pollution Load Index and Potential Ecological Risk Index

The contamination factor (CF) has been used to assess the pollution level of trace elements in the soil since the 1980s (Tomlinson et al., 1980; Kowalska et al., 2018). The CF values of PTE in soil were calculated as follows:

$$CF_i = C_i / C_{REF_i} \tag{1}$$

where C_i and C_{Refi} are the contents of element "i" (mg/kg) in the soils and background value of the PTE in Mashan County, which was obtained from this study and a geochemical survey of land quality in 2016, respectively (**Table 1**).

Correspondingly, the pollution degree of a single element is grouped into four levels: low (CF < 1), moderate (1 ≤ CF < 3), equivalent (3 ≤ CF < 6), and extremely high (CF F 6) (Hakanson, 1980; Egbueri et al., 2021b; Egbueri and Agbasi, 2022).

To evaluate the overall degree of heavy metal contamination across all sampling sites, the pollution load index (PLI) was proposed to represent total pollution of all PTE in the soil, which is calculated as follows:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times \cdots \times CF_n} \tag{2}$$

where n is the total number of the studied PTE consisting of As, Cd, Cr, Cu, Hg, Pb, and Zn. The contamination degrees were further classified as PLI <1, 1 ≤ PLI <2, 2 ≤ PLI <3, and PLI ≥3, which indicated low, moderate, high, and very high contamination, respectively (Egbueri et al., 2021b).

The potential ecological factor (PEF) has been widely applied to assess the ecological risk of toxic PTE in soils (Hakanson, 1980; Gu et al., 2021). The PEF values are calculated as follows:

TABLE 1 | Descriptive analysis of the heavy metal contents in rhizosphere soil and rice samples.

Plantation type	Item	As	Cd	Cr	Cu	Hg	Pb	Zn
Soil (*N* = 38)	Min	1.75	0.22	35.50	12.10	0.07	15.00	47.30
	Max	20.72	7.72	177.00	45.80	0.34	57.80	324.00
	Mean	7.45	1.52	83.13	24.30	0.17	32.67	137.47
	SD	4.97	1.48	33.45	7.53	0.07	10.75	70.75
	CV (%)	66.76	97.35	40.24	30.99	37.55	32.89	51.47
	Skewness	1.186	2.466	1.066	0.947	0.882	0.779	0.983
	Kurtosis	0.463	7.851	0.734	0.858	0.215	0.255	0.527
	Soil background value	22.15	2.38	140.39	40.13	0.197	44.43	199.48
	Surface soil in Guangxi (Hou, 2020)	8	0.144	50	18	0.083	24	43
Rice (N = 38)	Min	0.06	0.01	0.03	1.15	0.00	0.01	10.20
	Max	0.21	1.04	1.54	14.10	0.01	0.60	21.10
	Mean	0.10	0.28	0.36	4.12	0.00	0.15	14.64
	SD	0.03	0.26	0.29	3.12	0.00	0.17	2.28
	CV(%)	30.26	92.88	80.18	75.87	31.57	109.21	15.56
	Skewness	1.621	1.358	2.083	1.772	0.106	1.146	0.665
	Kurtosis	3.356	1.521	6.781	2.821	-1.424	0.444	0.660

N is the number of samples (there are 22 Hg data in the rice sample); CV is the coefficient of variable; CV = SD/mean×100%; the units of elements are mg/kg.

$$\mathrm{PEF_i = Tr_i \times CF_i = Tr_i \times C_i / C_{REF_i}} \tag{3}$$

where $\mathrm{Tr_i}$ is the biological toxicity coefficient for heavy metal i (10, 30, 2, 5, 40, 5, and one for As, Cd, Cr, Cu, Hg, Pb, and Zn, respectively) (Hakanson, 1980). The potential ecological risk index (RI) can be calculated by the following function:

$$\mathrm{RI} = \sum_{i=1}^{n} \mathrm{PEF_i} \tag{4}$$

The classification standards of ecological risks for PEF and RI are shown in **Supplementary Table S1**.

Nemeiro Comprehensive Pollution Index

Single pollution index (Pi) is calculated to assess heavy metal pollution in soils and rice as follows:

$$\mathrm{Pi} = \frac{C_i}{S_i} \tag{5}$$

where $\mathrm{C_i}$ represents contents of the element i in the soil or rice sample, $\mathrm{S_i}$ represents contents of component i in risk screening values for soil contamination of agriculture land GB 15618-2018 (MEEPRC Ministry of Ecology and Environment of the People's Republic of China, 2018), or maximum levels of contaminants in foods GB 2762-2017 (NHFPCPRC and CFDA, National Health and Family Planning Commission and China Food and Drug Administration, 2017) in China, respectively. The risk screening values for soil and maximum levels of contaminants for rice were listed in **Supplementary Table S2**. As GB 2762-2017 only stipulates the content limits of As, Cd, Cr, Hg, and Pb in rice (**Supplementary Table S2**), these elements were assessed by Pi in this study. Soil or crop are polluted by metal i if Pi > 1 (Hu et al., 2017).

The Nemerow Comprehensive Pollution Index (NCPI) is simple in form and has good applicability. It is commonly used for heavy metal comprehensive pollution evaluation, and expressed as:

$$\mathrm{NCPI} = \sqrt{\left(\mathrm{P^2_{i\,max} + P^2_{i\,ave}}\right)/2} \tag{6}$$

where Pimax and Piave represent the maximum and average Pi value of PTE, respectively. According to NCPI, five levels are used to classify the pollution level of PTE: clean (≤0.7), prevention (0.7 ~1.0), light pollution (1.0~2.0), moderate (2.0 ~3.0), and heavy pollution (>3.0) (Hu et al., 2017; Kowalska et al., 2018).

Bioaccumulation factor

The transfer ratio of PTE from soil to the crop could be quantified by bioaccumulation factor (BAF) (Kumar et al., 2019) as follows:

$$\mathrm{BAF}_i = \frac{C_{i\,rice}}{C_{i\,soil}} \tag{7}$$

where $\mathrm{C_{i\,rice}}$ and $\mathrm{C_{i\,soil}}$ are the contents of element i in the rice and the corresponding rhizosphere soils, respectively.

Human Exposure and Risk Assessment

Health risk for three groups of people—children, adult women, and adult men—through rice consumption was evaluated by estimated daily intake (EDI), targeted hazard quotient (THQ), and hazard index (HI), as proposed by (USEPAU.S. Environmental Protection Agency, 1989)

$$\mathrm{EDI_i = (C_i \times DI)/BW} \tag{8}$$

$$\mathrm{THQ_i = EDI_i/RfD_i} \tag{9}$$

$$\mathrm{HI} = \sum_{i=1}^{n} \mathrm{THQ_i} \tag{10}$$

where $\mathrm{EDI_i}$ is the total daily exposure of element i [mg/(kg bodyweightday)], $\mathrm{C_i}$ is the content of i in polished rice (mg/kg), and DI is the recommended dose of rice intake for residents during 2013–2018 [0.25 and 0.40 kg/day for children and adults, according to the minimum and maximum recommended amounts of cereals by Chinese Nutrition Society (CNS Chinese Nutrition Society, 2021)]; BW is the body weight of children (9 years old), adult men and women,

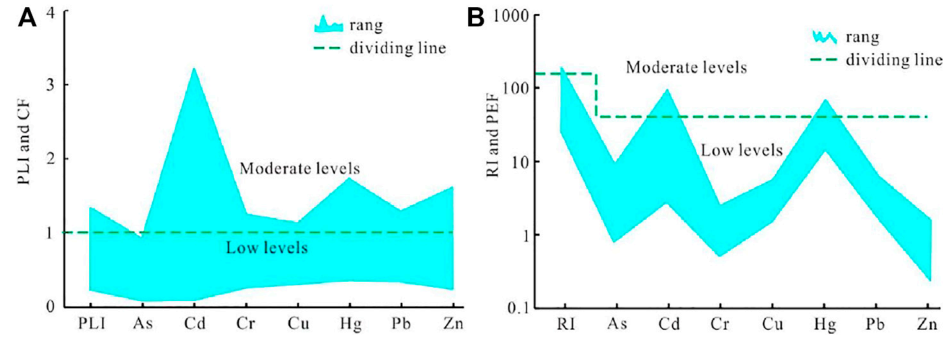

FIGURE 2 | Contamination levels **(A)** and potential ecological risk **(B)** of each PTE in the soils of the karst. The blue bands indicate the range of contamination factor (CF) and pollution load index (PLI) **(A)**, and potential ecological factor (PEF) and potential ecological risk index (RI) **(B)** of PTE in soils; and the green dotted line divides the low and moderate levels.

which are 30, 66.2, and 57.3 kg on average, respectively (Zuo et al., 2019). THQ_i is the ratio of element i between EDI and reference dose (RfDis). The RfD is considered safe for lifetime exposure to PTE and was enumerated in **Supplementary Table S3**. It may cause side effects to health when THQ >1. HI assumes that eating certain types of food may result in simultaneous exposure to multiple PTE. If HI < 1, harmful health effects are assumed to be unlikely to happen, while there are non-carcinogenic risks that could arise when HI > 1 (Zeng et al., 2015).

Data Analysis

Chemometric analysis including correlation analysis, unrotated principal component analysis, and varimax-rotated factor analysis were performed for source apportionment of soil PTE and risk assessment of soil-rice system by SPSS Statistics 18 (IBM, United States). Boxplots were performed by Origin 8.5 (Origin Lab, United States).

RESULTS AND DISCUSSION

Contents and Contamination Levels of PTE in the Soil

The statistical analysis results of PTE are exhibited in **Table 1**. On average, the contents of As, Cd, Cr, Cu, Hg, Pb, and Zn in soils were 7.45 ± 4.98, 1.53 ± 1.49, 83.13 ± 33.45, 24.3 ± 7.53, 0.18 ± 0.07, 32.67 ± 10.75, and 137.47 ± 70.75 mg/kg, respectively. Soil pH ranged from acidic (4.83) to alkaline (8.18). The results showed that the averaged contents of all PTE in soil samples were significantly lower than the corresponding local background values of Mashan County but higher than the background value of surface soil in Guangxi except for As (Hou Q. Y. et al., 2020) (**Table 1**). There were 6, 2, 2, 11, 6, and 7 in 38 samples of Cd, Cr, Cu, Hg, Pb, and Zn that exceeded the local background values.

The coefficient of variations (CV) of the PTE in the soils was, in a decreased order, Cd (97.35%), As (66.76%), Zn (51.47%), Cr (40.24%), Hg (37.55%), Pb (32.89%), and Cu (30.99%), respectively (**Table 1**), suggesting that Cd was obviously enriched in some soil samples, while Zn, Cr, Hg, Pb, and Cu were slightly enriched in some areas. In addition, results of the Kolmogorov-Smirnov test for normality also showed that all the studied soil element contents were skewed distributions.

PTE in almost all soil samples had a CF value below 3, except for one sample with CF_{Cd} of 3.24 (**Figure 2A**; **Table 2**), indicating that the contamination levels of PTE were low or slightly moderate (Kowalska et al., 2018). The average PLI value was 0.60 ± 0.27, and 5 out of 38 samples had a PLI value greater than 1, with the maximum value of 1.35. The relatively low PLI value indicated that the soil was mildly polluted due to the high geological background (Kowalska et al., 2018).

The PEF of soil samples was 3.37 ± 2.25, 19.24 ± 18.73, 1.18 ± 0.48, 3.03 ± 0.94, 35.59 ± 13.37, 3.68 ± 1.21, and 0.69 ± 0.35 for As, Cd, Cr, Cu, Hg, Pb, and Zn, respectively (**Figure 2B**). Only 3 samples of Cd and 11 samples of Hg had a moderate potential risk in the study area (**Figure 2B**). The RI values ranged from 23.70 to 190.30, with an average value of 66.77 ± 35.00, demonstrating that all soil samples were at a pollution-free level.

However, according to the risk screening values of As, Cd, Cr, Cu, Hg, Pb, and Zn stipulated in GB 15618-2018, the contents of Cd in 84.21% of soil samples were above the risk screening values, followed by Zn, with 10.53% of samples exceeding the risk screening values, while As, Cr, Cu, Hg, and Pb in paddy soils were lower than the guideline (**Figure 3**). NCPI of 21.05 and 26.32% soil samples showed moderate and heavy pollution (**Table 3**), which is common in karst areas (Wen et al., 2020b). With the increase of weathering intensity, the content of Fe/Al/Mn oxides, organic carbon, and clay minerals increases, and leads to the enrichment of Cd in soil (Wen et al., 2020b; Yang et al., 2021b).

Chemometric Analysis for Source Identification and Risk Assessment of PTE in Soil

Correlation Analysis

The correlation coefficients between soil pH, SOC, effective state, and heavy metals (As, Cd, Cr, Cu, Hg, Pb, and Zn) in the studied soils were calculated to study the influencing factors on the enrichment of heavy metals in soils (**Supplementary Table S4**). Contents of As, Cd, Cr, Cu, Hg, Pb, Zn, A_{Si}, and A_{Mn} in

TABLE 2 | Number of soil samples with PTE pollution assessed by contamination factor (CF) and pollution load index (PLI) in the study area.

Pollution level		As	Cd	Cr	Cu	Hg	Pb	Zn	PLI
Low degree	Number	38	32	36	36	27	32	31	33
	Percentage	100%	84.21%	94.74%	94.74%	71.05%	84.21%	81.58%	86.84%
Moderate degree	Number	0	5	2	2	11	6	7	5
	Percentage	0.00%	13.16%	5.26%	5.26%	28.95%	15.79%	18.42%	13.16%
Equivalent degree	Number	0	1	0	0	0	0	0	0
	Percentage	0.00%	2.63%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%

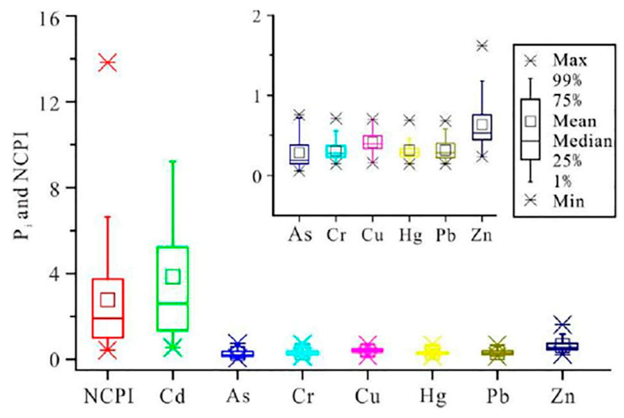

FIGURE 3 | Boxplots of heavy metal single pollution index (Pi) and Nemerow Comprehensive Pollution Index (NCPI) of soil in the study area.

soils were significantly positively correlated with each other ($p < 0.01$). High E_{Ca} and E_{Mg} content can increase the adsorption of heavy metal ions (Kokkinos et al., 2020), can also increase soil pH, and indirectly immobilize heavy metals (Hussain et al., 2021). The Corg was significantly positively correlated with Cd, Cu, Hg, and Pb, consistent with the results of previous studies (Mu et al., 2020; Zhang et al., 2021). Available Fe was significantly ($p < 0.01$) negatively correlated with pH, E_{Ca}, E_{Mg}, A_{Si}, and all studied PTE, but significantly positively correlated with A_{Cu} and A_{Zn}, indicating higher Fe availability in lower pH soils, similar to those reported for paddy soil in Bangladesh (Rahman et al., 2018) and India (Baruah et al., 2021). All the studied PTE were almost significantly negatively correlated with A_{Fe} in soils, which indicated that the activity of Fe is not conducive to the accumulation of heavy metals (Yu et al., 2016). The ferromanganese nodules have a strong ability to enrich heavy metals. The change of redox conditions results in the layered distribution of iron, manganese, and heavy metals in the nodules. Different mineral species in the nodules have different release and adsorption capacities of elements in the face of environmental changes, which results in different correlations (Frierdich and Catalano, 2012; Liu et al., 2021).

Principal Component Analysis

PCA can be used to identify potential sources of the PTE (Egbueri and Agbasi, 2022; Mallongi et al., 2022). The correlation coefficients of most variables in this area were relatively high, and common factors can be extracted from them; the corresponding probability P is close to 0, and the Kaiser-Meyer-Olkin test value is 0.831, which is suitable for PCA to establish an adequate understanding of the sources of heavy metals and other parameters in the analyzed samples. Results of the PCA are presented in **Table 4**. It can be seen from **Table 4** that the information of the sources of PTE can be represented by 3 PCs, and the 3 PCs can explain 86.6% of the total variables, indicating that the first three factors can reflect most of the information of all the data. It was clear that As, Cd, Cr, Cu, Hg, Pb, Zn, pH, A_{Si}, and A_{Fe} have significant loadings in PC1. This suggests that there may be a closer correlation between these parameters. The average content of all PTE did not exceed the local background value, and the excess rate was very low, indicating a main natural source of these PTE (Kowalska et al., 2018). They could be attributed to the weathering of carbonate minerals (Egbueri et al., 2021a). Various degrees of soil pollution of PTE were reported in the karst regions (Zhang et al., 2013). During the weathering and pedogenesis of heavy metal-rich carbonate rocks, alkaline Earth elements were leached, and heavy metals in soil were enriched by residues such as Fe/Mn oxides and clay minerals (Wen et al., 2020b). The carbonate rocks weathered soil characterized by high pH, high calcium carbonate, and soil organic matter content, which play an essential role in immobilizing PTE in soil (Guo et al., 2006; Zhao et al., 2010; Wang et al., 2015).

In PC2, significant loadings were observed on the A_{Cu}, Corg, A_{Zn}, and Cu (**Table 4**). Rice roots and straws are the main sources of organic matter in paddy soils. The enrichment coefficients of Cd, Cu, and Zn in the soil-rice system are relatively high. Previous studies believed that heavy metals mainly accumulated in the

TABLE 3 | Number of soil samples with PTE pollution assessed by Nemerow composite pollution index (NCPI) according to GB 15618-2018 in the study area.

	Clean	Precaution	Light pollution	Moderate	Heavy pollution
Number	4	5	11	8	10
Percent	10.53%	13.16%	28.95%	21.05%	26.32%

TABLE 4 | Data dimensionality reduction extractions.

Parameter	Unrotated principal components			Varimax-rotated factor loadings			Communality
	PC1	PC2	PC3	Factor 1	Factor 2	Factor 3	
As	0.928	–0.151	-0.115	0.771	0.550	–0.027	0.898
Cd	0.915	0.206	0.130	0.698	0.502	0.397	0.897
Cr	0.861	–0.125	–0.079	0.703	0.519	0.003	0.763
Cu	0.817	0.550	–0.069	0.807	0.138	0.552	0.975
Hg	0.921	0.033	0.076	0.696	0.564	0.228	0.855
Pb	0.916	0.121	–0.185	0.859	0.354	0.155	0.887
Zn	0.975	0.117	0.061	0.766	0.541	0.297	0.967
Corg	0.314	0.694	0.396	0.173	0.054	0.839	0.737
pH	0.904	–0.227	0.105	0.611	0.711	0.028	0.880
E_{Ca}	0.570	–0.466	0.607	0.010	0.953	0.051	0.911
E_{Mg}	0.697	–0.535	0.371	0.229	0.918	–0.113	0.909
A_{Si}	0.838	0.217	–0.407	0.944	0.121	0.098	0.915
A_{Mn}	0.639	0.059	–0.693	0.914	–0.085	–0.222	0.891
A_{Fe}	–0.824	0.407	–0.037	–0.547	–0.719	0.171	0.846
A_{Zn}	–0.635	0.557	0.148	–0.47	–0.576	0.427	0.736
A_{Cu}	–0.156	0.850	0.227	–0.071	–0.406	0.792	0.798
NCPI	0.780	0.468	0.190	0.613	0.319	0.621	0.863
PLI	0.990	0.107	-0.005	0.813	0.515	0.255	0.992
RI	0.980	0.115	0.070	0.764	0.551	0.302	0.979
Eigenvalue	12.238	2.942	1.520	8.365	5.547	2.788	
Variance %	64.412	15.482	7.998	44.026	29.193	14.674	
Cumulative %	64.412	79.894	87.893	44.026	73.219	87.893	

roots, and there was a good correlation between Corg and PTE. For instance, human activities such as water irrigation and application of fertilizers and pesticides may have a significant impact on the enrichment of metals in farmland (Yang et al., 2013). Thus, PC2 can be attributed to agricultural activity.

Furthermore, PC3 was noticed to have obvious loadings on A_{Mn} and E_{Ca} (**Table 4**), having a negative and positive loading, respectively. The variation showed differences in their origin or impact. As discussed above, E_{Ca} affects the mobility of heavy metals by buffering pH. While A_{Mn} was significantly positively correlated with organic matter and clay content, extremely significantly negatively correlated with pH and calcium carbonate content, and extremely significantly positively correlated with cation exchange capacity (Pu et al., 2010).

Varimax-Rotated Factor Analysis

The Varimax twiddle factors extracted in this study for soil heavy metal association and source identification are shown in **Table 4**. Similar to PCA, 86.6% of the information about the heavy metal data was explained by three-factor categories. Factor 1 has high loadings for As, Cd, Cr, Cu, Hg, Pb, Zn, pH, A_{Si}, A_{Fe}, PLI, and RI (**Table 4**). Combined with the fact that there are only individual quarries in the locality and no other industries, therefore, Factor 1 was judged to be the “weathering residual source”. Meanwhile, the correlation between As, Cd, Cr, Hg, Pb, Zn, SPI, and RI in Factor 2 became stronger than in PC3. This observation seems to confirm that they may have the same origin. The extremely positive correlation of E_{Ca} and E_{Mg} with Factor 2 suggested the source of carbonate rock, the nearby limestone quarries. Furthermore, leaded gasoline, diesel combustion, fossil fuel burning, braking, and vehicular emission were potentially elevated PTE levels in the soil. Therefore, Factor 2 may be attributed to the mixture of mineral powder and fuel exhaust particles in the farmland soil in the form of dry and wet deposition. Moreover, recent studies found that several elements such as Zn, Cd, Pb, and As in alluvial deposits are related to their easily transportable forms (soluble forms) (Fonseca et al., 2021). Toxic elements in soils developed from carbonate rocks can also be transported and deposited in downstream alluvial plains (Hou Q. et al., 2020). Factor 3 explained about 14.674% of the total variance and was considered loaded for Corg, A_{Cu}, Cu, and A_{Zn} (**Table 4**), which is the same as PC2 related to agricultural resources. They can come from wastewater irrigation, fertilizer application, pesticides, organic manures, compost, and sewage sludges.

Contents and Risk Assessment of PTE in Rice

The mean contents of As, Cd, Cr, Cu, Hg, Pb, and Zn in rough rice were 0.10 ± 0.03, 0.28 ± 0.26, 0.36 ± 0.29, 4.12 ± 3.12, 0.0045 ± 0.0014, 0.15 ± 0.17, and 14.64 ± 2.28 mg/kg, respectively (**Table 1**; **Figure 4A**). The Pi of the As, Cd, Cr, Hg, and Pb of rice samples varied from 0.29 to 1.05, 0.03 to 5.20, 0.03 to 1.54, 0.01 to 0.35, and 0.03 to 3.00, respectively. The average Pi decreased in the order of Cd (1.38) >Pb (0.77) > As (0.52) > Cr (0.36) > Hg (0.13) (**Figure 4B**). In the present study, 55.26% of Cd (21 samples) and 31.58% of Pb (12 samples) were higher than the maximum allowable value of 0.2 mg/kg for cereal grains recommended by NHFPCPRC and CFDA, National Health and Family Planning Commission and China Food and Drug Administration (2017), respectively, and 15.79% (6 samples) of the samples had both Cd and Pb exceeding the maximum

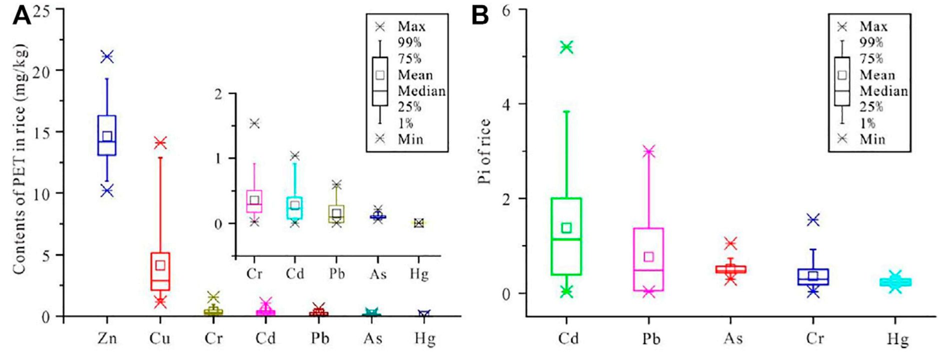

FIGURE 4 | Boxplots of heavy metal contents **(A)** and single pollution index (Pi) **(B)** of rice in the study area (mg/kg).

TABLE 5 | The number of samples with non-carcinogenic risk [targeted hazard quotient (THQ)≥1] caused by rice intake of different groups in the study area.

Groups		As	Cd	Cr	Cu	Hg	Pb	Zn
Child	Number	38	23	16	11	0	3	0
	Percentage	100%	60.53%	42.11%	28.95%	0%	7.89%	0%
Women	Number	38	22	12	8	0	2	0
	Percentage	100%	57.89%	31.58%	21.05%	0%	5.26%	0%
Men	Number	38	21	10	6	0	1	0
	Percentage	100%	55.26%	26.32%	15.79%	0%	2.63%	0%

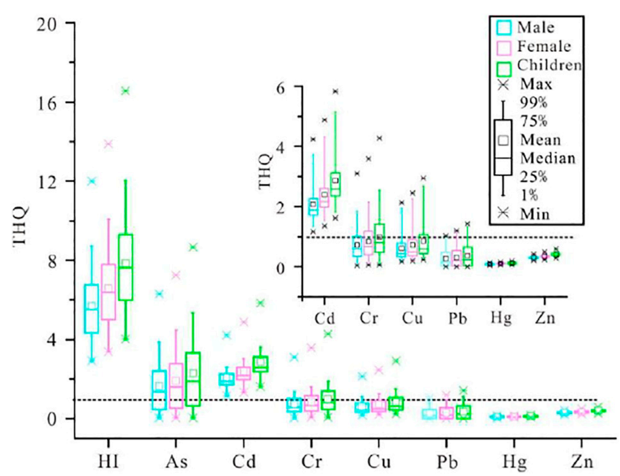

FIGURE 5 | Box plots of targeted hazard quotient (THQ) for individual heavy metals and hazard index (HI) of men, women, and children (horizontal dotted line indicates the threshold value of the hazard quotient).

allowable value. The exceedance rate of inorganic As and Cr was 2.6%. This is consistent with the low exceedance rates of As, Cr, and Hg in rice grain in the karst areas of Guangxi (Yang et al., 2021a). The excess rate of Pb in this study was relatively high but does not exceed the maximum allowable value in Yang et al. (2021a). The Cd in 26.67% (75 in total) of the rice samples exceeded the maximum allowable value in karst regions of Liujiang County, Guangxi, with the mean contents of 0.16 mg/kg (Tang et al., 2021). Even higher excessive rates were found in the karst area of Jinchengjiang, Guangxi, 95% (40 in total) of rice grains harvested from limestone soil had a Cd content that surpasses the maximum permissible concentration (Li et al., 2018). The CVs of PTE in rice decreased in an order of Pb (109.21%), Cd (92.88%), Cr (80.18%), Cu (75.87%), Hg (31.57%), As (30.26%), and Zn (15.56%) in this study. The high spatial heterogeneity of Cd may lead to different results of the exceeded rate in different areas.

Human Health Risk Assessments

The results of using EDI, THQ, and HI to assess the potential non-carcinogenic effect of long-term exposure to PTE of edible rice are shown in **Table 5** and **Figure 5**. The average EDIs of As, Cd, Cr, Cu, Hg, Pb, and Zn for inhabitants by consuming rice were 0.00062, 0.00166, 0.00216, 0.02487, 0.00002, 0.00191, and 0.08849 mg/(kg BWday) for men, and 0.00072, 0.00192, 0.00250, 0.02874, 0.00002, 0.00107, and 0.10223 mg/(kg BWday) for women, and 0.00086, 0.00230, 0.00298, 0.03430, 0.00004, 0.00128, and 0.12204 mg/(kg BWday) for children. The average THQ values of PTE decreased in an order of As (2.08) >Cd (1.66) >Cr (0.72) >Cu (0.62) >Zn (0.29) >Pb (0.27) >Hg (0.09) for men, As (2.4) >Cd (1.92) >Cr (0.83) >Cu (0.72) >Zn (0.34) >Pb (0.31) >Hg (0.1) for women, and As (2.86)>Cd (2.3) >Cr (0.99) >Cu (0.86) >Zn (0.41) >Pb (0.37) >Hg (0.12) for children. The EDIs and THQs values of the PTE decreased in the order of children > women > men owing to the increasing body weight. The dietary risk of Cd and As in children is the highest, and decreases with the increasing body weight. The same results were reported by Chen et al. (2018), Baruah et al. (2021), and Mallongi et al. (2022). Children are also at higher health risks

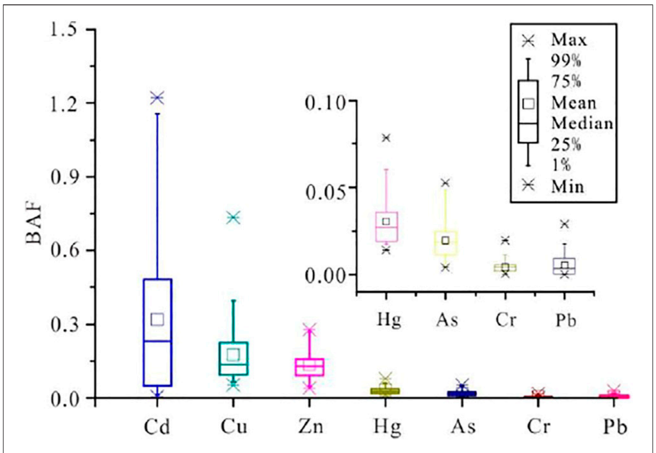

FIGURE 6 | The bioaccumulation factor (BAF) values of PTE in rice samples.

than adults by drinking substandard water. The HI, THQ_{As}, and the average THQ_{Cd} in all the samples were greater than 1 (**Figure 5**), indicating that residents suffer from non-carcinogenic risk by rice consumption. As and Cd were the biggest contributors to high HI. This is consistent with previous studies reporting that As and Cd intake of rice is the main contributor to health risks (Chen et al., 2018; Baruah et al., 2021; Tang et al., 2021). Given the high dietary Cd intake, effective agronomic measures should be considered to solve Cd pollution in the soil and reduce the transfer of Cd from the soil to edible crops (Hussain et al., 2021).

Influencing Factors of PTE Enrichment in Soil-Rice System

The BAF values of As, Cd, Cr, Cu, Hg, Pb, and Zn in rice were 0.02, 0.318, 0.005, 0.173, 0.030, 0.005, and 0.135, respectively, on average (**Figure 6**). The results are consistent with the fact that cadmium seems to prefer to be absorbed by the rice, although it is not an essential element. The average enrichment index for Cd, Zn, and Cu was 0.269, 0.160, and 0.083 in a soil–rice system in Wenling, Zhejiang Province, respectively, and varied significantly with heavy metals in paddy fields (Zhao et al., 2010). Cd can form a complex with plant peptide transporters; thus, it can be transported to the rice grains (Rizwan et al., 2012). Cd^{2+} could replace Ca^{2+} more easily than other PTE owing to their similar ion radius and same valence, and Cd would be transported actively into the grain through the Ca channel, while other PTEs could only be transported passively (Kim et al., 2002; Chang et al., 2014).

To determine the relationship between the PTE in rice and the corresponding rhizosphere soils, correlation analysis was performed. There was a certain correlation of PTE between rice and soil (**Supplementary Table S5**). The concentrations of Cd ($p < 0.01$), Hg ($p < 0.01$), Pb ($p < 0.01$), and Zn ($p < 0.01$) in soil correlated positively with As in rice, and the concentrations of As ($p < 0.01$), Cr ($p < 0.05$), Hg ($p < 0.05$), Pb ($p < 0.05$), and Zn ($p < 0.05$) in soil correlated positively with Hg in rice, indicating that these elements in soil promoted the accumulation of As and Hg in rice grains. However, the correlation of other heavy metals in rice and soil was not significant, even A_{Cu} was not significantly correlated with Cu in rice, indicating that the accumulation of heavy metals in the soil-rice system was also affected by other factors. Heavy metals are absorbed by soil organic matter and reduce the accumulation of heavy metals in crops. For example, the Hg content of rice, $lgBAF_{Hg}$, and $lgBAF_{Zn}$ are negatively correlated with Corg (**Supplementary Table S5**). But the high Corg content will also increase the accumulation of As in rice (Norton et al., 2013). This study also found a significant positive correlation between As in rice and Corg in soil (**Supplementary Table S5**). Content of As, Cd, and Zn in rice and their lgBAF were significantly negatively correlated with pH, E_{Ca}, and E_{Mg} in soil, respectively, at different confidence levels (except that Cd was not significantly correlated with E_{Ca}) (**Supplementary Table S5**). Soil pH affects the dissolution of heavy metals, especially in acidic rice fields; low pH may result in increased solubility and high availability of heavy metals in rice. High exchangeable calcium and magnesium content can increase soil pH and indirectly immobilize heavy metals (Hussain et al., 2021), and also promote the adsorption capacity of heavy metals (Kokkinos et al., 2020), leading to negatively correlated results. However, the correlation between Hg in rice and elements in the soil is opposite to them. Hg in rice was significantly positively correlated with pH, E_{Ca}, and E_{Mg} in soil, but significantly negatively correlated with A_{Fe}, A_{Zn}, and A_{Cu} (**Supplementary Table S5**). Meanwhile, Cd and Zn in rice were significantly positively correlated with A_{Fe}, A_{Zn}, and A_{Cu}; lgBAF of As, Cd, and Zn were significantly positively correlated with A_{Fe} and A_{Zn} (**Supplementary Table S5**). This is consistent with previous reports that decreased rhizosphere Fe and Cd concentrations resulted in lower Cd concentrations in rice (Zhang et al., 2018). Iron is an essential and important element in plants, and the chemical properties and pathways into rice of Fe and Cd are similar, resulting in their high correlation in crops (Sharma et al., 2004; Chen et al., 2017; Liu et al., 2017). Changes in the redox environment affect the dissolution and bioavailability of heavy metals with different irrigation methods. Concentrations of iron oxides change due to redox changes in paddy fields, so it is reasonable that Fe oxide was significantly and positively correlated with BAF of As, Cd, and Zn since heavy metals may release from stable Fe oxide bound fraction which would increase the availability of heavy metals to rice. The correlation of A_{Mn}, A_{Fe}, and lgBAF of heavy metals can also be traced back to their correlation with heavy metal content in soil (**Supplementary Tables S5 and S4**), which may be related to changes in pH and redox conditions affecting the formation and evolution of iron-manganese nodules. Significantly negative correlations between A_{Si} and $lgBAF_{As}$, $lgBAF_{Cd}$, $lgBAF_{Hg}$, and $lgBAF_{Zn}$ indicate that Si can effectively alleviate the bioaccumulation of PTE (**Supplementary Table S5**), as suggested by a previous study (Li et al., 2018). In natural environments, soil properties such as pH, CEC, redox potential, minerals (phosphates, metal hydroxides, metal oxides, and clays), and SOM jointly affect the BCF of PTE (Ata-Ul-Karim et al., 2020). Future studies are recommended to investigate the interactions between soil properties to gain a comprehensive understanding of the bioavailability of PTE in soil-crop systems. For farmers, the use of unqualified mineral fertilizers or excessive use of pesticides should be avoided. Although the excess rate of As in soil and rice was very low, its non-carcinogenic risk to humans is high, so organic fertilizers should be used with caution to reduce the risk of As enrichment in rice. Meanwhile, attention should be paid to soil acidity and alkalinity, as well as the impact of irrigation methods on the accumulation of heavy metals in rice.

CONCLUSION

The average concentration of all studied PTE in rhizosphere soil of rice samples was below the local background value of Mashan County, but higher than the background value of surface soil in Guangxi except for As. Results of contaminant risk assessment using background values as reference values indicated a low-risk status. However, Cd in 84.21% of the samples exceeded the risk screening value of GB 15618-2018, and 21.05 and 26.32% of the samples were moderately and heavily polluted in the NCPI assessment. Weathering of parent rocks and alluvial deposits are the major source of heavy metals in soils, while fossil fuel combustion and agricultural activities also contribute to the accumulation of soil PTE. Cd in 55.26% and Pb in 31.58% of rice samples exceed the maximum allowable value of rice of China. The high excessive rate of Cd and Pb could be attributed to their high bioaccumulation factor and high content in the soil. Residents may be exposed to As and Cd through rice consumption, resulting in significant non-carcinogenic health risks, especially children. Health risks caused by excessive consumption of wild heavy metal-enriched rice should be avoided. Residents are expected to apply appropriate agricultural products and irrigation methods to mitigate the risk of PTE enrichment in rice, and future research should place a high value on rice cultivars and bioavailability of PTE in agricultural soils in the karst areas.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

XZ had the original ideas, designed the research, and acquired financial support for the project leading to this publication. CZ collected the sample, carried out the data analysis, and prepared the original draft. HY, JL, and TZ analyzed data for figures and tables, and helped to prepare the original draft. All authors contributed to manuscript development and edited the final version.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenvs.2022.866427/full#supplementary-material

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