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ORIGINAL ARTICLE

Sources and environmental risks of cadmium in soils affected by high geochemical background and artisanal zinc smelting activities

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Abstract Soil cadmium (Cd) pollution is a global environmental issue of significant concern. In southwestern China, soil Cd content is notably influenced by high geochemical background and mining/smelting activities. However, the specific contributions of these Cd sources to Cd enrichment and environmental risks in soils remain poorly understood. Therefore, this study investigated the total and bioavailable Cd and other metals in the topsoil and subsoils surrounding Caohai Lake in northwestern Guizhou Province. This research aimed to identify Cd sources, assess pollution characteristics, and evaluate the potential environmental risks. The results revealed that the carbonate bedrock has average Cd content of 0.66 mg/kg, confirming a naturally high geochemical background of Cd in the study area. Soil Cd content ranged from 0.14 to 6.69 mg/kg, with topsoil exhibiting higher average Cd content (2.29 mg/kg) than subsoil (0.71 mg/kg). Statistical analyses indicated that Cd in subsoil is primarily of geogenic origin. In contrast, approximately 87% of the total Cd in topsoil originates from atmospheric deposition linked to historical artisanal zinc smelting activities. The study found that Cd in topsoil reaches a moderate pollution level and poses a high potential ecological risk. Furthermore, the proportion of bioavailable Cd (DTPA-extractable) was significantly higher in topsoil (26%) than in subsoil (13%). This elevated Cd bioavailability in topsoil is attributed to atmospheric Cd deposition, lower soil pH, and higher organic matter content. These findings provide critical insights for managing Cd risks in soils from regions with high geochemical backgrounds and smelting activities.

Keywords Karst region · Soil pollution · Caohai Lake · Heavy metals · Bioavailability

1 Introduction

Cadmium (Cd) is a widespread toxic pollutant that poses significant risks to plants, organisms, and ecosystems (El Rasafi et al. 2022; Larison et al. 2000; Satarug et al. 2003). Soil contamination by Cd is a global environmental issue, garnering considerable attention due to its adverse impacts (Akesson et al. 2014; Ma et al. 2021). Cd is highly mobile in soils, making it readily adsorbable by food crops, transferable to water and sediment systems, and ultimately posing potential health risks to the ecosystems and residents (Akesson et al. 2014; Kubier et al. 2019; Liu et al. 2015). Recognizing the sources of Cd and understanding its pollution characteristics in soils is essential for developing effective strategies to mitigate Cd-related risks.

Chao Luo and Wangwang Zhou have contributed equally to this work.

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The sources of Cd in soils can be categorized into geogenic and anthropogenic inputs. Geogenic Cd enrichment in soils commonly results from the weathering of Cd-rich black shale and carbonate rock, driven by geochemical inheritance and secondary enrichment processes (e.g., Liu et al. 2021b; Quezada-Hinojosa et al. 2015; Wen et al. 2020a; Yang et al. 2021a). On the other hand, anthropogenic Cd pollution primarily arises from the application of phosphate fertilizer (Bigalke et al. 2017; Salmanzadeh et al. 2016), mining and smelting operations (Liu et al. 2022; Wen et al. 2015), and atmospheric deposition (Hernandez et al. 2003; Liu et al. 2023a, 2024). To effectively reduce Cd accumulation in soil and mitigate its environmental risks, it is crucial to recognize and quantify the contribution of these sources (Xia et al. 2024; Zhao et al. 2020). In addition to total Cd content, the environmental risk of Cd in soils is highly dependent on its bioavailability (Kim et al. 2015). Metals from different sources usually exhibit varying environmental availability due to differences in their chemical forms and input pathways (Chlopecka 1996; Ding et al. 2022; Laveuf et al. 2009). Generally, geogenic Cd in soils has been reported to exhibit lower bioavailability than anthropogenic Cd (Chlopecka 1996; Ma et al. 2020). For instance, in soils derived from carbonate rocks, the 0.01 M $CaCl_2$-extractable and exchangeable Cd fractions were found to be negligible (Quezada-Hinojosa et al. 2009; Wen et al. 2020a). In contrast, these fractions accounted for 5.94% and 48.1% of the total Cd, respectively, in soils derived from black shale (Liu et al. 2021b, 2022). Furthermore, anthropogenic Cd tends to exert higher bioavailability than geogenic Cd (Ma et al. 2020). Therefore, it is essential to not only apportion Cd sources but also evaluate their influence on Cd bioavailability in soils. However, the bioavailability of Cd in soils subject to both geogenic enrichment and anthropogenic disturbance remains poorly understood.

In southwestern China, a vast region spanning approximately 69000 km^2 exhibits abnormally high soil Cd concentrations (> 1.5 mg/kg), primarily attributed to the weathering of carbonate bedrocks (Xia et al. 2022). The geogenic enrichment of Cd in these areas and its associated environmental risks have garnered increasing attention (e.g., Liu et al. 2023b; Wen et al. 2020b; Xia et al. 2020; Yang et al. 2021b). Additionally, southwestern China is one of the large-scale low-temperature metallogenic domains in the world (Huang et al. 2011), with widespread nonferrous metal mining activities. Consequently, mining and smelting activities have also contributed to Cd accumulation in soils in certain regions. Particularly, fine particles emitted from Pb–Zn–Cd smelters can disperse into the atmosphere and deposit onto soils, especially during periods of lax environmental regulations. This process has led to additional Cd accumulation in soils with high geochemical backgrounds, affecting large areas (Luo et al. 2023b). For example, in northwestern Guizhou Province, artisanal Zn smelting persisted for over 300 years until its complete cessation in 2000. The atmospheric deposition of Cd-rich dust caused severe Cd pollution in local soils (Bi et al. 2006b). Such atmospheric inputs not only increase total Cd content but may also alter its environmental availability in soils. Therefore, distinguishing between anthropogenic and geogenic Cd sources in these regions is critical for effective soil pollution control. Furthermore, the impact of mining-related activities on Cd bioavailability warrants greater attention to better understand and mitigate the associated environmental risks.

In this study, we investigated the total and bioavailable content of Cd and other trace metals in both topsoil and subsoil around Caohai Lake, located in northwestern Guizhou Province, southwestern China. The sources of Cd and related metals were quantified by statistical analyses. The potential environmental risks were assessed, and the factors influencing the bioavailability of Cd were discussed. The findings of this study are expected to provide essential guidelines for soil management in the study area, as well as in other regions with high geochemical backgrounds and anthropogenic contamination.

2 Materials and methods

2.1 Study area

The study area is situated in Weining County, northwestern Guizhou Province, southwestern China (Fig. 1). It lies within the Wumeng Mountains area on the central Yunnan-Guizhou Plateau. The lithology of the region is dominated by Carboniferous carbonate rocks, and the soils are classified as yellow–brown soil, primarily used for upland agriculture. The area experiences a subtropical monsoon climate, with a mean annual precipitation of ~900 mm and a mean annual temperature of ~10 °C. This region is characterized by a high geochemical background of Cd (Luo et al. 2023a; Meng et al. 2022). Additionally, long-term artisanal Zn smelting activities have contributed to the atmospheric deposition of Cd and other metals into the soil (Bi et al. 2006b; Yu et al. 2022b). Caohai Lake, the only natural lake in Guizhou Province, is the largest wetland in the area and serves as a critical habitat for numerous rare species and a vital resource for the local population. Consequently, the soil quality surrounding Caohai Lake holds significant environmental significance.

2.2 Sample collection and preparation

A total of 27 sampling sites were established around Caohai Lake. At each site, the topsoil (0–20 cm depth) and corresponding subsoil (> 60 cm depth) samples were collected (Fig. 1). The land use types of sampling sites included

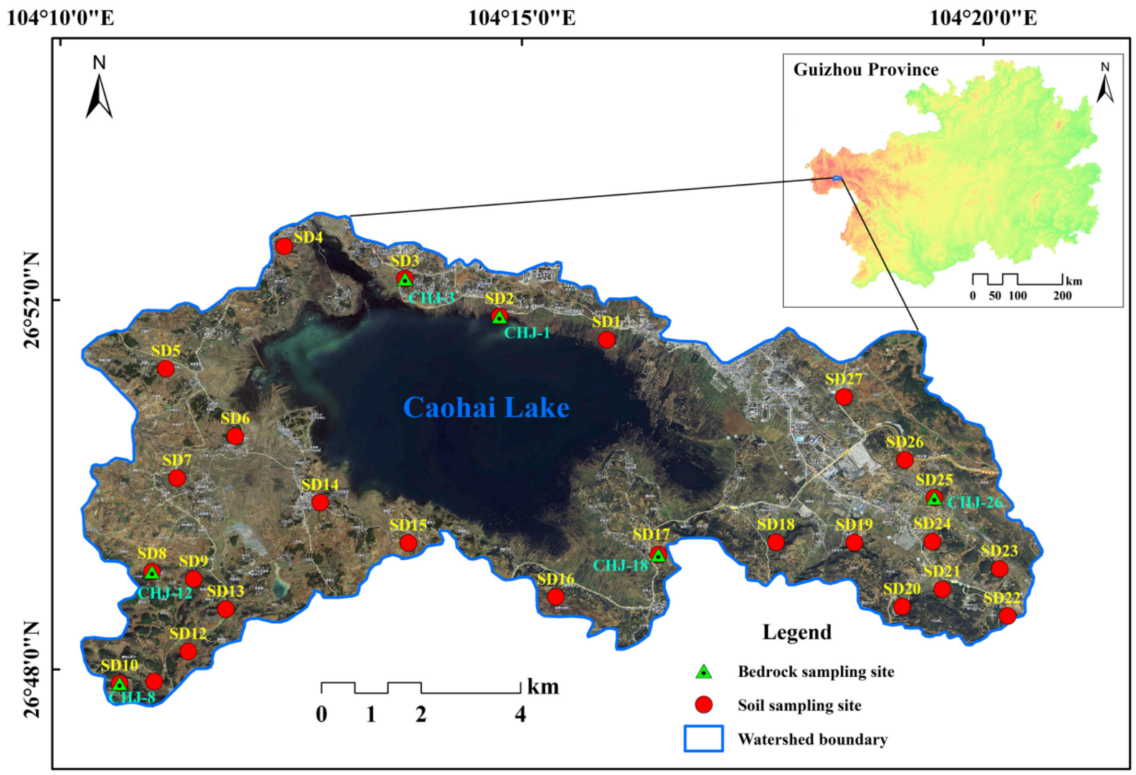

Fig. 1 Location of the study area and soil sampling sites

agricultural fields, forest, and grassland. Additionally, six bedrock samples were collected from four different locations within the study area. All bulk soil samples were air-dried and ground to remove extraneous materials such as roots and stones. Both soil and bedrock samples were initially ground to a particle size of <0.85 mm and further to <74 μm for subsequent geochemical analysis.

2.3 Analysis of geochemical composition and soil properties

Soil pH was measured using a glass electrode (Harveson pH 600 pH meter) in a 1:2.5 (w/v) suspension. Soil organic matter (SOM) content was determined using the $K_2Cr_2O_7$-$FeSO_4$ titration method (Zhang et al. 2024). Bulk mineralogy was analyzed using powder X-ray diffraction (XRD, Empyrean). Powdered samples (<74 μm) were packed into front-loading sample holders, and XRD patterns were collected under the following conditions: Cu Kα radiation ($\lambda = 1.5406$ nm), 40 kV, 30 mA, with a 2θ angle range of 5–60°, step scanning at 0.02°/step, and scanning speed 2°/min. The major elements (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, Ti, and Mn) in the soil samples were quantified using an energy-dispersive X-ray fluorescence (XRF) spectrometer (ARL Perform'X 4200).

2.4 Measurement of heavy metals in samples

To determine the total concentrations of heavy metals in solid samples, 50 mg of each sample was digested using a mixed acid (HNO_3-HF) in an automated microwave digestion system (Auto DigiBlock S60 UP) for 3.5 h. The bioavailable metals were extracted with 0.005 mol/L DTPA-0.01 mol/L $CaCl_2$-0.1 mol/L triethanolamine (TEA) at a solid-to-solution ratio of 1:10. The concentrations of heavy metals in the digested solution and extractants were measured using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700).

2.5 Data processing

2.5.1 Geo-accumulation factor

The geo-accumulation factor (I_{geo}) was applied to evaluate the contaminant levels of heavy metals (Müller 1979). It was calculated as Eq. 1:

$$I_{geo} = \log_2\left(\frac{C_i}{1.5S_i}\right), \quad (1)$$

where C_i is the content of elements in soil samples (mg/kg), and S_i represents the Cd, Zn, Pb, Cr, Ni, and Cu content in the subsoil of northwestern Guizhou Province (Meng et al.

2022), which is 0.244, 116, 27.4, 137.6, 61.3, and 65.1 mg/kg, respectively. The value 1.5 is the correction constant. The I_{geo} was graded into seven levels, as described in Table S1 (Müller 1979).

2.5.2 Enrichment factor

The enrichment factor (EF) was applied to distinguish between the influence of anthropogenic and geological sources on heavy metals in soil. In this study, Al was chosen as the reference element as it has been generally regarded as a lithogenic element and immobile in soil (Wen et al. 2020b). The background value was 81.8 g/kg in the study area (Meng et al. 2022). EF is calculated using the following Eq. 2:

$$\mathrm{EF} = \frac{\left(\frac{M_i}{M_{\mathrm{Al}}}\right)}{\left(\frac{B_i}{B_{\mathrm{Al}}}\right)}, \tag{2}$$

where M_i and M_{Al} are the concentrations of elements i and Al in samples, respectively. B_i and B_{Al} are the background values of elements i and Al, respectively. In this study, the average concentrations of heavy metals in the subsoil of northwestern Guizhou Province (Meng et al. 2022) were used as the background values. The EF degree was divided into five levels from no or low to severe enrichment (Table S2).

2.5.3 Ecological risk factor

Ecological risk factor (E_{r}) was applied to evaluate the potential ecological risk of heavy metals in soil and was calculated according to Eq. 3 (Hakanson 1980):

$$E_{\mathrm{r}} = \frac{C_i}{B_i} T_i, \tag{3}$$

in which C_i is the measured concentration of heavy metals in the soil, B_i is the geochemical background of heavy metals in the soil (subsoil of northwestern Guizhou Province, Meng et al. 2022), and T_i is the toxic factor of heavy metals. The E_{r} was classified into five grades from low potential ecological risk to very high potential ecological risk (Table S3) (Hakanson 1980).

2.6 Source appointment by PCA-APCS-MLR

Principal component analysis (PCA) was applied to extract major factors that contribute to heavy metals in soils. The mathematical model can be expressed as Eq. 4:

$$\begin{cases} X_1 = a_{11}\ F_1 + a_{12}F_2 + \cdots + a_{1m}F_m + \varepsilon_1 \\ X_2 = a_{21}\ F_1 + a_{22}F_2 + \cdots + a_{2m}F_m + \varepsilon_2 \\ \qquad\qquad \cdots \\ X_p = a_{p1}\ F_1 + a_{p2}F_2 + \cdots + a_{pm}F_m + \varepsilon_p \end{cases}, \tag{4}$$

where m indicates the quantity of heavy metals, n indicates soil samples, p integrated variables can be achieved after PCA calculation, a is the component loading, and F is the measured value of the variable.

Based on the principal factors obtained from PCA analysis, the absolute principal component scores (APCS) obtained from the eigenvectors and standardized data were further calculated by multiple linear regression (APCS-MLR) to obtain the contribution rate of each factor to the soil heavy metals. The contribution rate C_{j} of each factor to the heavy metals is expressed as Eq. 5:

$$C_j = \left(r_0\right)_j + \sum_{k=1}^{n} r_{jk} \times \mathrm{APCS}_K, \tag{5}$$

where $(r_0)_j$ is a constant term of multiple regressions for pollutant j; r_{jk} is the regression coefficient of multiple linear regression; $\mathrm{APCS_k}$ is the scale value of the rotated factor K for the considered sample. The combined term $r_{jk} \times \mathrm{APCS_k}$ represents the contribution of source k to C_j.

2.7 Correlation analysis

Pearson's correlation analysis was used to assess the linear relationship among variables of soils. The r is Pearson's correlation coefficient, and the p values refer to the significance of the linear relationship.

3 Results

3.1 Geochemical composition of bedrock

The XRD patterns of the bedrock are presented in Fig. S1. Most bedrock samples were predominantly composed of calcite (87%–100%), except CHJ3, which contained 82% dolomite. The total Cd content in the bedrock ranged from 0.15 to 2.1 mg/kg, with an average content of 0.66 mg/kg (Table 1). The average content of other heavy metals decreased in the order of Zn (11.05 mg/kg) > Cr (7.73 mg/kg) > Ni (3.35 mg/kg) > Pb (2.19 mg/kg) > Cu (0.45 mg/kg).

3.2 Soil chemical composition and selected properties

The major chemical composition of the soil samples included SiO_2 (33.9%–68.7%), Al_2O_3 (14.2%–27.3%), and Fe_2O_3 (3.77%–14.0%), and the loss on ignition (LOI) ranged from 4.75% to 20.2%. The average content of CaO, MgO,

Table 1 Total content of heavy metals in bedrock samples

Sample	Cd (mg/kg)	Zn	Pb	Cr	Ni	Cu
CHJ1	0.29	5.27	0.32	9.38	4.19	0.68
CHJ3	0.83	3.07	0.08	7.32	3.89	0.14
CHJ8	0.23	10.2	8.10	4.00	0.91	0.38
CHJ12	0.15	BDL	0.21	2.53	1.69	0.13
CHJ18	2.10	23.3	1.87	8.34	3.96	0.75
CHJ26	0.35	13.4	2.55	14.8	5.48	0.62
Carbonate[a]	0.035	20	9	11	20	4

BDL: below detection limit

[a]Turekian and Wedepohl (1961)

Table 2 Major chemical composition and selected chemical properties of the studied soil samples

Statistics	Min	Max	Median	Average	SD
Topsoil (0–20 cm, $N=27$)					
SiO_2 (%)	39.9	61.5	53.8	52.8	6.20
Al_2O_3 (%)	15.9	27.3	19.2	19.5	2.89
Fe_2O_3 (%)	5.62	12.9	8.52	8.52	1.75
CaO (%)	0.09	8.96	0.41	0.76	1.66
MgO (%)	0.78	2.90	1.31	1.42	0.46
Na_2O (%)	0.11	0.55	0.15	0.17	0.08
K_2O (%)	1.05	4.12	1.65	1.92	0.73
Ti (g/kg)	4.01	8.46	6.73	6.5	1.32
Mn (g/kg)	0.11	1.10	0.39	0.47	0.26
LOI (%)	7.25	20.2	14.1	14.1	3.16
pH	4.46	7.92	5	5.45	1.04
SOM (g/kg)	8.89	144	41.3	46.2	23.5
Subsoil (> 60 cm, $N=27$)					
SiO_2 (%)	41.2	68.7	50.8	52.2	8.55
Al_2O_3 (%)	14.2	25.1	21.5	20.6	3.45
Fe_2O_3 (%)	3.77	14.0	9.10	8.62	2.32
CaO (%)	0.09	13.1	0.25	1.15	2.99
MgO (%)	0.79	2.59	1.44	1.51	0.44
Na_2O (%)	0.09	0.55	0.15	0.18	0.09
K_2O (%)	1.12	5.03	1.97	2.28	0.99
Ti (g/kg)	3.80	8.71	6.14	6.09	1.45
Mn (g/kg)	0.09	2.16	0.36	0.47	0.44
LOI (%)	4.75	19.2	12.4	12.7	4.12
pH	4.18	8.14	5.36	5.52	0.96
SOM (g/kg)	BDL	45.9	12.3	14.3	10.5

SD: standard deviation; BDL: below detection limit

Na_2O, and K_2O was generally below 5% (Table 2). The average content of CaO, MgO, Al_2O_3, K_2O, and Fe_2O_3 was higher in subsoil than in topsoil. In contrast, the average LOI was higher in topsoil than in subsoil.

Soil pH ranged from 4.46 to 7.92 in topsoil and from 4.18 to 8.14 in subsoil; 81.5% of topsoil and 85.2% of subsoil samples were acidic (pH ≤ 6.5). The median and average pH values were higher in subsoil than in topsoil, and ~74% of the sampling sites exhibited lower pH in topsoil than in subsoil. Soil organic matter (SOM) content in topsoil ranged from 8.89 to 144 g/kg, while in subsoil, it ranged from undetected to 45.9 g/kg in subsoil. The average SOM content was higher in topsoil (46.2 g/kg) than in subsoil (14.3 g/kg).

3.3 Content of total and bioavailable heavy metals in soil

The total and bioavailable content of Cd, Zn, and Pb in the collected soils is summarized in Table 3. The total Cd content (Cd_{tot}) in topsoil ranged from 0.47 to 6.97 mg/kg, with an average of 2.29 mg/kg, which was significantly higher than that in subsoil (0.47–6.97 mg/kg, average of 0.71 mg/kg) ($p < 0.01$). Similarly, the total Zn content (Zn_{tot}) in topsoil (average of 193 mg/kg) was higher than in subsoil (average of 183 mg/kg). The average Pb content in topsoil (85.4 mg/kg) was lower than in subsoil (93.2 mg/kg), although the median Pb content showed the opposite trend. No significant differences were observed between the topsoil and subsoil in the total content of Cr, Ni, and Cu.

The bioavailable Cd content (Cd_{DTPA}) in topsoil (0.56 mg/kg) was significantly higher than in subsoil (0.07 mg/kg) ($p < 0.01$, Table 3). Similarly, the average bioavailable Zn content (Zn_{DTPA}) in topsoil (3.79 mg/kg) exceeded that in subsoil (1.85 mg/kg). The content of bioavailable Pb, Cr, Ni, and Cu was generally below 1 mg/kg. The average proportion of bioavailable metals decreased in the order of Cd (25.7%) > Zn (2.74%) > Cu (0.6%) > Ni (0.29%) > Pb (0.12%) > Cr (0%) in topsoil, and Cd (12.9%) > Zn (2.59%) > Ni (0.44%) > Pb (0.32%) > Cu (0.29%) > Cr (0%) in subsoil. The proportion of bioavailable Cd in topsoil (average of 25.73%) was significantly higher than that in the subsoil (average of 12.95%) ($p < 0.01$) (Fig. 2a). Additionally, 37% of the topsoil in sampling sites had bioavailable Cd, accounting for > 30% of total Cd, compared to 14.8% in

Table 3 Content of total and DTPA-extractable heavy metals in studied soils

Sample	Statistics	Cd_{tot} (mg/kg)	Cd_{DTPA}	Zn_{tot}	Zn_{DTPA}	Pb_{tot}	Pb_{DTPA}	Cr_{tot}	Ni_{tot}	Cu_{tot}
Topsoil ($N=27$)	Min	0.47	–	57.6	–	32.6	–	77.7	12.6	9.51
	Max	6.69	2.48	699	34.8	359	1.42	245	115	67.0
	Average	2.29	0.56	193	3.79	85.4	0.15	121	54.4	31.7
	Median	2.00	0.45	130	2.14	54.9	0.01	119	53.2	27.3
	SD	1.48	0.61	157	6.59	80.9	0.35	32.7	19.4	12.9
Subsoil ($N=27$)	Min	0.14	–	18.6	–	18.9	–	91.7	4	7.04
	Max	3.25	0.39	1126	13.0	1082	19.3	232	142	58.7
	Average	0.71	0.07	183	1.85	93.2	0.82	131	58.0	27.8
	Median	0.54	0.05	89.8	0.95	36.6	–	129	51.4	23.2
	SD	0.70	0.09	254	2.88	207	3.71	33.4	27.7	13.8
GZ[a]		0.66	–	99.5	–	35.2	–	95.9	39.1	32.0
NWGZ[b]		0.224	–	116	–	27.4	–	138	61.3	65.1

[a]Background value of Guizhou Province obtained from CNEMS (1990)

[b]Background value of northwest Guizhou Province obtained from Meng et al. (2022). SD refers to standard deviation. The subscript tot refers to the total content, and DTPA refers to DTPA-extractable content. The DTPA-extractable content of Cr, Ni, and Cu is not listed because their total content was close to the background values, and the bioavailable content was very low

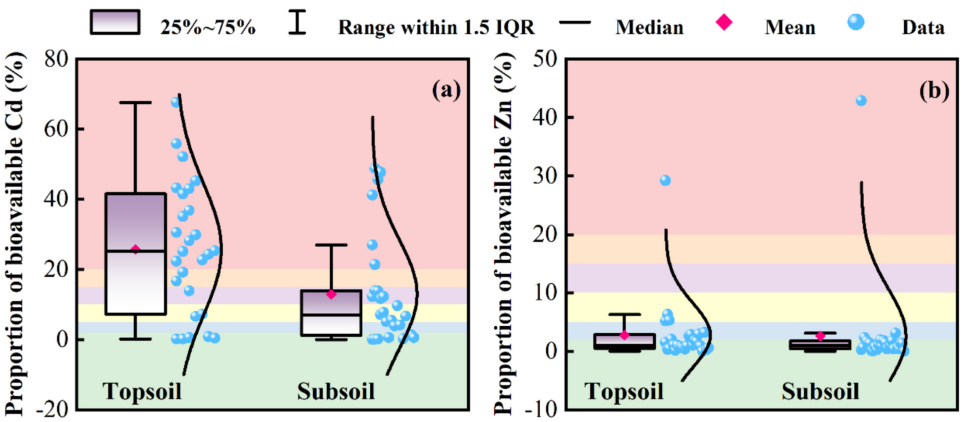

Fig. 2 Proportion of bioavailable Cd (**a**) and Zn (**b**) in topsoil and subsoil

the subsoil. The proportion of bioavailable Zn accounted for < 10% of the total Zn in both soil layers (Fig. 2b).

3.4 Geo-accumulation index and enrichment factors

The average I_{geo} value for heavy metals decreased in the order of Cd (2.34) > Pb (0.71) > Zn (−0.16) > Cr (−0.86) > Ni (−0.86) > Cu (−1.73) in topsoil, and the order of Cd (0.46) > Pb (0.21) > Zn (−0.61) > Cr (−0.69) > Ni (−0.86) > Cu (−2.01) in subsoil (Fig. 3a, b). In topsoil, 70.37% of samples had I_{geo} values above 2 for Cd, compared to 11.11% in subsoil. For Zn and Pb, the proportions of samples with $I_{geo} > 2$ were 3.7% and 7.41% in topsoil, and 11.11% and 7.41% in subsoil, respectively.

The average EF value decreased in the order of Cd (7.69) > Pb (2.55) > Zn (1.36) > Ni (0.73) > Cr (0.72) > Cu (0.40) in topsoil, and in the order of Pb (2.37) > Cd (2.14) > Zn (1.12) > Cr (0.72) > Ni (0.70) > Cu (0.31) in subsoil (Fig. 3c, d). The proportion of samples with EF > 2 for Cd was 96.3% in topsoil and 59.3% in subsoil. For Zn and Pb, most soil samples had EF < 2, with 85.2% and 66.7% in topsoil, and 85.2% and 85.2% in subsoil, respectively. The EF values for Cr, Ni, and Cu were consistently below 2 in both topsoil and subsoil.

The E_r of Cd was significantly higher than that of other metals. Cadmium exhibited a high potential ecological risk in topsoil, with E_r values ranging from 58 to 857 and an average of 282 (Fig. S2a, b). In subsoil, Cd posed a considerable potential ecological risk. In contrast, the average E_r values for other heavy metals were below 40, indicating a low potential ecological risk for these elements.

The spatial distribution of both total and bioavailable Cd content in topsoil revealed elevated content in the southwest and northeast regions of the study area (Fig. 4a).

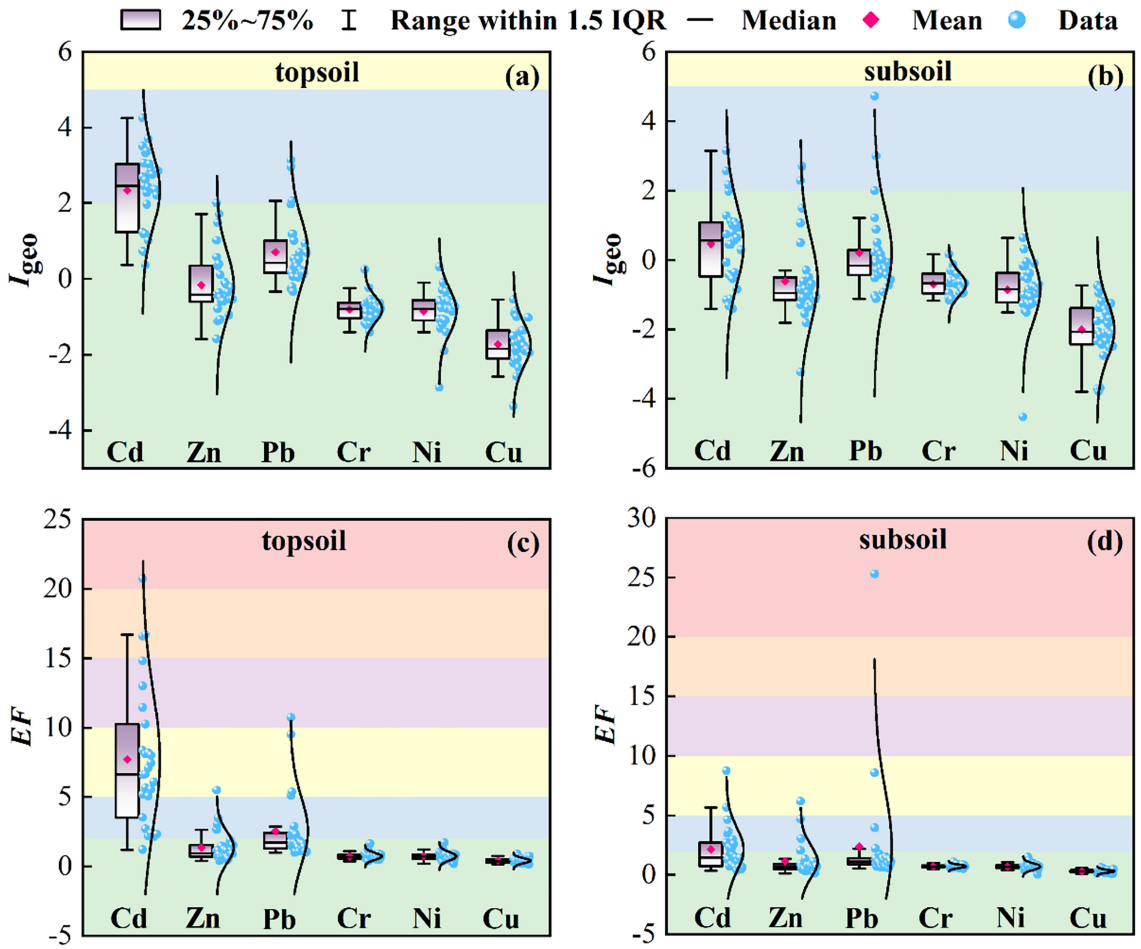

Fig. 3 The I_{geo} values of heavy metals in topsoil (**a**) and subsoil (**b**), and the EF values of heavy metals in topsoil (**c**) and subsoil (**d**) in the study area

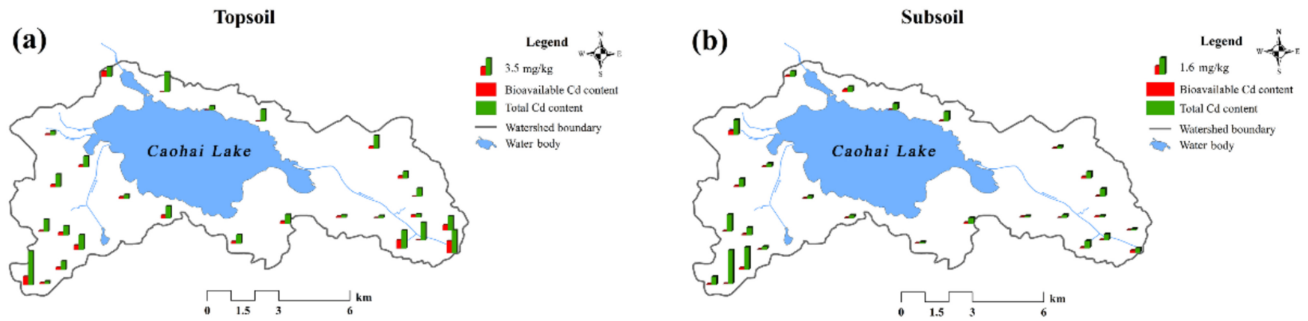

Fig. 4 Spatial distribution of Cd in the study area. Red refers to bioavailable and green refers to total Cd distribution in the topsoil (**a**) and subsoil (**b**)

A similar pattern was observed for total Cd content in subsoil, with particularly extreme content detected in the southwest (Fig. 4b). The spatial distribution of total Zn and Pb is similar to that of total Cd. However, the content of bioavailable Zn and Pb was low in both topsoil and subsoil (Fig. S3).

3.5 Correlation analysis

Pearson correlation analysis revealed distinct relationships among heavy metals and soil properties in topsoil and subsoil. In topsoil, Cd showed a significantly positive correlation only with Pb. Zn was significantly positively

correlated with Pb and Ni, while Pb was significantly correlated with Cr and Ni. Additionally, significantly positive correlations were found among Cr, Ni, and Cu (Table 4). In the subsoil, all analyzed heavy metals exhibited significant correlations with one another. For topsoil, the total Cd content was significantly correlated with SOM ($r = 0.619$, $p < 0.01$, Table S4). The DPTA-extractable Cd content was positively correlated with both total Cd content ($r = 0.635$, $p < 0.01$) and SOM ($r = 0.730$, $p < 0.01$), but negatively correlated with pH ($r = -0.481$, $p < 0.05$). The proportion of DTPA-extractable Cd was also negatively correlated with soil pH ($r = -0.747$, $p < 0.01$, Table S4). For subsoil, the total Cd content was positively correlated with Mn ($r = 0.526$, $p < 0.01$, Table S5). The DPTA-extractable Cd showed a weak correlation with total Cd ($r = 0.184$) but a significantly negative correlation with pH ($r = -0.489$, $p < 0.01$). Similarly, the proportion of DTPA-extractable Cd was negatively correlated with soil pH ($r = -493$, $p < 0.01$, Table S5). The content of residual Cd ($Cd_{Res} = Cd_{Tot} - Cd_{DTPA}$) exhibited a positive correlation with residual Pb in topsoil (Table S6). In contrast, the Cd_{Res} was positively correlated with Pb_{Res}, Ni_{Res}, Cu_{Res}, and Mn in subsoil (Table S7).

3.6 Principal component analysis

The Kaiser–Meyer–Olkin (KMO) values of the dataset were 0.622 for topsoil and 0.869 for subsoil, indicating that the data were suitable for PCA (KMO > 0.6). Effective principal components with eigenvalues greater than 1 were extracted, resulting in two factors for topsoil and one factor for subsoil. The cumulative variance contribution rates were 84.33% for topsoil and 67.9% for subsoil, capturing most information related to major pollution sources (Table 5).

Table 5 Loading of principal components

Element	Topsoil		Subsoil
	PC1	PC2	PC1
Cd	0.139	**0.934**	**0.655**
Zn	**0.898**	0.214	**0.840**
Pb	**0.767**	0.541	**0.821**
Cr	**0.921**	−0.293	**0.912**
Ni	**0.874**	−0.341	**0.929**
Cu	**0.756**	−0.223	**0.756**
Variance (%)	59.971	24.362	67.895
Cumulative (%)	59.971	84.333	67.895

Significant loading (>0.6) is indicated in bold

4 Discussion

4.1 Enrichment and potential risks of Cd in the soils

It is widely accepted that heavy metals in overlying soil in unpolluted karst landforms primarily originate from the weathering of bedrock (Liu et al. 2023b; Quezada-Hinojosa et al. 2009; Wen et al. 2020b; Yang et al. 2021a). Consequently, the heavy metal content in bedrock determines the local geochemical background. In the study area, the average levels of Zn, Pb, Cr, Ni, and Cu in bedrock were lower than those in global carbonate rocks (Turekian and Wedepohl 1961, Table 1), while Cd levels were higher. Specifically, the Cd content in the bedrock ranged from 0.15 to 2.1 mg/kg, with an average of 0.66 mg/kg, which exceeds the levels found in carbonate rocks from Guangxi in China (0.09–1.54 mg/kg, average of 0.45 mg/kg; Wen et al. 2020a), northwestern Guizhou Province (0.12–0.4 mg/kg, average of 0.23 mg/kg; Yu et al. 2022a), and the Jura Mountains of Switzerland (0.03–4.91 mg/kg, average of 0.28 mg/kg; Quezada-Hinojosa et al. 2009). This confirms the high

Table 4 Pearson's correlation coefficients between heavy metals in the studied soils

		Cd	Zn	Pb	Cr	Ni	Cu
Topsoil ($N = 27$)	Cd	1					
	Zn	0.258	1				
	Pb	**0.520****	**0.793****	1			
	Cr	−0.147	**0.728****	**0.577****	1		
	Ni	−0.143	**0.686****	**0.448***	**0.924****	1	
	Cu	−0.012	**0.557****	0.377	**0.674****	**0.636****	1
Subsoil ($N = 27$)	Cd	1					
	Zn	**0.386***	1				
	Pb	**0.499****	**0.635****	1			
	Cr	**0.512****	**0.705****	**0.727****	1		
	Ni	**0.502****	**0.806****	**0.706****	**0.856****	1	
	Cu	**0.459***	**0.553****	**0.456***	**0.639****	**0.646****	1

*$p < 0.05$; **$p < 0.01$. The significant correlation coefficients are in bold

geochemical background of Cd in the study area. The significant positive correlation between total Cd and total Mn content in subsoil ($r = 0.526$, $p < 0.01$, Table S5) suggests the co-enrichment of Cd and Mn in carbonate regions, consistent with previous studies conducted in karst regions of southwestern China (Liu et al. 2023b; Wen et al. 2020a; Yang et al. 2021b). In topsoil, total Cd was positively correlated with SOM ($r = 0.619$, $p < 0.01$, Table S4), likely due to the abundance of negatively charged sites (e.g., carboxylates, phenolics, and thiols) in organic matter, which enhance Cd retention (Loganathan et al. 2012).

In the study area, 100%, 66.67%, and 100% of topsoil samples exceeded the background values for Cd, Zn, and Pb, respectively (Meng et al. 2022). For subsoil, the exceedance rates were 81.48%, 25.93%, and 85.19%, respectively. Compared to the risk screening values for Chinese agricultural land (GB15618-2018), 100%, 22.22%, 25.93%, 7.41%, 29.63%, and 11.11% of topsoil samples exceeded the screening values for Cd, Zn, Pb, Cr, Ni, and Cu, respectively. For subsoils, the corresponding exceedance rates were 66.67%, 18.52%, 14.81%, 22.22%, 25.93%, and 7.41%. The average Cd content in topsoil (2.29 mg/kg, Table 3) was also higher than in carbonate regions of Guangxi (1.00 mg/kg; Yang et al. 2021b) and France (1.34 mg/kg; Rambeau et al. 2010), while the average Cd content in subsoil (0.71 mg/kg) was lower. The I_{geo} indicated that Cd and Pb exhibited higher pollution levels than Zn, Cr, Ni, and Cu in topsoil (Fig. 3). Cadmium was classified as moderately polluted ($I_{geo} > 2$), and the E_r results confirmed its high potential ecological risk, identifying Cd as the primary pollutant in the studied soils. In this study, EF ≥ 2 was considered indicative of anthropogenic influence (Acosta et al. 2009). Over 96.3% of sampling sites in the study area showed EF ≥ 2 for Cd, suggesting significant anthropogenic pollution. These findings indicate that Cd contamination in the study area results from a combination of high geological background and anthropogenic activities. This aligns with previous studies showing severe Cd, Zn, and Pb pollution in soils near Zn smelting areas (Bi et al. 2006b; Li et al. 2022) and high spatial variability of Pb, Cd, and Zn in soils of Bijie City (Yuan et al. 2017), highlighting the multiple sources of heavy metals in the studied soils.

4.2 Sources of Cd in soils

The heavy metal content in the studied soils is influenced by both geogenic and anthropogenic activities, making it essential to quantify the contribution of these sources. The significantly positive correlation between Cd and Pb in topsoil suggests that they may share similar sources, while the positive correlations among other metals indicate their common origins. In subsoil, the strong correlations among all heavy metals point to a shared source, most likely of geogenic origin. The significantly positive correlation between Cd_{Tot} and Mn, as well as between Cd_{Res} and Mn in subsoil, suggest the co-enrichment of Cd and Mn in soils from karst regions. This further supports the geogenic origin of Cd, likely derived from the weathering of carbonate bedrock in the study area.

PCA identified two distinct influencing metal distributions in topsoil, while only one component was identified in subsoil. In subsoil, PC1 had loading values above 0.6 for Cd, Zn, Pb, Cr, Ni, and Cu (Table 4), confirming their geogenic source (Li et al. 2022; Yu et al. 2022a). In topsoil, PC1 was dominated by Zn, Pb, Cr, Ni, and Cu, with contribution rates of 80.77%, 58.53%, 75.86%, 71.93%, and 77.22%, respectively (Fig. 5). The levels of Cr, Ni, and Cu in the studied soils were close to the background values in northwestern Guizhou Province (Table 3). In contrast, Zn and Pb were identified as pollutants in the study area, primarily due to artisanal Zn smelting activities, and these metals are predominantly found in smelting slag (Bi et al. 2006b; Li et al. 2022; Yu et al. 2022b). Therefore, PC1 for topsoil was identified as a mixed source of geological materials and smelting slag.

PC2 was dominated by Cd, with a contribution rate of 87.05%. Artisanal zinc smelting activities have been prevalent in the study area from the seventeenth century until 2004 (Bi et al. 2006b; Li et al. 2022; Luo et al. 2018). The smelting process involves burning coal and Zn-bearing minerals at high temperatures to produce Zn vapor, which is then recovered through condensation. Because the boiling point of Cd (767 °C) is lower than that of Zn (907 °C), and Zn is the primary product, a significant amount of Cd is emitted into the atmosphere during smelting (Feng et al. 2006). Additionally, the differing boiling points of these metals

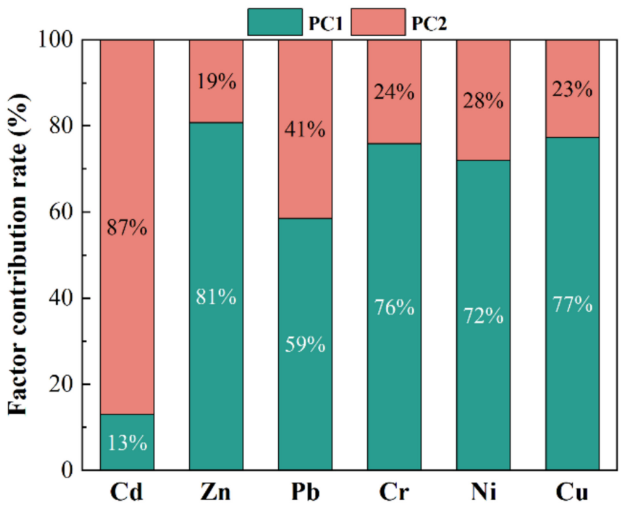

Fig. 5 Contribution rate of two principal components to heavy metals in topsoil

result in distinct Zn/Cd and Pb/Cd ratios in the gas and slag phases, which can serve as indicators of heavy metal sources in soils (Bi et al. 2006b; Lin et al. 2009; Meng et al. 2021). In the study area, the Zn/Cd ratio in subsoil ranged from 30 to 1536 (average of 335), while the Pb/Zn ratio ranged from 21 to 501 (average of 134). In topsoil, the Zn/Cd ratio ranged from 25 to 578 (average of 116), and the Pb/Cd ratio ranged from 10 to 264 (average of 49). Because the average content of Zn and Pb was similar between topsoil and subsoil, the lower Zn/Cd and Pb/Cd ratios in topsoil likely reflect additional Cd input from atmospheric deposition. Similar findings were reported by Lin et al. (2009), who observed lower Pb/Cd and Zn/Cd ratios in polluted soils than in background soils in the artisanal Zn smelting area. These ratio changes were also evident in local sediments (Meng et al. 2021). A mass balance calculation by Bi et al. (2006a) estimated that ~450 tons of Cd was released into the environment from artisanal smelting activities in a small area (< 150 km^2) in Hezhang County between 1989 and 2001. Atmospheric deposition may also contribute to Pb enrichment (~41%) in the studied soils (Table 4, Fig. 5), likely originating from coal combustion during smelting activities (Bing et al. 2016; Liu et al. 2023a; Pan et al. 2021). This is supported by elevated Pb content and Pb isotopic fingerprints observed in the sediment of Caohai Lake (Bi et al. 2007). These results collectively suggested that atmospheric Cd deposition (PC2) from Zn smelting significantly contributes to the elevated Cd levels in topsoil in the study area. Although the amendment of fertilizers can result in Cd accumulation in agricultural soils (Bigalke et al. 2017), it may not be a major Cd source in the studied soils because Cd inputs from the application of mineral fertilizers are usually low (Bigalke et al. 2017).

4.3 Factors influencing Cd bioavailability in soils

The environmental risks of heavy metals in soils are highly dependent on their bioavailability (Kim et al. 2015; Shahid et al. 2016). In the study area, Cd is the primary pollutant and exhibits greater bioavailability than other metals. Therefore, this section focuses on identifying the factors influencing Cd bioavailability in soils. Previous studies have shown that Cd in soils from karst regions commonly exhibits low bioavailability (Lin et al. 2024; Ma et al. 2020; Wen et al. 2020b). Our results revealed that DTPA-extractable Cd accounted for 0.002%–48.87% (average of 12.95%) of the total Cd in subsoil, where Cd is predominantly of geogenic origin (Fig. 3). In contrast, this proportion was higher in topsoil (average of 25.73%), where Cd is influenced by both high geochemical background and atmospheric deposition from artisanal Zn smelting. These findings align with previous studies indicating that topsoil generally exhibits greater Cd bioavailability than subsoil (Liu et al. 2023b; Quezada-Hinojosa et al. 2015). Several factors contribute to the difference in Cd bioavailability. First, the sources of heavy metals play a critical role. Anthropogenic heavy metals are generally more labile than geogenic metals (Chlopecka 1996; Giráldez et al. 2020; Laveuf et al. 2009; Ma et al. 2020). For example, Mao et al. (2014) demonstrated that petrol-derived Pb in rural roadside surface soils had a higher isotopically exchangeable fraction (35%) than geogenic Pb (27%). Recent studies have also shown that Cd from atmospheric deposition is more bioavailable than legacy Cd in soils, and Cd deposition significantly increased the bioavailable Cd pool (Liu et al. 2022; Zhou et al. 2024). In the studied soils, atmospheric deposition from artisanal Zn smelting contributed 87% of total Cd in topsoil (Fig. 5). This suggests that atmospheric Cd deposition is a critical factor driving the higher Cd bioavailability in topsoil compared to subsoil. Once deposited into the soil, Cd from atmospheric sources tends to adsorb onto the surface of soil aggregates rather than being incorporated into the aggregates or bound in stable chemical forms (Liu et al. 2021a; Sungur et al. 2021). This surface-bound Cd is more readily available for plant uptake and poses greater environmental risks.

In addition to the distinct contribution of Cd sources, topsoil and subsoil exhibit contrasting chemical properties due to weathering, biological disturbances, and agricultural activities. Topsoil has lower pH and higher SOM than subsoil (Table 2), and both properties are correlated with the content and proportion of bioavailable Cd (Tables S4 and 5). The content and proportion of bioavailable Cd were negatively correlated with soil pH in both topsoil and subsoil. Soil pH is a primary factor controlling Cd bioavailability (Huang et al. 2021; Wen et al. 2020a), as it influences Cd adsorption/desorption by soil minerals. Low soil pH reduces the surface negative charge of soil colloids, decreasing their capacities to adsorb Cd^{2+} (Hou et al. 2017). Additionally, higher concentrations of H^+ can compete with Cd^{2+} for adsorption sites on soil particles (Young 2012). In this study, the proportion of bioavailable Cd in soils with pH above 7 was less than 1%, consistent with findings by Shahid et al. (2016), who reported that Cd tends to form insoluble hydroxides or carbonates in alkaline environments. Therefore, a decrease in pH in topsoil, caused by factors such as the removal of base cations, root and microbial activities, accumulation and decomposition of organic matter, and fertilization (Weil and Brady 2017), can increase Cd bioavailability. Given this, prevention of soil acidification and adjustment of soil pH could be effective strategies to combat Cd risks in the study area.

In topsoil, the bioavailable Cd content was positively correlated with both the total Cd content ($r = 0.635$, $p < 0.01$) and SOM ($r = 0.730$, $p < 0.01$). However, this strong correlation between bioavailable Cd and SOM was not observed in subsoil. SOM plays a complex and dual role in Cd bioavailability in soils (Azeez et al. 2010; Dhaliwal et al. 2023).

On one hand, solid organic matter can provide adsorption sites, immobilizing Cd and reducing its bioavailability. On the other hand, dissolved organic matter (DOM), particularly low-molecular-weight hydrophilic compounds, can form complexes with Cd, enhancing its bioavailability (Halim et al. 2015; Li et al. 2024; Loganathan et al. 2012). In addition, organic acids from plant root exudates, such as citric acid and oxalic acid, have been shown to increase Cd bioavailability in soils (Huang et al. 2024; Qin et al. 2021; Rezwan et al. 2024; Zhan et al. 2020). For example, Wang et al. (2020) reported that DOM derived from straw and farmyard manure promoted Cd desorption and increased the proportion of exchangeable Cd in soil, leading to higher Cd accumulation in Pak Choi. These results implied that the application of straw and manure amendments could influence Cd bioavailability and thus should be approached with caution in the study area. Most of the studied soils were collected from farmland and forests, where plant litter and manure are primary sources of organic matter. However, the effects of different plant species and organic acid on Cd bioavailability remain poorly understood and warrant further investigation.

5 Conclusions

This study delved into the sources and potential environmental risks of heavy metals in topsoil and subsoil around Caohai Lake, an area characterized by high geochemical background and artisanal Zn smelting, with a particular focus on Cd. The findings indicated that the carbonate bedrock in the study area exhibits high Cd content, corroborating the high geochemical background of Cd. Cadmium emerged as the principal soil pollutant in the study area, presenting a case of moderate pollution alongside high potential ecological risks. Through the application of PCA-APCS-MLR source apportionment, it was discerned that 87% of the total Cd in topsoil could be traced back to atmospheric deposition associated with historical artisanal zinc smelting activities. Conversely, Cd in subsoil was predominantly of geogenic origin. Furthermore, the study uncovered that additional atmospheric Cd deposition, coupled with lower soil pH and higher organic matter content, served to enhance the bioavailability of Cd in topsoil. The outcomes of this study underscore the significant impact of atmospheric Cd deposition on both the total and bioavailable Cd in karst regions with a high geochemical Cd background.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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