



A large and overlooked Cd source in karst areas: The migration and origin of Cd during soil formation and erosion

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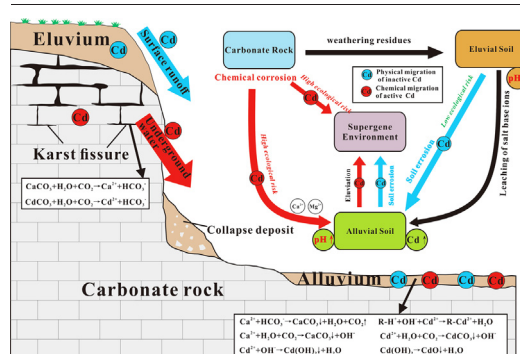
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HIGHLIGHTS

- Mechanical migration of Cd does not influence spatial redistribution of soil Cd concentration.
- Chemical migration of Cd elevated Cd concentration and bioavailability in alluvium.
- Active Cd in alluvium mainly originates from carbonate corrosion rather than leaching of eluvium.
- Carbonate weathering poses Cd risks to karst areas due to its significant Cd release flux.

GRAPHICAL ABSTRACT



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ABSTRACT

There is increasing concern regarding the substantial enrichment of Cd during the weathering of carbonate rocks and subsequent risks posed to the ecological environment and food security in karst areas. However, the incomplete understanding of Cd migration mechanisms and material sources restricts soil pollution control and land management. This study investigated the migration regulation of Cd during soil formation and erosion in karst areas. The results demonstrate that soil Cd concentration and bioavailability are both significantly higher in alluvium compared with those in eluvium. This increase is primarily attributed to the chemical migration of active Cd, rather than the mechanical migration of inactive Cd. Additionally, we analyzed the Cd isotopic characteristics of rock and soil samples. The isotopic composition of the alluvial soil was $-0.18\text{‰} \pm 0.01\text{‰}$, which is obviously heavier than the $\delta^{114/110}\text{Cd}$ value of the eluvium ($-0.78\text{‰} \pm 0.06\text{‰}$). The Cd isotopic fingerprint revealed that the active Cd in the alluvium of the study profile was probably derived from the corrosion of carbonate rocks rather than by eluviation of the eluvium. Moreover, Cd tends to occur in soluble mineral components of carbonate rocks rather than in residues, which suggests that carbonate weathering has a great potential to release active Cd into the environment. It is estimated that the Cd release flux caused by carbonate weathering is $5.28\text{ g Cd km}^{-2}\text{ yr}^{-1}$, accounting for 9.30 % of the anthropogenic Cd flux. Therefore, the corrosion of carbonate rocks is a substantial natural Cd source and poses significant potential risks to the ecological environment. It is suggested that the contribution of Cd from natural sources should be considered during ecological risk assessments and studies of the global Cd geochemical cycle.

Abbreviations: BCR, European Community Bureau of Reference; CCSF, carbonate weathering carbon-sink flux; ICP-MS, inductively coupled plasma-mass spectrometry; XRF, X-ray fluorescence.

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1. Introduction

Cadmium (Cd) is a toxic non-essential element that seriously threatens the environment and human health (Lin et al., 2015). The generation, distribution, and migration of Cd in soils have attracted considerable academic attention because of its non-biodegradability and persistence in the environment (Deng et al., 2019; Holm et al., 2003; Wen et al., 2020). Rapid economic development and a lack of effective environmental protection are considered to be the main factors causing soil Cd contamination in China (Hu et al., 2016; MEEC and MLRC, 2014; Wang et al., 2019), especially human factors such as industrial operations, mining and metallurgy, agricultural production, and activities of urban residents (Borah et al., 2018; Liu et al., 2005; Shi et al., 2019; Wen et al., 2015; Xu et al., 2010a). However, the distribution of soil Cd concentration is not significantly correlated with factors such as economic development, urbanization, and population distribution (Cheng et al., 2005; Liu et al., 2013). For example, areas with the fastest economic growth and largest population in China (southeastern coastal regions) do not have the highest Cd levels; the highest levels occur in southwest provinces with an underdeveloped economy and a relatively small population (Xie et al., 2012). Geochemical anomalies of Cd are widely present in southwest China, including in Yunnan, Guizhou, and Guangxi Province. An area larger than 235,000 km² has an average Cd concentration of approximately 2 mg/kg (Tian and Xu, 2014), surpassing the background value of soil Cd in China (0.097 mg/kg; Wei et al., 1991). Therefore, the geological background plays a critical role in elevating Cd concentrations (Liu et al., 2017a; Wen et al., 2020; Ye et al., 2012).

Recent research suggests a link between the elevated Cd geological background in southwest China and the widespread distribution of carbonate rocks. Soil Cd content is notably higher in karst areas than in non-karst areas (Xia et al., 2020; Xia et al., 2022; Yamasaki et al., 2013; Yang et al., 2021). The Cd migration capacity of karst soils remains controversial, despite the general perception of high Cd concentrations in carbonate weathering soils. Some studies indicate that soil Cd in karst areas is primarily associated with a low mobility residual form (Quezada-Hinojosa et al., 2009; Tian and Xu, 2014; Wen et al., 2020). However, other studies contradict this finding, suggesting that carbonate weathering soils could exhibit high Cd mobility and bioavailability (Liu et al., 2017b; Li et al., 2018). Diverse study profiles likely account for the contrasting conclusions. Most previous studies reporting low mobility of soil Cd in karst areas focused on eluvium, where highly active Cd was strongly leached and transferred during weathering (Guo et al., 2019; Ma et al., 2021; Xing et al., 2015; Zhang et al., 2010). However, recent studies have confirmed that the total concentration and bioavailability of soil Cd in the lowland alluvium are significantly higher than those in the upland eluvium (Xia et al., 2020). Additionally, over half of the rice grown on the alluvium exceeds the national food standard for Cd concentration, which further confirms the mobility and bioavailability of soil Cd in karst areas, highlighting the associated risk. Therefore, understanding the migration mechanism and material source of Cd in carbonate rock weathering and pedogenesis is crucial for developing effective measures to mitigate Cd ecological risks in karst areas and advancing the global Cd cycle theory. Although many studies have reported the enrichment characteristics and risk assessment of soil Cd based on large-scale geochemical sampling and testing in karst areas (Jia et al., 2020; Luo et al., 2018; Yang et al., 2015; Yang et al., 2021), few studies have illustrated the migration mechanism and source tracing of Cd during soil formation and erosion on a relatively microscopic profile scale. The advancement of isotope analysis technology offers a new and precise research approach for Cd source identification. Numerous studies have employed Cd isotope analysis methods to trace environmental Cd contamination sources (Cloquet et al., 2006; Liao et al., 2022; Yang et al., 2019; Yin et al., 2021). However, current studies on Cd source apportionment predominantly concentrate on anthropogenic contaminant sources, with limited exploration of natural Cd sources (Gao et al., 2021). Additionally, previous studies have focused on Cd input–output fluxes and budget balances of anthropogenic contaminant sources, such as smelters (Li et al., 2023), river sediments (Lu et al., 2022), runoff (Yang et al., 2008),

atmospheric deposition (Fang et al., 2018), farmland (Fan et al., 2022), and forest ecosystems (Huang et al., 2011). However, research on the Cd flux of natural source in global is scarce.

In this study, we selected and investigated southern Guizhou Province in China, which is a representative karst area unaffected by atmospheric Cd deposition resulting from lead and zinc mining and smelting. The primary objectives of this study were to (1) comprehensively examine the migration characteristics and mechanisms of Cd in carbonate rock weathering and pedogenesis, while identifying key factors driving increased Cd concentration in alluvium; (2) use a stable Cd isotope as a tracer for source apportionment, and determining the main natural Cd source in the karst area; and (3) assess potential risks of Cd caused by weathering of carbonate rocks by constructing a calculation model of Cd release flux. The findings will enhance our understanding of the migration patterns of soil Cd and the potential ecological risks associated with natural Cd sources in karst areas. In future work, identifying the detailed fate and risk of active Cd released by carbonate weathering in karst ecosystems will be helpful for improving land use management, Cd ecological prevention and control, and green sustainable development.

2. Study area and sampling

The study area is located in southern Guizhou Province, China, and includes Ziyun, Anshun, Pingtang and Duyun cities or counties (Fig. 1). The study area exhibits a dominant geomorphic combination of karst peak forest and depression, leading to significant soil erosion and rock desertification. It is characterized by a warm and humid subtropical monsoon climate, with an average annual temperature of 16.1 °C and annual rainfall ranging from 1200 to 1400 mm. The exposed strata are complex owing to multi-stage tectonic movements in geological history; however, the lithology remains relatively homogeneous (Xu et al., 2010b; Zhou et al., 2017). Carbonate rocks dominate the Cambrian strata in the northeastern of the study area and the Carboniferous and Permian strata in the central area. By contrast, the northern and western regions feature extensive distributions of Devonian and Triassic strata, characterized by a lithological combination of carbonate and clastic rocks (Fig. 1). Additionally, influenced by lithology and climate, the main soil types in the study area are lime and yellow soil.

Since the objective of this study is to investigate the natural migration regulation of soil Cd, sampling was conducted at remote locations far from villages and towns. Nine representative carbonate-weathering crusts from the Cambrian, Carboniferous, and Permian periods were selected for investigation and sampling. (Table S1). Profile S1 was located in an abandoned quarry that ceased operation in 2010. Runoff continuously eroded the upland eluvium, and the eroded soil was deposited on the lowland platform. Alluvium gradually formed with a soil thickness of approximately 40 cm after several years of accumulation (Fig. S1A). This profile offers favorable conditions for studying the process and mechanism of Cd migration in the karst area owing to its singular material source for the alluvium. Typical residual soil profiles (Profiles S2–S9) developed above the carbonate highlands were selected as study profiles to avoid interference from human activities and exogenous substances. For each profile, samples of bedrock, weathering crust, and topsoil were collected from bottom to top at 20 cm intervals (Figs. S1B and S2). This study involved the collection of 9 rock samples and 38 soil samples, weighing 5 kg and 2 kg per sample, respectively.

Samples were packed in Ziplock bags and transported to the laboratory. The rock samples were cleaned with deionized water, air-dried, and ground to 200 mesh (<0.074 mm) with a ball mill. Soil samples were passed through a 10 mesh (diameter 2 mm) sieve to remove plant roots and gravel. Then, the air-dried samples were ground to 200 mesh with an agate mortar.

3. Test and analysis methods

3.1. Extraction of acid insoluble matter

Carbonate rocks have unique mineral compositions and weathering processes compared with other rocks. An acid-insoluble extraction test

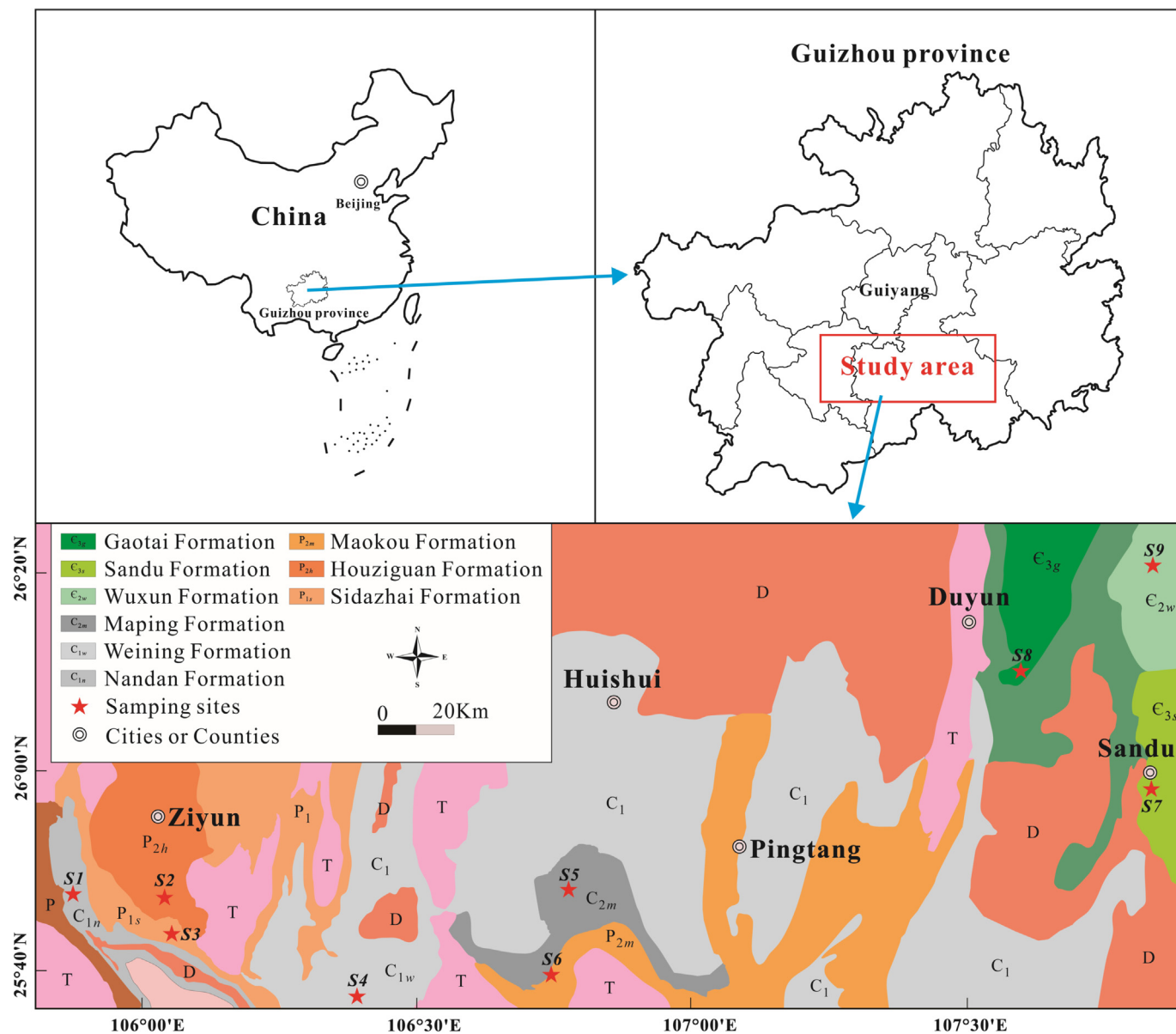


Fig. 1. Geological map of the study area in southern Guizhou Province, China showing the locations and strata of sampling sites.

was performed to clarify the distribution characteristics of Cd in different mineral components of carbonate rocks. The test steps were as follows: 2 kg of rock powder sample was weighed and then reacted with an appropriate amount of 1 M HCl at 25 °C. The dissolution of the rock powder produced many air bubbles. The test was stopped when the remaining sediment no longer bubbled. New HCl was constantly added during this process to ensure that the solution remained acidic. The sediment was separated from the acid solution by centrifuge (5000 rpm, 20 min) to obtain the acid insoluble matter. The acid-insoluble matter was cleaned with ultrapure water, dried, and weighed (Wang et al., 1999).

3.2. Separation of soil aggregates

A 20 g soil sample was placed into the top of the aggregate soil analyzer (sieve apertures of 0.5 mm, 0.25 mm, and 0.053 mm from top to bottom), soaked for 5 min by injecting deionized water into the analyzer to cover the soil sample, and continuously oscillated at a frequency of 30 times/min and an amplitude of 3 cm for 5 min. The soil on the sieve was

transferred and dried, and four water-stable soil aggregates with different particle sizes (>0.5 mm, 0.25–0.5 mm, 0.053–0.25 mm, and <0.053 mm) were obtained. The Cd concentrations of soil aggregates containing different particle sizes were measured in each sample.

3.3. Sequential extraction of Cd speciation

The eluvial and alluvial soil samples in Profile S1 were treated using a modified BCR sequential extraction method to obtain four different forms of soil Cd (Rao et al., 2008; Rauret et al., 1999). The following specific test procedures were used: F1 (water-soluble state or acetic-acid-soluble fraction), extracted with 0.1 M acetic acid solution; F2 (reducible fraction), extracted with 0.5 M hydroxylamine hydrochloride solution; F3 (oxidizable fraction), extracted with 30 % w/v H₂O₂ and 1 M ammonium acetate solution; and F4 (residual), digested using mixed acid (HF–HNO₃–HCl). Subsequently, Cd concentrations in different forms were measured using inductively coupled plasma mass spectrometry (ICP–MS). Sample recoveries ranged from 88.97 % to 95.41 %, with an average of 91.93 %.

3.4. Major composition/element analysis

The rock and soil samples were ground to 200 mesh. The main elemental concentrations were determined using X-ray fluorescence (XRF) spectrometry (ARL Perform X 4200; Thermo Fisher Scientific, United States). The concentrations of Cd and other trace elements were measured using the Quant MS Elite ICP-MS (Jena Analytical Instruments AG, Germany). The sensitivity of ICP-MS was 1.0×10^8 cps (1 ppm In, U), and the detection limits for Fe, La, and Bi were 20 ppt, 1.0 ppt, and 2.0 ppt, respectively. Soil pH was measured using a pH Meter (Mettler-Toledo International Inc., U.S.A.) at a soil-to-water mass ratio of 1:2.5. Particle size was determined using a Battersize 3000 Plus laser particle size analyzer (Dandong Baxter Instrument Co., Ltd., China).

3.5. Calculation of mass balance

The mass transfer coefficient τ was utilized to characterize the deficit or enrichment characteristics of elements in weathering crusts using the following equation (Chadwick et al., 1990; Feng, 2010; Ji et al., 2004; Nesbitt and Markovics, 1997):

$$\tau_{j,zr} = (C_{j,w}/C_{zr,w}) / (C_{j,p}/C_{zr,p}) - 1 \quad (1)$$

where $C_{j,w}$ and $C_{j,p}$ represent the concentrations of element j in the weathering crust (w) and parent rock (p), respectively; $C_{zr,w}$ and $C_{zr,p}$ represent the concentrations of zr in the weathering crust and parent rock, respectively. A $\tau_{j,zr}$ value > 0 denotes the external addition of element j . If $\tau_{j,zr} < 0$, element j in the sample is lost during weathering, and $\tau = -1$ means that element j was completely removed.

3.6. Cd isotopic determination

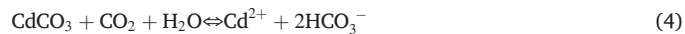
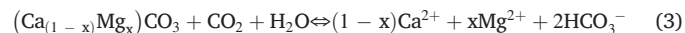
For testing accuracy, the Cd in each sample must be chemically separated from the sample matrix before analysis. All samples were weighed and placed in Teflon digestion vessels for chemical purification. Firstly, samples were reacted with 8 mL of aqua regia + double spike solution (sample/spike ratio of ~ 1) at 110 °C for >24 h, and transferred into 15 mL polypropylene centrifuge tubes. After centrifugation (4000 r/min, 10 min), each residue was digested with 3 mL concentrated HNO_3 + 3 mL concentrated HF, and heated to dryness on a hotplate at 110 °C. Afterward, the corresponding supernatant + 3 mL 30 % H_2O_2 was added, and the solution was evaporated to dryness. Finally, 5 mL 2 mol/L HCl was added and purified on columns containing 3 mL AG MP-1 M (100–200 mesh, Bio-Rad, USA) resin. The procedure for chemical purification of Cd was described by Zhu et al. (2013), with a Cd recovery of >98 %.

The Cd isotopic composition was determined using a Neptune Plus MC-ICP-MS instrument at the State Key Laboratory of Ore Deposit Geochemistry (SKLOGD; Institute of Geochemistry Chinese Academy of Science [IGCAS], Guiyang, China). The double-spike consisted of a mixture of ^{110}Cd and ^{111}Cd , which was used for the mass bias correction. The Nancy Spex and JMC Cd reference materials were employed as secondary Cd isotope standards for quality control. According to the Cd concentrations, all samples and standards were diluted to 200 ng mL^{-1} , and the ^{114}Cd signal was $\sim 3 \text{ V}$ at an uptake rate of $\sim 50 \mu\text{L min}^{-1}$. Detailed information on instrument parameters and computing Cd isotopic compositions using the double-spike technique is detailed in Zhu et al. (2021). In this study, the Cd isotopic compositions reported are relative to the NIST SRM 3108 solution and were using the formula (Liu et al., 2022):

$$\delta^{114/110}\text{Cd} (\text{‰}) = \left[\left(\frac{^{114}\text{Cd}}{^{110}\text{Cd}} \right)_{\text{sample}} / \left(\frac{^{114}\text{Cd}}{^{110}\text{Cd}} \right)_{\text{NIST-3108}} - 1 \right] \times 1000 \quad (2)$$

3.7. Calculation of Cd release flux from carbonate weathering

During the process of weathering of carbonate rocks, the formation mechanism of karst carbon sinks (Li et al., 2019, 2022) and Cd release (Xia et al., 2020) were expressed as follows:



Based on the stoichiometric relationship between CO_2 absorbed flux and Cd release flux during carbonate weathering, Cd release flux was expressed as:

$$\text{CWRF}_{\text{Cd}} = \text{CCSF} \cdot \frac{M_{\text{Cd}}}{M_{\text{C}}} \cdot A \quad (5)$$

$$A = \frac{n_{\text{Cd}}}{n_{\text{CO}_2}} = \frac{\omega \cdot \frac{M_{\text{Cd}}}{M_{\text{C}}}}{\frac{M_{\text{CaO}}}{M_{\text{CaO}}} + \frac{M_{\text{MgO}}}{M_{\text{MgO}}}} = \frac{\omega \cdot [\text{Cd}] \cdot M_{\text{CaO}} \cdot M_{\text{MgO}}}{M_{\text{Cd}} \cdot M_{\text{MgO}} \cdot [\text{CaO}] + M_{\text{Cd}} \cdot M_{\text{CaO}} \cdot [\text{MgO}]} \quad (6)$$

where CWRF_{Cd} is the carbonate weathering Cd release flux ($\text{g Cd km}^{-2} \text{ yr}^{-1}$), CCSF is the carbonate weathering carbon-sink flux (global mean CCSF is $4.3 \text{ t C km}^{-2} \text{ yr}^{-1}$; Zeng et al., 2019); A is the amount-of-substance ratio of removed CO_2 from the atmosphere and released Cd during carbonate weathering; n_{Cd} and n_{CO_2} are the amounts of Cd and CO_2 , respectively; ω is the mass percentage of Cd in soluble mineral components of carbonate rocks; M represents the mass of carbonate rock sample for testing; $[\text{Cd}]$, $[\text{CaO}]$, and $[\text{MgO}]$ are the concentrations of Cd, CaO, and MgO in the carbonate rock; and M_{C} , M_{Cd} , M_{CaO} , and M_{MgO} refer to the molar weights of C, Cd, CaO, and MgO, respectively.

4. Results and discussion

4.1. Migration of Cd during soil formation and erosion

The mass transfer coefficients of Cd in the eluvium of Profile S1 were all below 0 and tended to -1 (Fig. S3). This indicates that Cd is strongly leached and transported during the weathering of carbonate rocks. The major elements present in carbonate rocks (Ca and Mg) have higher leaching degrees than Cd, resulting in the relative accumulation of Cd in soils compared with the bedrocks (Alamgir, 2016; Niesiobedzka, 2012; Song et al., 2019). This was confirmed by the fact that Cd concentrations were significantly higher in the eluvium (0.278–0.448 mg/kg) than in the bedrock (0.174 mg/kg). The mass migration coefficients of Cd increased from top to bottom of the profile (Fig. S3), indicating that Cd has a significant vertical migration in the weathering profile. Variational chemical fields (e.g., increasing soil pH values) cause the precipitation and fixation of Cd at the bottom of the profile (Luo et al., 2018; Sun et al., 2019).

Soil erosion is an important mode of element migration in nature that results in enormous perturbations to the terrestrial element cycle (Liu et al., 2019). The alluvium in Profile S1 was formed by the accumulation of soil eroded from the eluvium. However, the Cd concentration was significantly higher in the alluvium (0.675 mg/kg) than in the eluvium (0.287–0.448 mg/kg, average value, 0.343 mg/kg; Table S2). This indicates that the migration of Cd during soil erosion can alter the spatial distribution pattern of soil Cd concentrations and pose potential risks to the environment in karst areas, which is consistent with the results of Xia et al. (2020).

We investigated particle size distribution characteristics of soil samples in Profile S1 (Fig. S4). The particle size of alluvium (0.23–78.26 μm , median = 10.24 μm) was significantly smaller than that of eluvium (0.23–244.70 μm , median = 14.61 μm), (Table S3), suggesting that the study profile shows obvious grain size differentiation during soil erosion. This corroborates the previously reported conclusion that the fine components of soil are more likely to be eroded and transported by surface running water (Lu et al., 2016; Nie et al., 2014; Wang et al., 2014; Zheng

et al., 2016). Therefore, inactive Cd occurring in clay mineral lattices or strongly adsorbed on the mineral surfaces (usually not involved in ion exchange) is prone to mechanical migration with fine soil particles. Contrary to previous findings indicating higher heavy metal concentrations in fine-grained soils and sediments than in coarse-grained soils (Acosta et al., 2011; Huang et al., 2017; Li et al., 2021; Qin et al., 2014; Quenea et al., 2009), this experiment yielded contrasting results. Specifically, the Cd concentration in the fine soil component of profile S1 was generally lower than that in the coarse component (Fig. 2 and Table S4). Consequently, the mechanical migration of inactive Cd is not the principal factor for increasing the soil Cd concentration in alluvium in the study area.

Morphological analysis of soil Cd showed that the acid-extractable and reducible forms of soil Cd increased in the alluvium compared with the eluvium (Fig. 3), in agreement with the results of Xia et al. (2020). Acid-extractable and reducible Cd occur primarily in carbonate and Fe/Mn hydroxides minerals (Rao et al., 2008), which are typical secondary minerals in soils. Therefore, besides the inactive Cd resulting from soil erosion in the eluvium, the alluvium likely received active Cd through the migration of weathering fluids. The active Cd likely co-precipitated with secondary carbonate and Fe/Mn hydroxides minerals, which is confirmed by the higher pH values and concentrations of Ca, Mg and Fe in the alluvium compared with the eluvium (Table S2). Furthermore, the alkaline soil environment is conducive to the accumulation and enrichment of Cd (Alamgir, 2016; Liu et al., 2017b; Mlangeni et al., 2022; Rambeau et al., 2010; Song et al.,

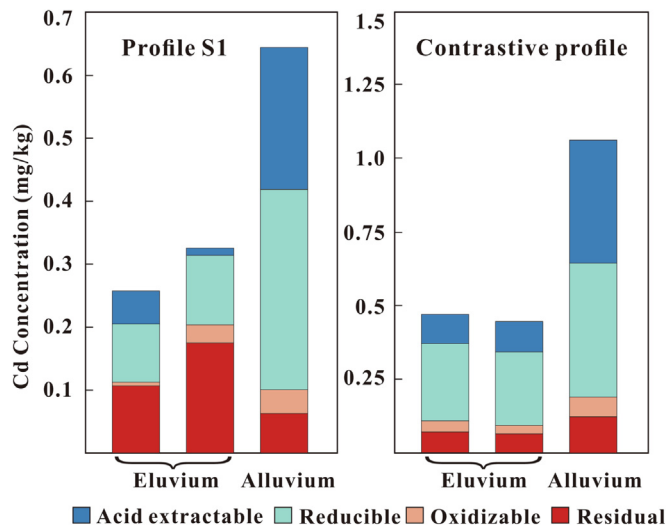


Fig. 3. Concentration distributions of soil Cd of various fractions in the eluvium and alluvium by BCR sequential extraction. The data of the contrastive profile are cited from Xia et al. (2022).

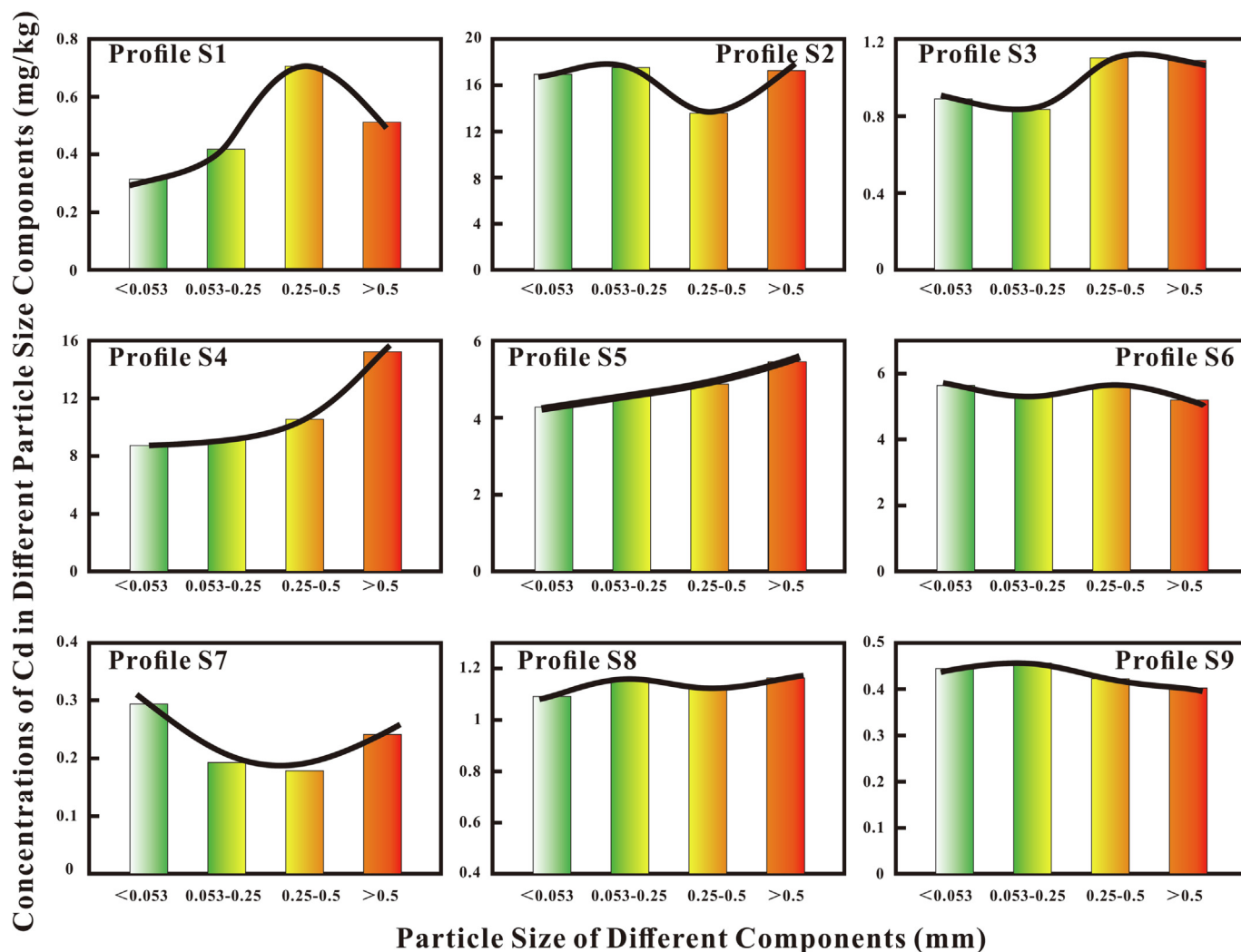


Fig. 2. Relationships between soil particle sizes and Cd concentrations in residual soil samples collected from 9 sampling sites in Cambrian strata (Profiles S7, S8, and S9), Carboniferous strata (Profiles S1, S4, and S5), and Permian strata (Profiles S2, S3, and S6).

2019). As such, the Cd migration in karst areas, involves both the mechanical migration of inactive Cd and chemical migration of active Cd. The latter is likely to be the crucial factor contributing to the elevation of Cd concentration and its bioavailability in the alluvium.

4.2. Source apportionment by Cd isotopes

Current research suggests that the chemical migration of active Cd in karst areas is an important cause of Cd exceeding the standards of soil and agricultural products in lowland alluvial areas (Li et al., 2018; Liu et al., 2017b; Xia et al., 2020). Hence, it is imperative to uncover the natural origin of active Cd to effectively mitigate potential ecological and environmental risks in karst areas. The high field strength elements Hf and Zr are commonly used to trace the material sources of soil and sediments owing to their geochemical inertness in supergene environments (Babechuk et al., 2015; Gong et al., 2010). The Hf and Zr concentrations in bedrock, eluvium, and alluvium samples exhibited a highly significant positive correlation ($R^2 = 0.996$; Fig. 4A), indicating clear inheritance and provenance characteristics. Consequently, the material source of soil in this profile is relatively straightforward, with minimal input from exogenous solid materials resulting from floods, atmospheric deposition, or mining activities. Hence, the Cd in the alluvium mainly originates from two end-members: active and inactive Cd (Fig. 4B). The isotopic composition of the inactive Cd endmember from the eluvium is $\delta^{114/110}\text{Cd} = -0.78\text{‰} \pm 0.06\text{‰}$, while the $\delta^{114/110}\text{Cd}$ value of mixed endmember in the alluvium is $-0.18\text{‰} \pm 0.01\text{‰}$ (Table S2), leading to the speculation that the isotopic composition of active Cd transported by weathering fluids should be heavy. Moreover, the Cd isotopic composition of weathered fluids must be at least heavier than that of the alluvium (i.e., $\delta^{114/110}\text{Cd}_{\text{fluid}} > -0.18\text{‰}$), as this is the only way to ensure that the isotopic composition of alluvium can reach the existing $\delta^{114/110}\text{Cd}$ values (Fig. 4B).

Excluding anthropogenic contributions, the remote sampling sites, free from nearby rivers, towns, mining areas, and smelting plants, suggest that the natural sources of active Cd are likely the soluble Cd released during the weathering of carbonate rocks and leaching of weathering crusts. Previous studies have demonstrated common Cd isotope fractionation in the weathering and leaching of rocks/minerals, resembling processes such as

precipitation (Horner et al., 2011), adsorption (Wasylenki et al., 2014; Yan et al., 2021), and crystallization (Yang et al., 2015) of minerals. Additionally, light Cd isotopes preferentially partition into the solid phase, whereas heavy Cd isotopes tend to remain in the liquid phase ($\Delta\delta^{114/110}\text{Cd}_{\text{fluid-solid}} = \delta^{114/110}\text{Cd}_{\text{fluid}} - \delta^{114/110}\text{Cd}_{\text{solid}} = 0.36\text{--}0.53\text{‰}$; Zhang et al., 2016; Zhu et al., 2018). Assuming that Cd isotope fractionation occurs in the leaching process of the eluvial soil, and according to the isotopic fractionation results of previous studies (Zhang et al., 2016; Zhu et al., 2018), the isotopic composition of leaching fluid from eluvium ranges from -0.42‰ to -0.25‰ . However, the active Cd from this source is too light to achieve the current $\delta^{114/110}\text{Cd}$ isotopic composition of the alluvium (Fig. 4B). We simulated the chemical corrosion of carbonate rocks using an acid-insoluble matter extraction test and showed that the $\delta^{114/110}\text{Cd}$ value of acid insoluble matter was $-0.05\text{‰} \pm 0.07\text{‰}$ (Table S2). Based on the isotopic fractionation results of previous studies, the estimated $\delta^{114/110}\text{Cd}$ value of weathering fluid of bedrock in the study profile should be between 0.31‰ and 0.48‰ (Fig. 4B). Obviously, the $\delta^{114/110}\text{Cd}$ value is more consistent with the actual situation. Therefore, the active Cd in the alluvium of the studied profile likely originated from the corrosion of carbonate rocks rather than the leaching of eluvium.

4.3. CWRFCd in karst regions and its potential risks

The rock survey results in the study area indicated that the mass percentage of Cd in the acid-soluble mineral components of carbonate rocks ranges from 28.37 % to 98.94 %, with a mean value of 74.12 % (Fig. 5). Cd was more likely to occur in acid-soluble components in Carboniferous and Permian carbonate rocks. We estimated that carbonate rocks corrosion (Eqs. (5) and (6)) has significant potential to release active Cd, posing ecological risks. By considering the stoichiometric relationship between carbon sink and Cd release, we estimated a global mean CWRFCd (carbonate weathering Cd release flux) of $5.28\text{ g Cd km}^{-2}\text{ yr}^{-1}$.

The total annual global amount of anthropogenic Cd emitted into the environment in the form of waste gas, wastewater, and solid waste is $28,200\text{ t yr}^{-1}$ (Jackson and Macgillivray, 1995). Most of the emitted Cd (approximately 70 %, $19,740\text{ t yr}^{-1}$) ends up in controlled areas, and the remaining 30 % anthropogenic Cd (approximately 8460 t yr^{-1}) is

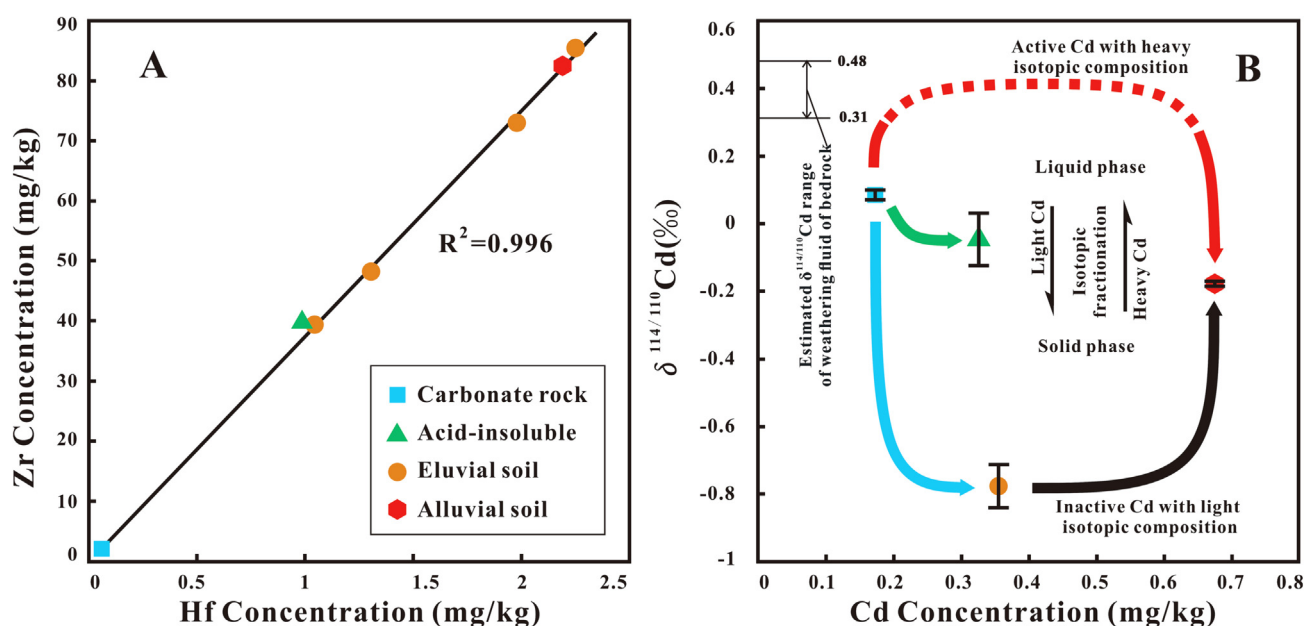


Fig. 4. (A) Distribution of Hf vs. Zr in bulk samples of eluvium, alluvium, and bedrock. The significant positive correlation is shown in the plot. (B) $\delta^{114/110}\text{Cd}$ vs. Cd concentration diagram of bulk samples from eluvium, alluvium, bedrock, and acid insoluble matter. The green arrow refers to the acid insoluble extraction test of carbonate rocks, blue arrow represents the weathering and pedogenesis process of carbonate rocks, black arrow is the soil erosion process, and red arrow indicates the chemical corrosion process of carbonate rocks. Soil erosion of the eluvium provides the alluvium with inactive Cd composed of relatively light isotopes, whereas the chemical corrosion of bed rock provides the active Cd with heavy isotopic composition.

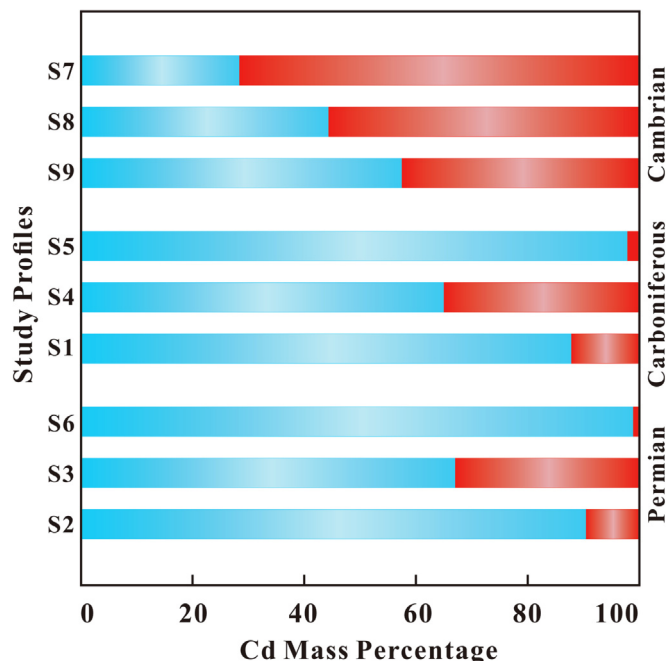


Fig. 5. Mass percentages of Cd in different mineral components of bedrocks in the study profiles exhibiting the occurrence characteristics of Cd in carbonate rocks. The blue and red blocks represent the acid soluble and acid insoluble mineral components in carbonate rocks, respectively.

uncontrollably released into the environment. Given that anthropogenic Cd discharge regions mainly focus on the continent (the global continental area is $149 \times 10^6 \text{ km}^2$), we obtained a total mean anthropogenic Cd emission flux of $56.78 \text{ g Cd km}^{-2} \text{ yr}^{-1}$. Therefore, the CWRFCd accounts for 9.30 % of the anthropogenic Cd emission flux. However, the CWRFCd is likely to be underestimated, as this study did not consider some special karst areas. For example, the maximum Cd concentration in the Jurassic limestone of Switzerland and France is 21.4 mg/kg (Efimenko et al., 2008), 2–3 orders of magnitude higher than that in common carbonate rocks (Chi and Yan, 2007).

The mechanical migration of inactive Cd during soil erosion did not result in obvious spatial distribution variations in regional soil Cd concentrations (Fig. 6). Part of the active Cd released by chemical corrosion of carbonate rocks is precipitated and enriched with secondary carbonate minerals and Fe/Mn oxides, thereby increasing the total concentration and bioavailability of soil Cd in the lowland catchment area. The remaining active Cd enters the supergene geochemical cycle with surface and subsurface runoff that may cause non-point source pollution of soil Cd and groundwater pollution over a larger range (Fig. 6). Additionally, the significant CWRFCd ($5.28 \text{ g Cd km}^{-2} \text{ yr}^{-1}$) has achieved 9.30 % of the anthropogenic Cd emission flux. Therefore, the chemical corrosion of carbonate rocks, as a significant natural source of Cd, has been overlooked for a considerable period, thereby presenting a substantial potential risk to the ecological environment in karst areas. Finally, we suggest in-depth studies to determine the migration mechanism and accurate levels of Cd release rate during the weathering of carbonate rocks and soil erosion. Additionally, ecological monitoring and scientific prevention of rocky karst desertification, soil erosion, acid rain, and soil acidification should be strengthened in karst areas.

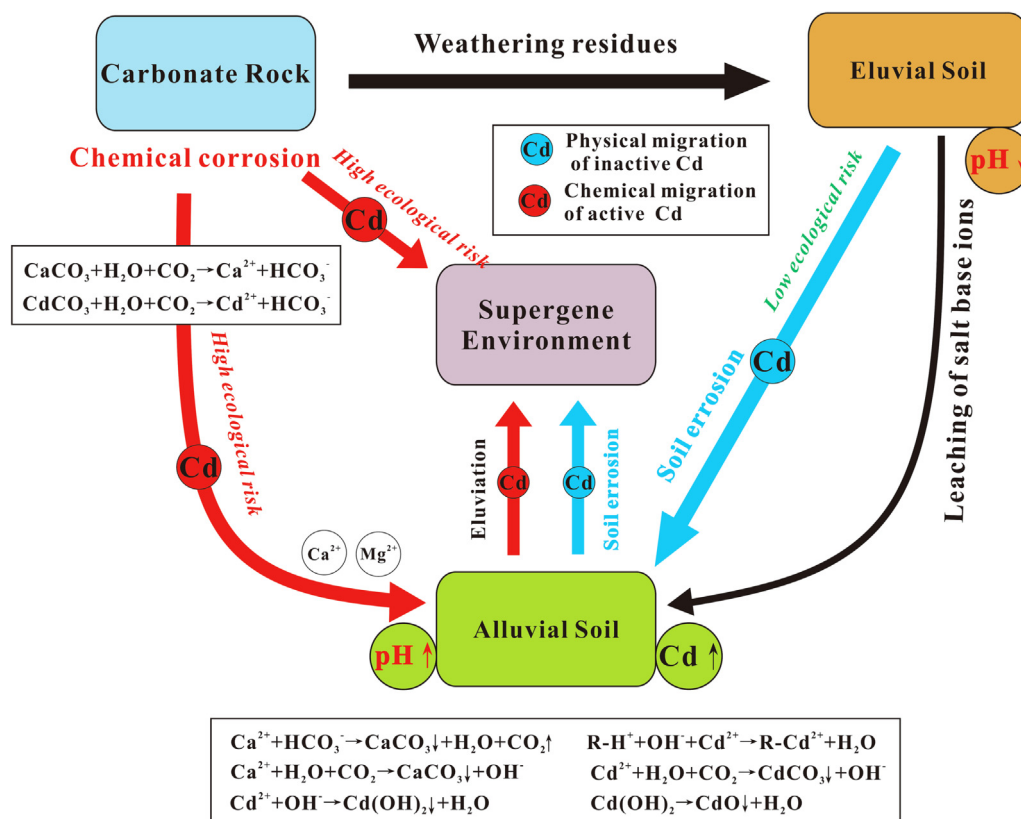


Fig. 6. Migration models and ecological risks of Cd during carbonate chemical corrosion and soil erosion in a karst supergene environment. The red and blue arrows indicate chemical corrosion of carbonate rocks, and soil erosion, respectively. The red and blue circles represent the chemical and physical migration of Cd, respectively. R-Cd^{2+} refers to the fixation of active Cd by adsorption of clay minerals, chelation of organic matter, and precipitation of iron/manganese oxides.

5. Conclusions

We identified the main factors causing the spatial redistribution of soil Cd in karst areas and proposed a new understanding of the ecological risk of Cd caused by the chemical corrosion of carbonate rocks based on the investigation and analysis of the geochemical characteristics, soil particle size, and Cd isotopic compositions of rock and soil samples from typical carbonate weathering profiles in southern Guizhou Province, China. The specific conclusions are as follows:

- (1) The chemical migration of active Cd plays a critical role in contributing to the elevation of Cd concentration and its bioavailability in the alluvium during soil erosion in karst areas. It is the main driving force for the spatial redistribution of Cd concentration in soil rather than the mechanical migration of inactive Cd.
- (2) The mass percentage of Cd in soluble mineral components of carbonate rocks in the study area ranged from 28.37 % to 98.94 %, averaging 74.12 %. This indicates that the chemical corrosion of carbonate rocks has a high potential to release active Cd. In addition, the isotopic data show that the active Cd in the alluvium of the study profile was probably derived from the chemical corrosion of carbonate rocks rather than the leaching of the eluvium.
- (3) The global mean CWRFC_d is estimated to be 5.28 g Cd km⁻² yr⁻¹, equivalent to 9.30 % of the Cd flux from human activities. This highlights the importance of carbonate weathering and corrosion as substantial sources of Cd in karst areas, posing significant threats to the ecological environment and food security. Therefore, we recommend conducting research, surveillance, and preventive measures to mitigate the risk associated with Cd release during the weathering of carbonate rocks.

CRediT authorship contribution statement

Xiao Wei: Conceptualization, Investigation, Methodology, Writing—original draft, Formal analysis. **Xiaoyong Bai**: Writing—review and editing, Supervision, Project administration, Funding acquisition. **Xuefeng Wen**: Validation, Investigation. **Li Liu**: Investigation, Data curation. **Jie Xiong**: Investigation, Validation. **Changlong Yang**: investigation. All authors have read and agreed to the published version of the manuscript.

Data availability

Data will be made available on request.

Declaration of competing 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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2023.165126>.

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