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Source apportionment of heavy metal(loid)s in sediments of a typical karst mountain drinking water reservoir and the associated risk assessment based on chemical speciation

Xue Chen
College of Agriculture, Guizhou University, Guiyang 550025, Guizhou Province, China
Pan Wu
Key Laboratory of Karst Georesources and Environment of Ministry of Education, Guizhou University, Guiyang 550025, Guizhou Province, China
Xue Chen
Guiyang Rural Revitalization Service Center, Guizhou Province, Guiyang 550025, Guizhou Province, China
Hongyan Liu
College of Agriculture, Guizhou University, Guiyang 550025, Guizhou Province, China
Xuexian Li (xxli5@gzu.edu.cn)
College of Agriculture, Guizhou University, Guiyang 550025, Guizhou Province, China

Research Article

Keywords: Reservoir sediments, heavy metal(loid)s, Risk assessment, Source apportionment, PMF

Posted Date: December 5th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-2311171/v1

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Additional Declarations: No competing interests reported.

Version of Record: A version of this preprint was published at Environmental Geochemistry and Health on July 2nd, 2023. See the published version at https://doi.org/10.1007/s10653-023-01676-8.

Abstract

As important place for water storage and supply, karst reservoirs play a key role in ensuring human well-being, and its water quality safety has attracted much attention. Source apportionment and ecological risks of heavy metal(loid)s in sediments of drinking-water reservoir are of great significance to ensure the safety of water quality and public health, especially in karst mountain areas where water resources are scarce. To expound the accumulation, potential ecological risks and sources of heavy metal(loid)s in a drinking-water reservoir from Northwest Guizhou, China, the surface sediments were collected and analyzed based on the combined use of the geo-accumulation index (I_{geo}), sequential extraction (BCR), ratios of secondary phase and primary phase (RSP), risk assessment code (RAC), modified potential ecological risk index (MRI), as well as the Positive Matrix Factorization (PMF) methods. Results showed that the concentrations of Cd, As, Pb, Cr, Cu, Ni, and Zn in sediments exceeded the corresponding background values of soils in Guizhou Province. The I_{geo} indicated that the accumulation of Cd was high, approximately 61.9% of the samples were at moderate and above accumulation levels, followed by Pb, Cu, Ni, and Zn, whereas the As and Cr were at low level. Based on the sum of toxic units (STU), the surface sediments in the reservoir showed a moderate level of toxicity. A large proportion of BCR-extracted acid extractable and reducible fraction was found in Cd (72.5%) and Pb (40.3%), suggesting high bioavailability. Combined RSP, RAC and MRI results showed that Cd was the major pollutants, which had a higher potential risk, while the other elements were at a lower risk level. Source apportionment of heavy metal(loid)s in the drinking-water reservoir indicated that Cd (75.76%) and Zn (23.1%) mainly originated from agricultural activities; As(69.82%), Cr(50.05%), Cu(33.47%), and Ni(31.87%) were associated with domestic sources related to residents' lives; Cu (52.36%), Ni (44.57%), Cr (34.33%), As (26.51%), Pb (24.77%), and Zn (23.80%) were primarily from natural geological sources; and Pb (47.56%), Zn (22.46%) and Cr (13.92%) might be introduced by mixed sources of traffic and domestic. The contribution ratios of the four sources were 18.41%, 36.67%, 29.48% and 15.44%, respectively.

1. Introduction

As important water sources for drinking, industry, agriculture and ecosystem services, karst water resources have met the drinking water demand of approximately a quarter of the world’s population, and their importance is increasing (Ford and Williams, 2007; Koit et al., 2022; Kalhor et al., 2018; Ravbar et al., 2021). However, the originally fragile and sensitive ecological environment, coupled with the impact of human activities, has exacerbated the pollution and shortage of karst water resources (Li et al., 2022a; Qin et al., 2021; Zhou et al., 2021). Especially in the karst mountain areas with engineering water shortage in developing countries, semi-urbanization, intensive industry, agricultural non-point source pollution, arbitrary stacking of rural household garbage and direct discharge of untreated sewage have increased the discharge of pollutants, posing a great threat to the quality of karst water (Zhou et al., 2021; Qin et al., 2021). Karst reservoirs, as important place for water storage and supply in karst mountain areas, play a key role in ensuring human well-being, and its water quality safety has attracted much attention (Zhou et al., 2021; Ma et al., 2021). In recent years, heavy metal(loid)s pollution of karst water resources has

become a worrying problem of water security (Miao et al., 2021; Qin et al., 2021). As potentially hazardous pollutants with high toxicity and bioaccumulation, heavy metal(loid)s can cause direct or indirect harm or risk to human health or ecosystem through multiple exposure pathways such as sediment and water (Magesh et al. 2021, Akindele et al. 2020). According to incomplete statistics, more than 80% of the sediments of rivers and lakes have been contaminated by heavy metal(loid)s in China (Lu and Peng 2019). Heavy metal(loid)s such as Pb, Zn, Ni, Cu, As and Cd, which are closely associated with natural sources (geological weathering, precipitation, erosion) and anthropogenic activities (domestic sewage discharge, industrial pollution and agricultural runoff, traffic and transportation, mining, urban activities as well as combustion of fossil fuel) are enriched continuously in the sediments of many important rivers, lakes and reservoirs, causing water pollution, which has been highly concerned by many researchers worldwide(Chen et al. 2022a, Li et al. 2022c, Li et al. 2022b, Marziali et al. 2021).

As important carriers and ‘storage tanks’ of pollutants in aquatic environment, the sediment is not only the sink of heavy metal(loid)s in overlying water such as reservoirs, rivers, and lakes, but also vital source of them in water (Bastami et al. 2012, Yao et al. 2021). It has been proved that only a small amount of exogenous heavy metal(loid)s remains in dissolved state after entering the water, while most of them are adsorbed and aggregated by sediment (Chen et al. 2021, Lee et al. 2021). However, these heavy metal(loid)s can be released again into the water due to the changes of water conditions, a series of physical and chemical reactions, resulting in ‘secondary pollution’ of water environment (Kim et al. 2021, Zhang et al. 2019). Drinking-water reservoir is important source of water supply in karst mountain areas, and the water quality protection is particularly important to ensure the safety of water supply for those who draw on the water resource(Blake et al. 2020, Lee et al. 2017; Zhou et al., 2022). Additionally, pollution with heavy metal(loid)s in drinking-water reservoir and sediment pose a serious threat to the environmental ecosystem and even affects the safety and health of human water supply due to its high toxicity, difficult to degrade, persistent and irreversible, which has raised public and special attention all over the world (Lee et al. 2017, Toller et al. 2022, Li et al. 2022b). Therefore, it is particularly important to investigate the concentration and distribution of heavy metal(loid)s in the sediments of drinking-water reservoirs and identify the sources of heavy metal(loid)s pollution.

However, the mobility, toxicity properties and bioavailability of heavy metal(loid)s in sediments is not only associated with the total concentrations of heavy metal(loid)s, but also related to its chemical speciation(Chen et al. 2022a, Zhuang et al. 2016). That is, different chemical speciations of heavy metal(loid)s have different chemical stability and bioavailability, which will pose different ecological risks to the ecosystem. Thus, determination of single concentrations of heavy metal(loid)s is insufficient to estimate whether its lead to environmental risk(Lee et al. 2017, Zhuang et al. 2016). Besides, the pH value, redox potential, salinity, hydraulic disturbance and microbial activities in sediments will promote the transformation of occurrence forms of heavy metal(loid)s(Teasdale et al. 2003, Toller et al. 2022), even affecting their bioavailability. Previous studies have shown that speciation analysis of heavy metal(loid)s in sediments can better evaluate their potential ecological hazards and mobility(Gao et al. 2016). To date, the sequential extraction procedures (SEP) have been widely used for heavy metal(loid)s speciation analysis in sediments to study different mobile fractions in detail(Liu et al. 2021, Toller et al.

2022, Tessier, Campbell and Bisson 1979, Chen et al. 2022a). Among them, the three-stage sequential extraction method, proposed by European Community Bureau of Reference (BCR) is often used to analyze the chemical speciations of heavy metal(loid)s in sediments due to due to its simple steps, high accuracy and good stability(Chen et al. 2021, Toller et al. 2022). Previous studies have demonstrated that heavy metal(loid)s dominated by residues are primitively related to regional geological background and are not easy to migrate and have little impact on the ecosystem(Liu et al. 2021), while heavy metal(loid)s produced by anthropogenic activities may have relatively high bioavailability and mainly exist in the forms of available(Nillos et al. 2020). It has been reported that the available occurrence forms, such as acid extractable/exchangeable fraction of heavy metal(loid)s in sediments can be absorbed on, ingested and accumulated by aquatic plants and microorganisms, and has high ecological risk(Jiang et al. 2018, Zhang et al. 2018). Therefore, chemical speciation-based risk assessment of heavy metal(loid)s pollution in sediments are increasingly favored in current studies, and the risk assessment code (RAC) and the modified potential ecological risk index (MRI) based on the acid extractable/exchangeable fraction of heavy metal(loid)s have become important means to effectively evaluate the ecological risk(Liu et al. 2021, Toller et al. 2022, Chen et al. 2022a). Additionally, the reduced and oxidizable heavy metal(loid)s in sediments will undergo morphological transformation or decomposition under the influence of redox conditions and microbial action, resulting in migration and transformation, and even be absorbed and utilized by aquatic organisms(Liu et al. 2021, Liang et al. 2017). Thus, the ratios of secondary phase and primary phase (RSP) of bioavailable heavy metal(loid)s is crucial method to effectively evaluate the potential ecological risk of heavy metal(loid)s in sediments(Liu et al. 2021, Zhan et al. 2020).

Accurate identification and quantification of heavy metal(loid)s source contributions in sediments is of great significance for timely blocking pollution sources(Wu et al. 2019, Zhang et al. 2020). At the same time, it also helps the government to formulate corresponding risk mitigation measures to prevent and control heavy metal(loid)s pollution from sources, which is the fundamental way to protect the ecological security of drinking-water reservoirs and reduce the potential harm of heavy metal(loid)s to human beings. At present, multivariate statistical methods and receptor-based models, mainly including factor analysis (FA), cluster analysis, principal component analysis(PCA), absolute principal component scores-multivariate linear regression (APCS-MLR), mass balance method (CMB), UNMIX model and positive matrix factorization (PMF), have been successfully used for sediment and soil heavy metal(loid)s source apportionment(Hao et al. 2022, Jiang et al. 2018, Shi et al. 2022, Zhang et al. 2019, Chen et al. 2022b, Proshad et al. 2022). Most of these methods are effective tools for classifying samples and identifying pollution sources by extracting meaningful information from large datasets, providing a clearer understanding of the natural and anthropogenic factors that influence the geochemical cycle of heavy metal(loid)s. The PMF receptor model approved by the U.S. Environmental Protection Agency can provide not only the number of pollution sources and the elements contributed by each pollution source, but also the contribution calculations of each pollution source to certain elements according to experimental uncertainty in the data matrix(Proshad et al. 2022). More importantly, PMF allows the discovery of quantitative information of variables controlling the distribution of heavy metal(loid)s(Chen et al. 2019),

therefore, it is very useful for effectively classifying heavy metal(loid)s pollution and developing corresponding remediation strategies.

The contamination of heavy metal(loid)s in regional soil caused by the superposition of high geological background and human activities is a prominent environmental problem in Northwest Guizhou, China. Many researchers have conducted considerable researches on the distribution, accumulation, ecological risk, and sources of heavy metal(loid)s in soils and crops(Li et al. 2022c, Luo et al. 2022, Wang et al. 2022). As we all know, contaminants in soils can easily enter the water environment through surface runoff and leaching, and finally accumulate in sediments(Hao et al. 2022). Unfortunately, the information available on the study of the content level, source and pollution risk of heavy metal(loid)s in sediments of drinking-water reservoir system is very limited. Reservoir sediments, as the central link of regional material circulatio, can not only reflect the pollution of heavy metal(loid)s in water environment, but also record the provenance information of heavy metal(loid)s in the sediments. Simultaneously, the water quality of drinking-water reservoir is directly related to human health and production activities, and plays an extremely important role in the evolution of ecological environment and social development. Thus, investigating the heavy metal(loid)s behaviors in the drinking-water reservoir can provide a new perspective, to improve the protection and management of regional ecological environment. Therefore, the purpose of this study is: 1) to investigate the concentrations and distribution of heavy metal(loid)s in the surface sediments of Yangwanqiao Reservoir; 2) to analyze chemical speciation and evaluate the ecological risk and the adverse biotoxicity of heavy metal(loid)s according to STU, RAC, RSP and MRI; 3) to identify the possible sources and corresponding contributions for heavy metal(loid)s in sediments based on PMF model. The research is expected to provide theoretical basis for water quality management in drinking-water reservoirs and source control of heavy metal(loid)s in sediments.

2. Materials And Methods

2.1 Study area

Yangwanqiao Reservoir (E104°07'30"~104°10'20", N26°48'30"~26°52'30") is 14 km away from Weining County, and the river basin belongs to the Yangtze River system. The reservoir has a catchment area of 97.35 km^2, with a total reservoir capacity of 36.22 million m^3, mainly to solve the domestic water supply of more than 200,000 people living in Weining County and surrounding towns. The reservoir is an important water source for urban water supply, agricultural irrigation and other functions. The terrain on both sides of the reservoir is relatively gentle, with a high south-east and low north-west terrain, and the water flows from south-east to north-west. The southern part of the reservoir is densely populated, and the surrounding land use type is mainly agricultural land. The lithologies of the exposed strata in the reservoir basin are mainly sandy shale, carbonaceous shale with thin coal seam, dolomitic tuff, flint limestone and limestone.

2.2 Sample collection

A total of 42 sampling points were laid out according to the reservoir topography. Taken into account the main surface runoff catchment areas, those points covered the whole reservoir as far as possible, and the distribution of sampling points is shown in Fig. 1. The surface sediments were collected in May 2021 by using a gravity mud collector, and each sample was mixed from three subsamples, placed in a clean polyethylene self-sealing bag, sealed after exhausting the air inside the bag, stored at low temperature and transported to the laboratory, then freeze-dried by LC-10N-50A vacuum freeze-dryer and ground through a 100-mesh nylon sieve for standby.

2.3 Sample preparation and analysis

Each sample was accurately weighed 0.1000 ± 0.0002 g in a 10 mL Teflon digestion tank, then 3mL HNO_3 (high purity) and 1 mL HF (high purity) were added, sealed in a stainless steel jacket, heated in an oven at 180 ℃ for 48 h. After the solution cooled down, acid-driving at 120 ℃ until it was viscous, and constant volume to 50ml for measurement. The contents of Cu, Ni, Pb, Zn, Cr and Cd were determined by inductively coupled plasma mass spectrometry (ICP-MS); the contents of As were determined by atomic fluorescence photometer (AFS-230E). The heavy metal forms were extracted by the modified BCR continuous graded extraction method (GBT 25282 – 2010), and the content of each form of heavy metals in the extracts was determined by ICP-MS. During the analysis, one sample was randomly selected as a parallel sample (repeated three times) for every 10 samples on average, and a blank experiment was performed at the same time, and the quality control was carried out with the analytical standard material for the composition of aqueous sediments (GBW07366). The relative standard deviations of the determination results of each heavy metal were less than 5%, and the recoveries of the quality control samples were maintained between 85% and 110%.

2.4 Assessment of the sediment pollution levels and ecological risks

2.4.1 Index of geo-accumulation (I_{geo})

Index of geo-accumulation (I_{geo}) is a quantitative indicator for studying the extent of heavy metal(loid)s accumulation in sediments, taking fully into account the influence of natural background and anthropogenic activities on the environment(Shu et al. 2021), and is calculated as follows

$$\mathrm{I_{geo}}=\log_2\ \mathrm{C_n}/\mathrm{k}\times\mathrm{B_n}$$

1

where C_n is the concentration of element n in the sample; B_n is the background concentration; in this study, the background values of soil elements in Guizhou province were taken as the evaluation benchmark; and 1.5 is the correction index (k) used to characterize sedimentary features, rock geology and other effects(Hao et al. 2022). The classification of I_{geo} is introduced in Table S1.

2.4.2 Biotoxicity Assessment

To evaluate the potential biotoxicity of heavy metal(loid)s in sediments of Yangwanqiao Reservoir, the heavy metal(loid)s concentrations measured in this study need to be compared with the corresponding threshold effect concentration (TEC) and probable effect concentration (PEC). When it is lower than TEC, it is considered that no biological toxic effect will occur; while if it is higher than PEC, it is considered that biotoxicity effect will occur frequently(Lacey et al. 2001). Besides, if the measured heavy metal(loid)s concentrations is between TEC and PEC, it is considered that heavy metal(loid)s pollution may cause harm to some benthic organisms(Li et al. 2022c). The TEC values for Cd, As, Pb, Cr, Cu, Ni, and Zn were 0.99, 9.79, 35.5, 43.4, 31.6, 22.7, and 121 mg/kg, respectively, and PEC values were 4.58, 33, 128, 110, 149, 48.6, and 459 mg/kg, respectively(Ma et al. 2013).

Toxic unit (TU) was used to standardize the toxicity of various heavy metal(loid)s in order to compare the relative effects, and it is defined as the ratios of the measured heavy metal(loid)s concentrations to PEC values(Pedersen et al. 1998). Furthermore, the sum of toxic units (STU), the sum of TU, is an important index to evaluate the potential acute toxicity of heavy metal(loid)s in sediments on aquatic ecosystems(Li et al. 2022b), and it is expressed as follows:

2

where C_i is the measured concentration of heavy metal(loid)s i in the surface sediments of the reservoir. In reference to the classification of(Pedersen et al. 1998), the evaluation criteria of different toxicity levels are listed in Table S2.

2.4.3 Ratios of secondary phase and primary phase (RSP)

Ratio of Secondary Phase and Primary Phase (RSP), as an assessment method based on the chemical speciations of heavy metal(loid)s, is widely used to evaluate the degree of heavy metal(loid)s contamination in sediments. In the present study, three-step sequential extraction method of the modified BCR was used to obtain the four fractions of heavy metal(loid)s in sediments, that is the acid-soluble/exchangeable fraction (F1), reducible fraction (F2), oxidizable fraction (F3), and residual fraction (F4). Refer to Table S3 for the specific extraction process involved. Among the four speciations, F1, F2 and F3 are bioavailable and are referred to as secondary phase, while F4 is not bioavailable and is classified as primary phase(Zhan et al. 2020). The distribution ratio of heavy metals in primary and secondary phases can, to a certain extent, reflect the characteristics of whether the sediment is contaminated and its contamination degree, thus proposing the use of RSP to evaluate the degree of heavy metal(loid)s contamination in sediments. The calculation formula is as follows:

$$\mathrm{RSP}=\frac{\mathrm{M}_{\mathrm{sec}}}{\mathrm{M}_{\mathrm{prim}}}$$

3

where M_{sec} = F1 + F2 + F3, is the secondary phases; M_{prim} = F4, is the primary phase. The pollution levels for the RSP method are classified in Table S4.

2.4.4 Risk assessment code (RAC)

The RAC value is a common ecological risk assessment index to evaluate the bioavailability of heavy metal(loid)s in sediments,which is defined as the proportion of the acid-soluble/exchangeable fraction (F1) in the total concentration of heavy metal(loid)s(Ji et al. 2019). The formula for calculation can be shown as follows:

$$RAC = \left(\frac{C_{F1}}{C_i} \right) \times 100\%$$

4

where the C_{F1} (mg/kg) represent the concentration of heavy metal(loid)s i in F1 fraction, C_i (mg/kg) is the total concentration of heavy metal(loid)s i. The classifications of RAC are presented in Table S5.

2.4.5 Modified potential ecological risk index (MRI)

The potential ecological risk index (PERI) has been widely used in the quantitative evaluation of ecological risk. However, the index of PERI does not take into account lithogenic sources and variations of heavy metal(loid)s concentrations in the geological background(Ji et al. 2019). Besides, RSP and RAC also lack consideration of background values of heavy metal(loid)s. Then the modified potential ecological risk index (MRI) was proposed in recent years to comprehensively assess heavy metal(loid)s contamination(Ji et al. 2019). In this index, the biotoxicity coefficient (T_r^i) and the risk coefficient (θ) of exchangeable fraction (F1) are introduced into PERI, which not only eliminated the influence of background value of heavy metal(loid)s, but also considered the the influences of biotoxicity, total concentration and bioavailability of heavy metal(loid)s, thus reflecting the comprehensive effects of multiple elements. The calculation formula of MRI was listed as follows:

$$MRI = \sum\nolimits_{i=1}^{n} E_r^i == \sum_{i=1}^{n} T_r^i \times \frac{C_D^i \times \theta}{C_r^i}$$

5

$$\theta = \mathrm{A}\,(\delta\text{-}1) + 1$$

6

where Ei r is the potential risk of the *i*th metal; Ti r is the toxicity coefficient of the *i*th metal, and the values of Pb, Cd, Cu, Zn, As, Cr and Hg are 5, 30, 5, 1, 10, 2, 40 and 2, respectively; Ci D is the average concentration of the *i*th metal(mg/kg); θ is the risk coefficient of F1 exchangeable fraction, A is the percentage of F1 fraction; δ is the toxicity index of F1 fraction of the given heavy metal(loid)s, and the δ

value depends on the RAC value as follows: δ = 1.0(1 < RAC ≤ 10), δ = 1.2 (11 ≤ RAC ≤ 30), δ = 1.4 (31 ≤ RAC ≤ 50),δ = 1.6 (50 < RAC). Ci r is the background values of the i^{th} heavy metal(loid)s, and the background value of Guizhou soil was chosen as the reference in this study. The classifications of MRI were shown in Table S6.

2.5 Source apportionment of heavy metal(loid)s in sediments

The positive matrix factorization (PMF) model is a multivariate factor analysis tool that can quantitatively identify different pollution sources of heavy metal(loid)s and the corresponding contributions, and has been extensively and successfully used in environmental pollutant source identification studies(Li et al. 2022b, Liu et al. 2021, Magesh et al. 2021).According to the EPA PMF 5.0 user's guide, the equation is shown below:

$$\mathrm{X_{ij}}=\sum_{\mathrm{k=1}}^{\mathrm{P}}\mathrm{G_{ik}F_{kj}}+\mathrm{E_{ij}}$$

7

where X_{ij} is the concentration of metal *j* in the sediment sample *i* (mg/kg); G_{ik} is the metal *i* in source *k* (mg/kg); F_{kj} is a factor profile of metal *j* for source factor *k*; E_{ij} represents the residual error matrix for each sample (mg/kg). Variable E_{ij} is calculated based on the defined objective function. The objective function Q_i is defined as (8):

$$\mathrm{Q}=\sum_{\mathrm{i=1}}^{\mathrm{n}}\sum_{\mathrm{j=1}}^{\mathrm{m}}\left(\frac{\mathrm{e_{ij}}}{\mathrm{u_{ij}}}\right)^{2}$$

8

where Q_i is the objective function and μ_{ij} is the uncertainty of metal *j* in the i^{th} soil sample. When the concentration of each metal is less than or equal to the corresponding method detection limit (MDL), the uncertainty is as per Eq. (9):

$$\mathrm{U_{ij}}=\frac{5}{6}\times\mathrm{MDL}$$

9

When the concentration of each metal is greater than the corresponding MDL, the uncertainty is as per Eq. (10):

$$\mathrm{U_{ij}}=\sqrt{(\text{error fraction}\times\mathrm{c})^{2}+\mathrm{MDL}^{2}}$$

where *error fraction* is the relative standard deviation (SD)(Li et al. 2022c), C is the elemental concentration (mg/kg), *MDL* is the method detection limit, and the detection limits for Cu, Ni, Pb, Zn, As, Cr, and Cd are 1, 2, 2, 4, 1, 5 and 0.03 mg/kg, respectively.

2.6 Data analysis

The data were analyzed and processed using Excel 2020, and the maximum (Max.), minimum (Min.), arithmetic mean (Mean) and coefficient of variation (CV) were calculated after the data passed the normal distribution test, and the correlation analysis was performed using SPSS 18.0. The graphs were drawn using Origin 2021 and ArcMap 10.5 software, and the EPA PMF5.0 receptor model was used for heavy metal(loid)s source identification.

3. Results And Discussion

3.1 Descriptive statistics of heavy metal(loid)s and pollution assessment

3.1.1 Heavy metal(loid)s concentrations in sediments

The descriptive statistics for heavy metal(loid)s concentrations in the surface sediments of the reservoir were presented in Table 1. The concentration ranges of Cd, As, Pb, Cr, Cu, Ni, Zn were found to be 0.79–14.9, 5.41–52.4, 18.6–164, 45.5-182.8, 25.5–75.3, 39.8–99.7, 87.4-448.6 mg/kg, which were 100%, 54.76%, 85.71%, 78.57%, 90.48%, 100%, 97.62%, and 6.1%, respectively, of the local soil background values, indicating massive accumulation of these heavy metal(loid)s in reservoir surface sediments. For the mean concentrations, Zn showed the highest concentration (215.5 mg/kg), followed by Cr (119.3 mg/kg), Ni (67.95 mg/kg), Pb (58.92 mg/kg), Cu (50.73 mg/kg), As (23.54 mg/kg), and Cd (3.71 mg/kg) (Table 1). It has been reported that the average concentrations of Zn, Cr, Ni, Pb, Cu, As, and Cd in lake sediments of China were 140.4, 73.4, 37.3, 46.3, 43.4, 32.4 mg/kg, and 0.667mg/kg, respectively (Li et al. 2022c). Obviously, the mean concentrations of heavy metals in Yangwanqiao reservoir sediments of the study area were higher than that those in lake sediments of China, which is mainly due to the fact that the study area is located inYunnan-Guizhou Plateau under the geological background of karst, and the regional sediments and soil have the characteristics of geological high background(Wang et al. 2022, Li et al. 2022c, Zhu et al. 2021). As shown in Table 1, the proportions of heavy metal(loid)s concentrations exceeding the TEC values in descending order were Cr = Ni (100%) > Cd = As (97.62%) > Zn (95.24%) > Cu (92.86%) > Pb (85.71%). Except for Zn and Cu, which did not exceed the PEC value, all other elements exceeded the PEC value to different degrees, among which 95.24%, 57.14%, 21.43%, 19.05%, and 2.38% of Ni, Cr, Cd, As, and Pb exceeded the PEC value, respectively.

Coefficient of variation (CV) reflects the average variation degree of all samples and regional spatial variability of heavy metal(loid)s, as well as the intensity of anthropogenic activities(Shi et al. 2022). The

detected heavy metal(loid)s exhibited a relatively high CV ranging from 19.55–88.21%, with Cd > Pb > As > Zn > Cr > Cu > Ni (Table 2). The results showed that extensive human activities play an important role in the accumulation and spatial variability of Cd, Pb, As and Zn. It also indicates that the accumulation of heavy metal(loid)s in reservoir sediments in the study area is not only affected by regional high geological background, but also strongly influenced by anthropogenic activities, especially for Cd. Previous studies have also shown that the Cd enrichment is relatively common in the sediments of some important lakes and reservoirs in China, and the non-point source pollution caused by anthropogenic activities, such as agricultural runoff may lead to the enrichment of Cd in sediments(Li et al. 2022c). Therefore, special attention should be paid to and control the source of Cd in the reservoir basin.

Table 1
Descriptive statistics of heavy metal(loid)s concentrations (mg/kg) in the sediments of Yangwanqiao reservoir (n = 42).

Metals	Min.	Max.	Mean	SD	CV %	BV	TEC	>TEC	PEC	>PEC
Cd	0.79	14.9	3.71	3.27	88.21	0.66	0.99	97.6%	4.58	21.4%
As	5.41	52.4	23.54	10.2	43.32	20	9.79	97.6%	33	19.0%
Pb	18.6	164	58.92	26.49	44.95	35.2	35.5	85.7%	128	2.4%
Cr	45.5	182.8	119.3	29.75	24.95	95.9	43.4	100.0%	110	57.1%
Cu	25.5	75.3	50.73	11.37	22.41	32	31.6	92.9%	149	0.0%
Ni	39.8	99.7	67.95	13.29	19.55	39.1	22.7	100.0%	48.6	95.2%
Zn	87.4	448.6	215.5	74.31	34.48	99.5	121	95.2%	459	0.0%

CV: coefficients of variation; BV: background values of heavy metal(loid)s in topsoil of Guizhou Province, which were obtained from CNEMC(Centre 1990); TEC: threshold effect concentration; PEC: probable effect concentration(Ma et al. 2013).

3.1.2 Pollution and toxicity assessment in sediments

The I_{geo} takes into account not only the difference in background caused by geological environment, but also the impact of anthropogenic activities, and is widely used to evaluate the level of pollution with heavy metal(loid)s in sediments(Wang et al. 2020). As shown in Fig. 2, the I_{geo} value of Cd, As, Pb, Cr, Cu, Ni, and Zn were ranged for − 0.33 ~ 3.91, -2.47 ~ 0.8, -1.51 ~ 1.64, -1.66 ~ 0.35, -0.91 ~ 0.65, -0.56 ~ 0.77, and − 0.77 ~ 1.59, respectively. According to the I_{geo} classification, Pb, Cu, Ni, and Zn showed unpolluted to moderate pollution, and As and Cr showed no pollution, whereas Cd in 61.9% of the sampling sites was at the level of moderate to heavily polluted (Fig. 2). This result implied that most of the surface sediments of the reservoir have been seriously polluted by Cd, however, as mentioned above, the pollution levels of Cd, Zn and Pb in sediments are relatively high, especially Cd, but it is difficult to determine the ecological risk of reservoir only by the total concentrations of heavy metal(loid)s.

STU is a powerful indicator to assess the acute toxicity of heavy metal(loid)s to macrobenthos, and when STU values are higher than 4, there is significant acute toxicity to aquatic organisms. The STU values in the sediments ranged from 2.69 to 8.72 with a mean value of 5.28, exhibiting moderate toxicity levels (Fig. 3). Ni, Cr and Cd in surface sediment showed great contributions to STU and the values were17.8%-37.9%,10.3%-27.9% and 3.1%-41.6%, respectively. It should be noted that the pollution degrees of Ni and Cr in I_{geo} evaluation results is not high, but their contribution to STU is large, which is mainly caused by the difference of evaluation indexes.

3.2 Bioavailability of heavy metal(loid)s and associated risk

3.2.1Geochemical fractionation of heavy metal(loid)s

It is well known that considering the total amount of heavy metal(loid)s alone cannot accurately reflect the bioavailability and environmental risks. The mobility, chemical activity, bioavailability and potential biotoxicity of heavy metal(loid)s were controlled by the geochemical fractionations(Liu et al. 2021, Chen et al. 2022a, Ji et al. 2019). The chemical fractions (F1, F2, F3, and F4) based on the BCR sequential extraction procedure for each heavy metal(loid)s were illustrated in Fig. 4. Among the four chemical fractions, heavy metal(loid)s in F1 fractions are the most mobile and bioavailable fraction, and mainly absorbed on humus and other components, which can be released into water under acid/neutral conditions and passively absorbed and utilized by plants, with great harm and portability(Liu et al. 2021) Heavy metal(loid)s in F2 fractions mainly exist in the forms of Fe and Mn oxides, sulfide and organic combinations, which are easy to migrate with the change of Eh and cause secondary pollution to overlying water for bioavailability(Liang et al. 2017). However, the heavy metal(loid)s in residual fraction are very stable, difficult to release under normal circumstances, and usually do not have bioavailability(Liu et al. 2022). In this study, Cr, Ni, Cu, Zn, and As are mainly in F4 fractions, with an average of 90.4%,89.3%,90.1%,80.3%,97.4% (Fig. 3), indicating that Cr, Ni, Cu, Zn, and As were relatively stable and not bioavailable, and may be derived from crustal material and in the form of aluminosilicate minerals(Xu et al. 2016). The results are consistent with the high geological background of heavy metal(loid) in the study area(Li et al. 2022c). However, what needs special attention is that the Cd and Pb in sediments are mainly present in F2, accounting for 59.4% and 39.7%, indicating high bioavailability, which may pose certain threat to the benthic environment(Xu et al. 2016, Nillos et al. 2020).

3.2.2 Risk assessment for heavy metal(loid)s

To comprehensively reflect the bioavailability and risk of heavy metal(loid)s in the surface sediments of reservoirs in the study area, RSP, RAC and MRI based on the geochemical fractionations of heavy metal(loid)s were jointly selected to assess the potential ecological risk of heavy metal(loid)s. The ecological risk evaluation of heavy metal(loid)s based on RSP is shown in Fig. 5. The mean values of RSP are Pb (4.53) > Cd (4.44) > Zn (0.25) > Cu (0.12) = Ni (0.12) > Cr (0.11), indicating that except Pb and Cd, most heavy metal(loid)s are not contaminated and the corresponding ecological risk is low. The Cd and Pb are mainly in the secondary phase, reflecting the high biological effectiveness in the surface

sediments of the reservoir and the higher risk of re-release into the water environment. At the same time, the results also indicate that anthropogenic activities in the study area are important sources of Cd and Pb in the sediments of Yangwanqiao Reservoir(Chen et al. 2022a, Ji et al. 2019, Liu et al. 2022). As depicted in Fig. 1, the population around the reservoir in the study area is dense, cultivated land is widely distributed, and traffic roads are densely covered. The pollution of Cd and Pb may be related to the emissions from agricultural activities, transportation, residential buildings and other anthropogenic activities(Chen et al. 2022a), and the specific sources of contamination will be detailed in section 3.3.

The RAC assessment based on F1 fraction of heavy metal(loid)s can effectively evaluate the bioavailability, migration and ecological risk of heavy metal(loid)s. RAC evaluation results of surface sediments in Yangwanqiao Reservoir are presented in Fig. 4. Similar to the RSP assessment results, Cr, Ni, Cu, Zn, and As pose low or no risk (RAC < 10%) to environment except for Cd. The RAC average values followed the order of Cd (18.00%) > Zn (0.95%) > As (0.82%) > Pb (0.56%) > Cu (0.52%) > Cr (0.37%). In particular, the overall RAC values of Cd were high, and the percentage of Cd in low risk, moderate risk and high risk are 38.46%, 30.77% and 23.08%, respectively. Compared with the other metals, the values of RAC suggested that Cd exhibited higher potential bioavailability and ecological risk. The ecological risk of the respective heavy metal(loid)s (E_r^i) and modified potential ecological risk (MRI) evaluation results are shown in Fig. 6. The order of Ei r values for all heavy metal(loid)s is: Cd > As > Ni > Pb > Cu > Cr > Zn, and the mean E^i_r values of As, Pb, Cr, Cu, Ni, and Zn were less than 40, suggesting low ecological risk. However, the E^i_r values of Cd at almost all sampling sites were greater than 40, and approximately 45.24%, 23.81% and11.9%of the sediments samples, respectively, posed considerable risk, high risk and extremely high risk to the ecosystem. This result was consistent with the above evaluation results of RSP and RAC. But it is worth noting that, the MRI values of reservoir surface sediments ranged from210.04 ~ 237.50, with an average of 217.40, indicating a moderate risk level, and Cd is the most important risk metal, which should be paid attention to strengthen the source control management in the future(Liu et al. 2021). Combined with the above results, it was found that although Cr and Ni contributed significantly to the toxicity unit sum (STU) in toxicity assessment, since more than 90% of Cr and Ni exist in residual fraction (Fig. 4), the risk of RSP, RAC and MRI assessment is low, and there is little impact on the environment. The results obtained above contradicted the conclusion based on total concentration, indicating that the chemical fractions of heavy metal(loid)s have a significant influence on the ecological risk assessment results. Furthermore, it is more accurate and comprehensive to evaluate the pollution and ecological risk of sediments by multiple assessment methods combined with geochemical fractions of heavy metal(loid)s.

3.3 Source apportionment of heavy metal(loid)s in the sediments

3.3.1 Correlation analysis

The relationships of each heavy metal(loid)s in surface sediments of Yangwanqiao Reservoir were analyzed by Pearson's correlation analysis (Fig. 7). Obviously, there are significant positive correlations between Cd and Zn; As and Cr, Cu; Pb and Zn, Ni; Cr and Ni, Cu; Cu and Ni; Ni and Zn ($P < 0.01$), indicating that these elements may have similar geochemical behaviors and controlling factors, or similar pollution sources(Hao et al. 2022, Chen et al. 2022b). Previous study has proven that the Cr, Ni, Cu, Pb, and Zn are enriched in soil and sediments of the study area due to the special geological background, which is generally considered to be of natural origin(Li et al. 2022c). In particular, except for the positive correlation between Cd and Zn, Cd has no significant correlation with other heavy metal(loid)s, suggesting that Cd and Zn may have independent sources.

3.3.2 PMF

Additionally, the PMF model was applied to identify the potential sources of heavy metal(loid)s in surface sediments of Yangwanqiao Reservoir quantitatively. Input each metal concentration and its associated uncertainty into the PMF model, after that, it runs several times randomly until lower converged Q_{robust} values and higher R^2 values are obtained, and finally, four factors were identified. There is a good correlation between the predicted value of the total variable and the observed value. With R^2 values ranging from 0.84 to 0.99, the difference of Q value is the smallest, and the residual values of all elements are − 3 ~ 3, indicating that the all the heavy metal(loid)s in the sediment are well interpreted. Therefore, the analysis results of the four sources in this study are reliable. The source profiles and percentage contributions of the four sources are shown in Fig. S1 and Fig. 8. Moreover, the spatial distributions of heavy metal(loid)s in sediments was depicted by ArcGIS inverse-distance weighting (Fig. S2), which not only provided intuitive information about heavy metal(loid)s pollution sources in reservoir sediments, but also important supplement and confirmation for PMF analysis results.

As shown in Fig. 8 and Fig. S1, Factor 1, accounting for 18.4% of the total contribution, has high composition of Cd (84.86%), followed by Zn (23.1%). According to the correlation analysis, strong positive correlation between Cd and Zn ($P < 0.01$) showed that they had similar source. Furthermore, the spatial distribution of Cd and Zn is very similar, with a high concentration in the southern part of the reservoir where agricultural production and residents gather (Fig. S2). As previously mentioned, contamination of Cd and Zn in sediments was associated with the extensive application of pesticides and fertilizers in agriculture production(Ke et al. 2017, Li et al. 2022c). Local residents are mainly engaged in agricultural planting, a large number of agricultural products such as pesticides and fertilizers are repeatedly put into the soil year after year to obtain higher yields, resulting in Cd and Zn residues in the soil(Wang et al. 2022). According to the field investigation, a large amount of livestock manure, compound fertilizer and pesticides are used by local residents in the agricultural cultivation process. Most notably, previous studies have confirmed that the contents of Cd and Zn in pig manure in the study area are very high, which is far higher than the standard values of Chinese organic fertilizer(MAPRC 2012). However, after a large number of heavy metals enter the soil, they migrate to the reservoir through surface runoff and eventually lead to the accumulation of heavy metals in surface sediments(Chen et al. 2021,

Liang et al. 2018). Consequently, factor 1 can be regarded as the category of local agricultural influence, which is consistent with the analysis results of Lin et al.(Lin et al. 2021) on the source of Cd in the surface sediments of Caohai wetland in the adjacent study area.

Factor 2, accounting for 36.7% of the total source contribution (Fig. 8b), is dominated by As (69.82%), Cr (50.05%), Cu (33.47%), and Ni (31.87%). It has been known that As is a environmental pollutant associated with anthropogenic activities. Atmospheric deposition, domestic garbage stacking, incineration, livestock manure, plastic film, wastewater discharges, as well as coal combustion were regarded as the anthropogenic inputs of As, Cu, Cr, Ni(Li et al. 2022c). As shown in Fig. S2, the spatial distribution of As, Cr, Ni and Cu in sediments is basically consistent with the water flow direction of the reservoir, showing a trend of low in the southwest of the upstream and high in the northeast of the downstream of the reservoir. It has to be pointed out that the residents living around the reservoir are concentrated, and a large amount of domestic garbage piled everywhere. After long-term leaching and runoff, the wastewater containing heavy metal(loid)s enters the reservoir and leads to the deposition in the sediment(Shi et al. 2018). In addition, the coal used by local residents in daily life contains high As and other heavy metals(Dai et al. 2005). The atmospheric deposition of heavy metal(loid)s produced by coal combustion is an important factor for the accumulation of heavy metal(loid)s in sediment and soil in the study area(Li et al. 2022c). Therefore, Factor 2 can be considered to represent the domestic sources of activities related to residents.

Factor 3, with total contribution of 29.5% (Fig. 8b), was characterized by Cu (47.27%), Ni (40.47%), Cr (38.80%), As (25.79%), Pb (16.32%), and Zn (15.30%). The coefficients of variation of Cu, Ni, Cr, and As in the surface sediments of the reservoir were low (Table 1), and according to the I_{geo} values for Cu, Cr, Ni, and As, most of the sediment samples were less polluted by these heavy metal(loid)s, suggesting that they were likely derived from natural sources. Besides, the study area is a typical carbonate geological high background area in southwest China,as well as a concentrated distribution area of Pb and Zn ores, thus, the there are obvious Pb and Zn high background geological characteristics in sediments and soils(Li et al. 2022c, Lin et al. 2021, Wang et al. 2022, Zhu et al. 2021). Therefore, Factor 3 can be considered to be a natural source caused by geological background.

Factor 4 accounted for 15.4% of the source contribution and was characterized by Pb (47.56%) followed by Zn (22.46%), Cr (13.92%), and Cd (11.04%). Pearson correlation analysis (Fig. 8) showed a significant correlation between Pb and Zn, and it is speculated that the sources of these elements were highly homologous. Numerous previous studies have proved that Pb and Zn are the main markers of traffic emissions, the automobile exhaust, wear and tear of asphalt on road surfaces, as well as tire wear and lubricant use can lead to an increase in Pb, Zn, Cr, and Cd in the environment(Xu et al. 2020, Dai et al. 2020, Li et al. 2022c). As shown in Figs. 1 and S2, the sediments with high concentrations of Pb and Zn were enriched in the south-east side of the reservoir, adjacent to the traffic artery, with frequent transportation, and the emissions from automobile exhaust are most likely to enter and accumulate in the sediments through atmospheric deposition or surface runoff. Thus, Factor 4 mainly represents the traffic emissions.

4. Conclusion

In this study, heavy metal(loid)s concentration, distribution, chemical fraction, pollution status, ecological risk and sources of Cd, As, Pb, Cr, Cu, Ni, and Zn in surface sediments of Yangwanqiao Reservoir, Southwest China were systematically evaluated and identified. The average concentrations of the studied heavy metal(loid)s in the sediments all exceed the soil background values in Guizhou Province. I_{geo} results showed that approximately 62% of the sediment samples of Cd were moderately polluted or above, and Pb, Cu, Ni and Zn were slightly polluted; As and Cr are at low pollution level. The STU revealed that the Ni, Cr, Cd and As were the most toxic elements in surface sediments in the study area. RSP, RAC and MRI evaluation results all indicated that the pollution risk of Cd was relatively high, while the rest of elements were at low risk level. The PMF analysis results show that the sources of heavy metal(loid)s include agricultural sources, domestic sources, geological sources and traffic sources, with the contribution of various sources accounting for 18.41%, 36.67%, 29.48% and 15.44%, respectively. Domestic sources are the main sources of heavy metals in reservoir sediments in the study area.

Declarations

Funding: This work was supported by the National Natural Science Foundation of China (U1612442), the High-Level Talent Training Program in Guizhou Province ([2016]5664), and the Science and Technology Project of Guizhou Province (Qian Ke He [2020]1Y186).

Competing Interests: The authors have no relevant financial or non-financial interests to disclose.

Author contribution: Xue Chen 1: Investigation, methodology and writing - original draft, Methodology and software. Pan Wu: Funding acquisition and project administration. Xue Chen 2:Project administration and software. Hongyan Liu: Conceptualization, funding acquisition. Xuexian Li: Visualization, Writing - review & editing.

Ethics approval: Not applicable

Consent to participate: Not applicable

Consent to publish: Not applicable

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Figures



Figure 1

Distribution of sampling points in the study area

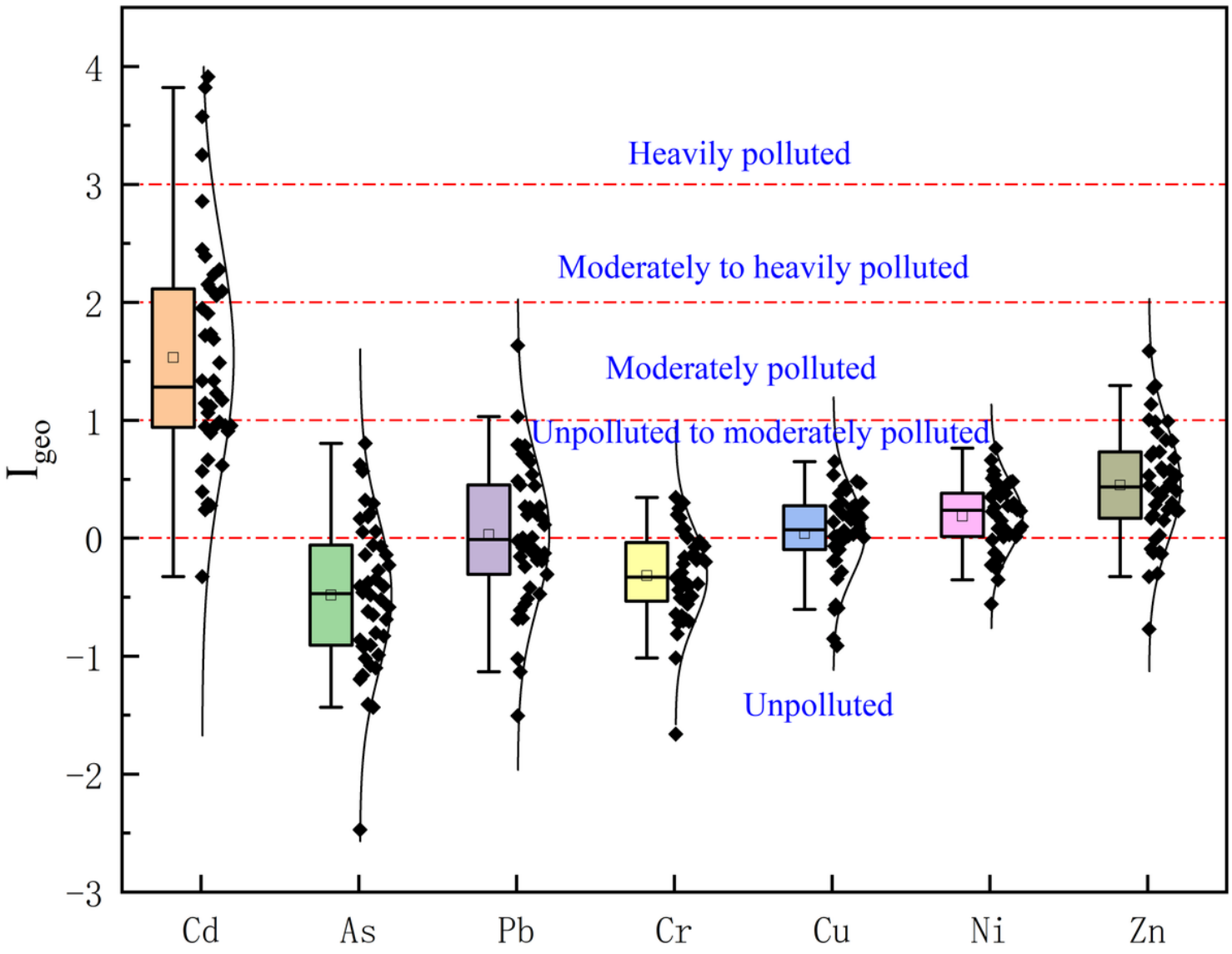


Figure 2

The geoaccumulation index (I_{geo}) of heavy metal(loid)s in sediments from Yangwanqiao Reservoir.

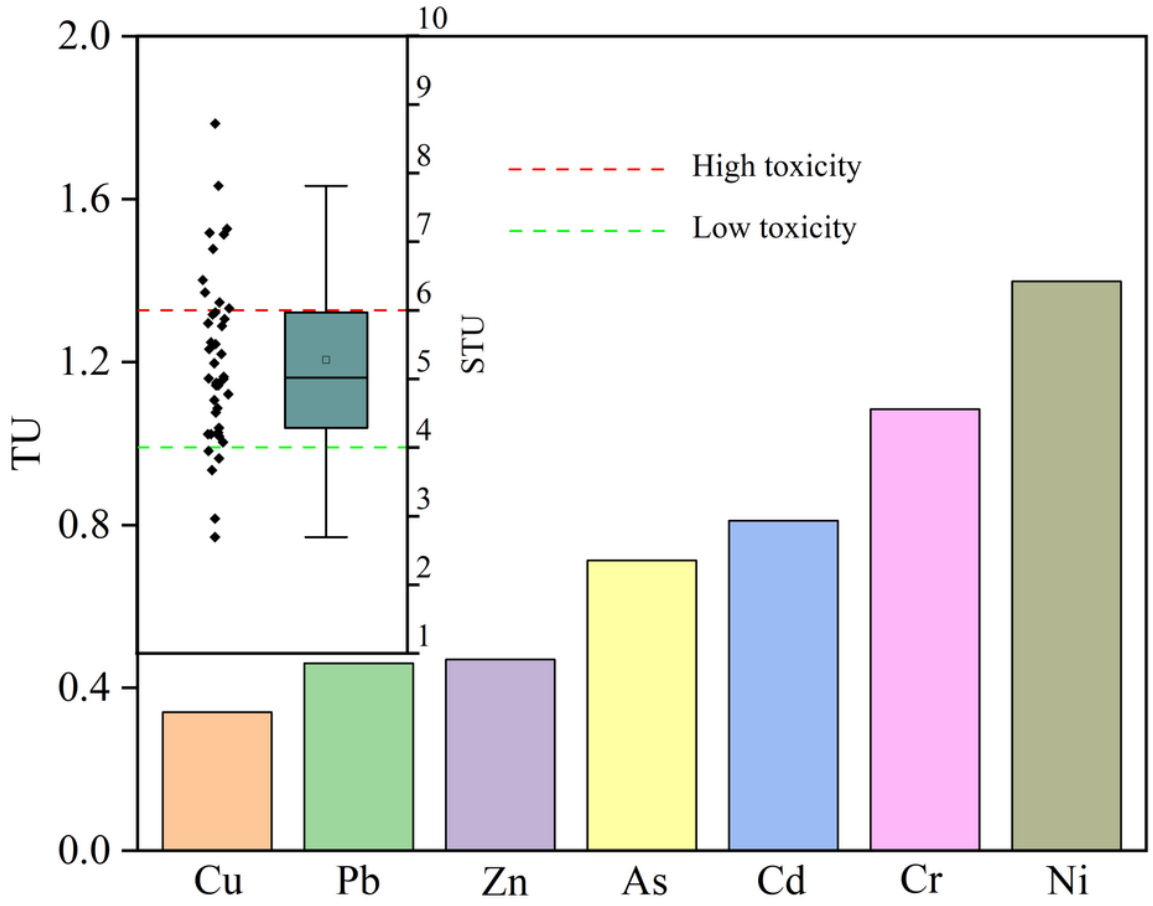


Figure 3

Toxic unit (TU) values of the heavy metal(loid)s and sum of toxic units (STU) results of reservoir sediments.

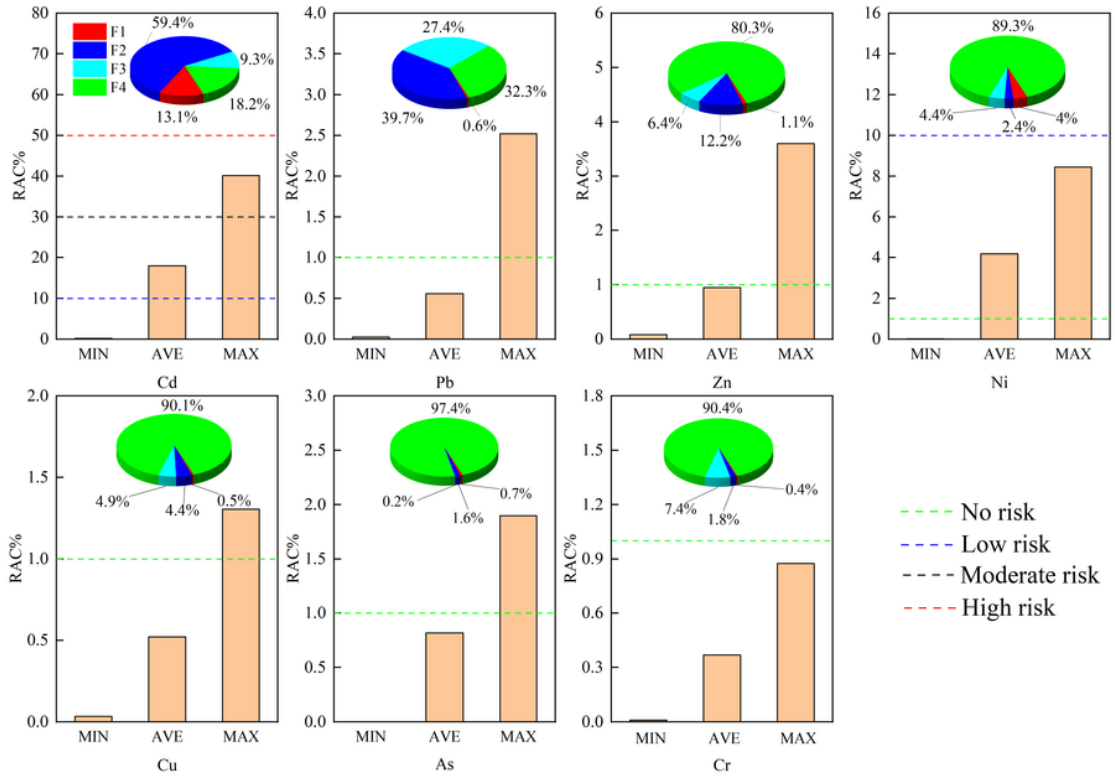


Figure 4

The four geochemical fraction percentages and the risk assessment code (RAC) values of heavy metal(loid)s in surface sediments. Dot lines of different colors divided those values into several pollution levels. The acid extractable/exchangeable fraction (F1), reducible fraction (F2), oxidizable fraction (F3), and residual fraction (F4).

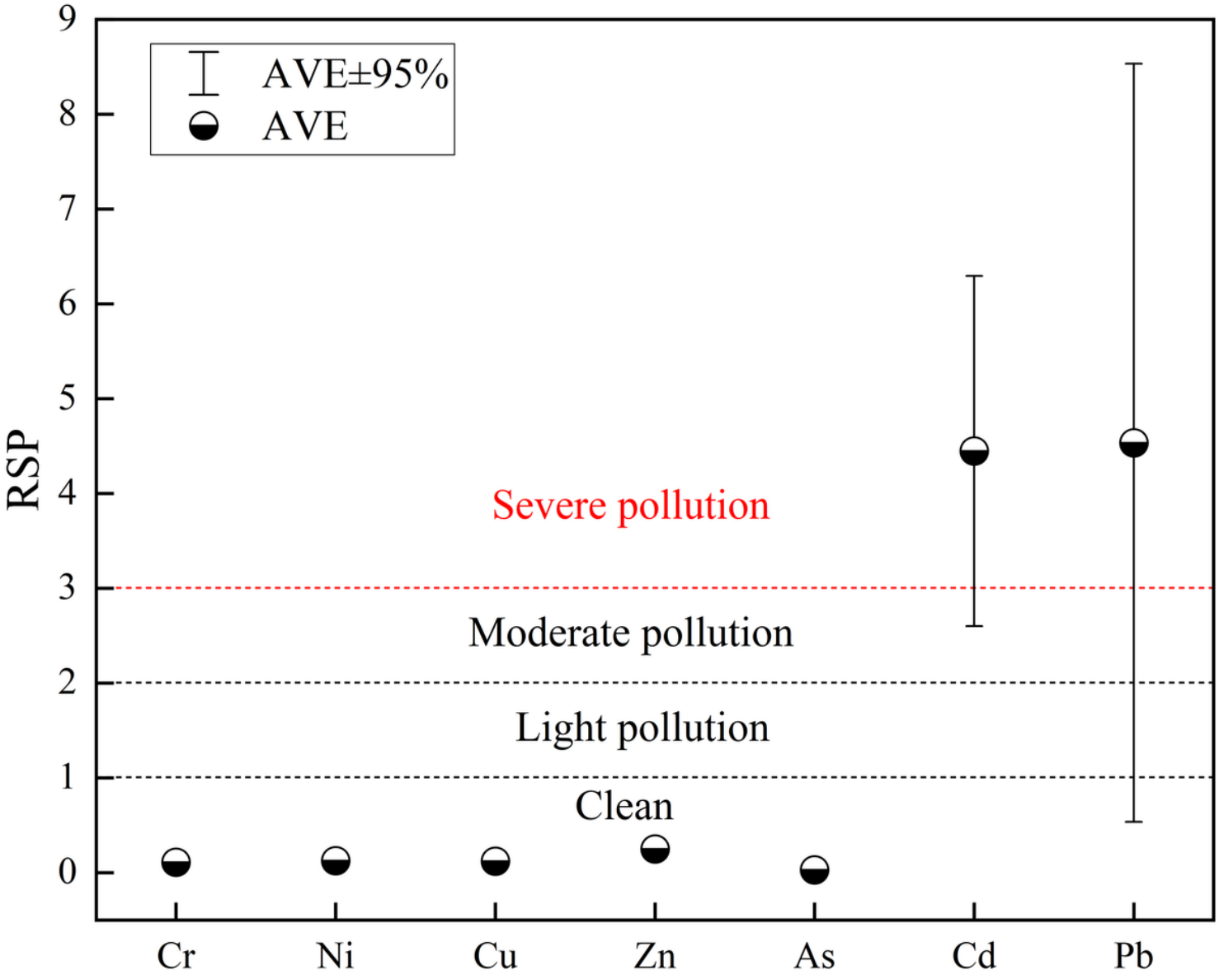


Figure 5

Ratio of secondary phase to primary phases (RSP)of heavy metal(loid)s in surface sediments from Yangwanqiao Reservoir.

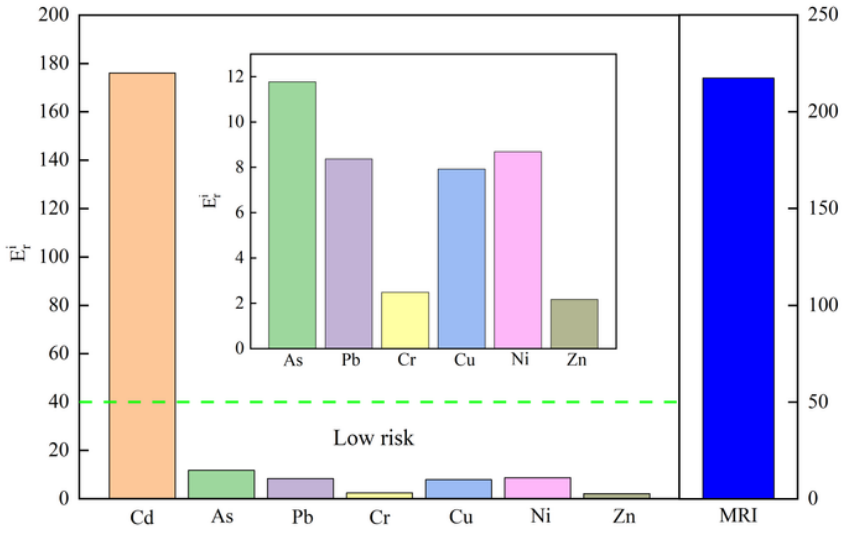
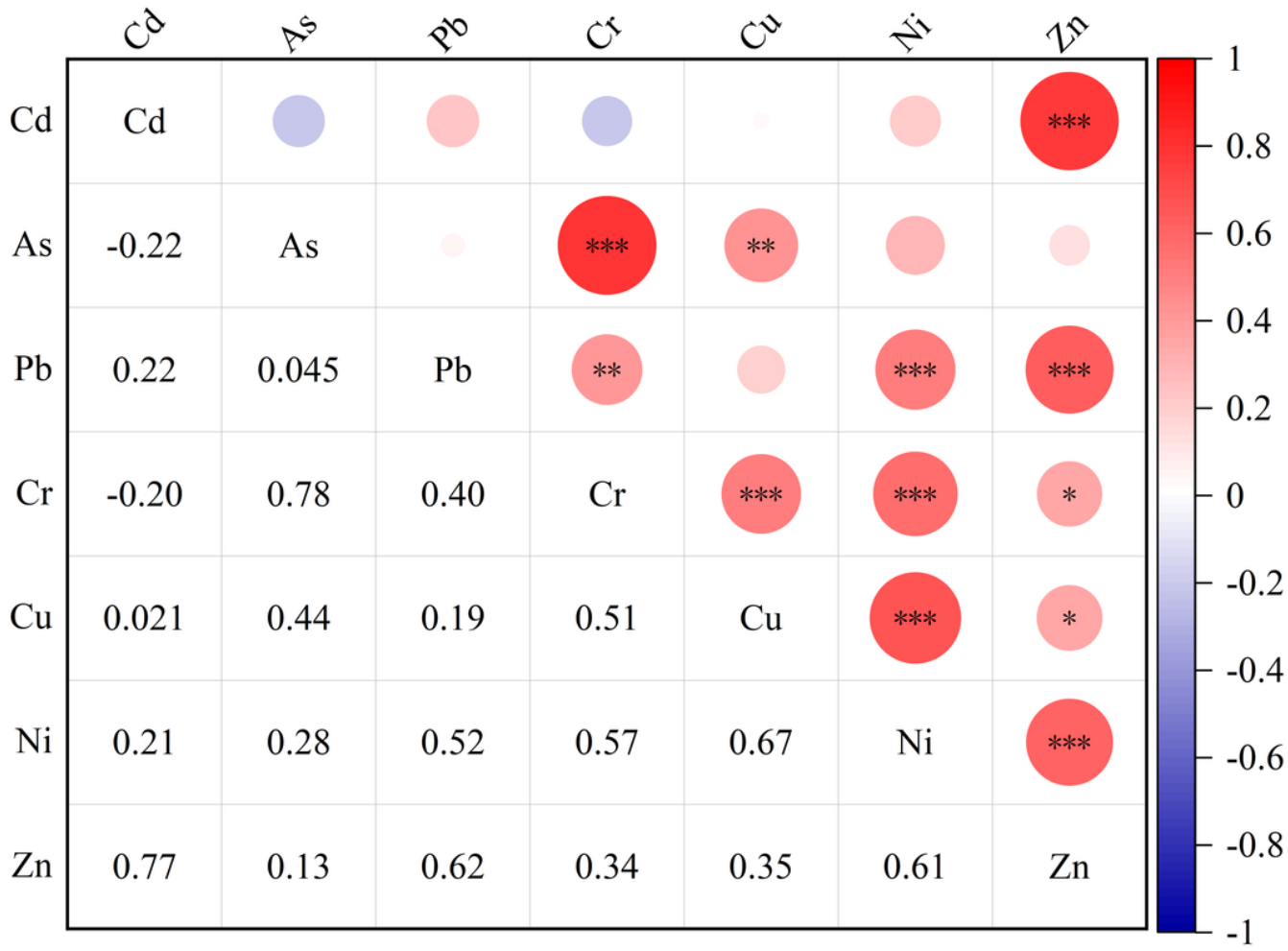


Figure 6

Ecological risk of the respective heavy metal(loid)s (E_r^i) and modified potential ecological risk (MRI) in the sediments of Yangwanqiao Reservoir.



* p<=0.05 ** p<=0.01 *** p<=0.001

Figure 7

Correlation matrix among heavy metal(loid)s in surface sediments of Yangwanqiao Reservoir (*p < 0.05, **p < 0.01, ***p < 0.001).

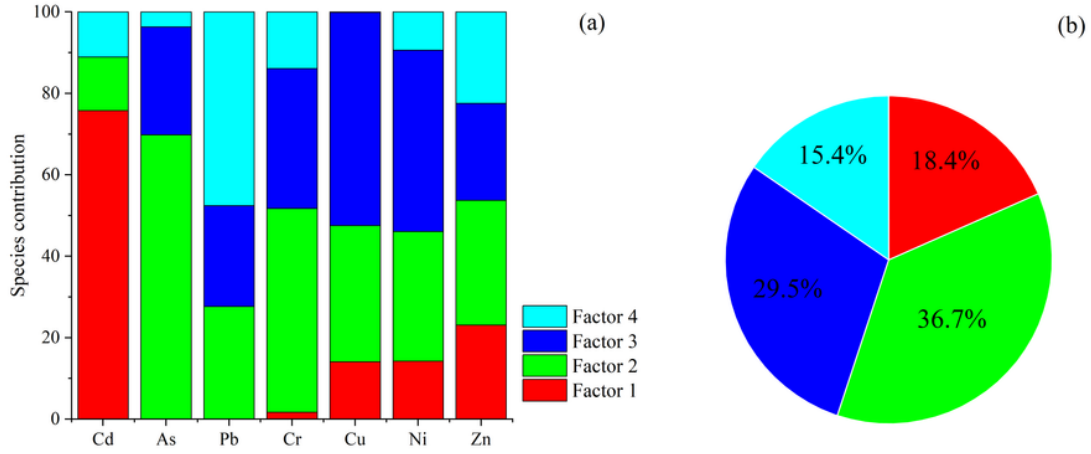


Figure 8

Source apportionment of heavy metal(loid)s in sediments of the study area. (a) Factor profiles of heavy metal(loid)s derived from the PMF model; (b) The percentage of contribution for each factor by the PMF model.

Supplementary Files

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- SupplementalMaterials.docx