



## Redistribution and isotope fractionation of endogenous Cd in soil profiles with geogenic Cd enrichment

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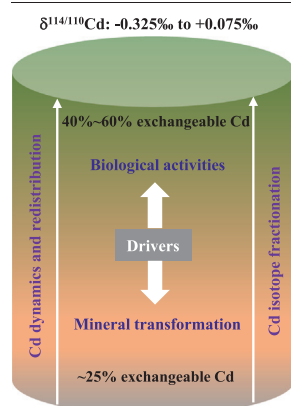
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### HIGHLIGHTS

- Soil erosion and deposition influence vertical Cd distribution in soil from valley.
- Mobility of Cd in profiles tends to increase from bottom toward surface.
- Distinct Cd isotopes were observed in soil developed on different parent materials.
- Biological activities result in Cd isotope fractionation in the upper layers of profile.

### GRAPHICAL ABSTRACT



Soil profiles with geogenic Cd enrichment

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### ABSTRACT

The concentration and speciation of endogenous cadmium (Cd) in soil systems derived from parent materials is continuously altered by rock-soil-plant interactions. Previous studies on the distribution of Cd primarily focused on surface soil at regional scale. However, it lacks a novel approach to provide a new perspective on dynamics and redistribution of Cd in soil profile. Therefore, this study tries to establish the linkage between isotope fractionation and environmental processes of Cd in soil profiles with geogenic Cd enrichment based on Cd isotopes. High Cd concentrations were observed in the profile from forest at accumulation zone and the one from farmland at ridge in a rural area, southwest China. Soil erosion and deposition substantially influence the vertical distribution of total Cd in soil from the accumulation zone. Accordingly, distinct Cd isotope compositions were observed in different layers ( $\delta^{114/110}\text{Cd}$ :  $-0.087\text{‰}$  to  $-0.066\text{‰}$  vs  $-0.325\text{‰}$  to  $-0.056\text{‰}$ ). Mineral transformation, pedogenesis and biological activities controlled the dynamics and redistribution of Cd. The mobility of Cd increased during weathering processes, with  $\sim 40\%$  to  $60\%$  of Cd residing in exchangeable fraction in the surface layers. Biological activity is a vital factor that drives Cd isotope fractionation in soil, resulting in depletion of heavy Cd isotopes in surface layers of the studied farmland profile. Contrasting fractionation effects were observed in profiles from forest and farmland due to the variance in soil-plant

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Cd cycling. Our study revealed the processes that control dynamics and redistribution of endogenous Cd in soil profiles, and proved that Cd isotope is a useful tool to investigate the bio-geochemical processes of Cd in soil systems.

## 1. Introduction

Cadmium (Cd) is one of the most toxic and mobile heavy metals in soils (Satarug et al., 2003; Kubier et al., 2019). Unfortunately, soil Cd pollution is a serious environmental issue in many regions of the world (Food and Agriculture Organization of the United Nations (FAO), 2018). The environmental geochemical processes of Cd in soil systems have attracted considerable attention. Many studies focused on Cd in soils from anthropogenic sources, such as metal mining and smelting (Wen et al., 2015; Zhao et al., 2021), e-waste recycling (Liu et al., 2021a), and fertilization (Bigalke et al., 2017). The geogenic enrichment of Cd in soils has also been widely reported (e.g., Lund et al., 1981; Wen et al., 2020; Yang et al., 2021; Liu et al., 2021b). For example, in southwestern China, >200,000 km<sup>2</sup> of area presents geogenic enrichment of Cd in soil (Xia et al., 2020). Understanding the bio-geochemistry of endogenous Cd in these soils is of great significance for risk control and land management.

Endogenous Cd, inherited and/or retained from parent materials, enters soil at the initial stage of soil formation (Liu et al., 2021b). Afterwards, Cd in these soils is continuously altered by natural turnover in rock-soil-plant systems (Kabala and Singh, 2001). Previous studies showed that the exchangeable fraction of Cd in soils increased with increasing weathering maturity, and topsoil presented a higher percentage of organic matter-bound Cd than subsoil (Wen et al., 2020; Quezada-Hinojosa et al., 2015). Topography was also demonstrated to be an important factor that influences Cd distribution in soils (Quezada-Hinojosa et al., 2015). Based on the comparison of soils from different topography, Xia et al. (2020) reported that soil derived from alluvium has a higher concentration and environmental availability of Cd than soil derived from upland eluvium. Our recent work found that average Cd concentration in residual soils was higher than alluvial soils (Liu et al., 2021b). However, most previous studies on environmental characteristics and behavior of endogenous Cd in soils focused on surface soils at regional scale. So far, little attention has been given to vertical scale, which precluded the understanding of redistribution of geogenic Cd. Additionally, the results of previous studies were primarily acquired via traditional approaches, such as elemental and mineralogical compositions, and sequential extraction. The application of novel tools may be helpful for providing new perspectives to understand environmental processes of Cd.

As an emerging geochemical tool, Cd isotopes have great potential in environmental tracing, not only for sources but also for environmental processes (Weiss et al., 2008; Wiederhold, 2015; Zhong et al., 2020). Because of the significant fractionation of Cd isotopes during smelting ( $\Delta^{114/110}\text{Cd}_{\text{fume-effluent}}$  up to 0.98 ‰, Shiel et al., 2010), Cd isotope fingerprint can be used for source tracing in surrounding soils of smelters. Previous studies showed that soils polluted by smelting dust showed a negative  $\delta^{114/110}\text{Cd}$ , while soils polluted by slag presented a heavier  $\delta^{114/110}\text{Cd}$  value (Cloquet et al., 2006; Gao et al., 2013; Chrastny et al., 2015; Wen et al., 2015; Yin et al., 2021). Based on Cd isotope signals of different endmembers and the understanding of processes that control Cd isotope fractionation (e.g., Wasylenki et al., 2014; Ratie et al., 2021; Xie et al., 2021; Yan et al., 2021), Cd isotopes also can be applied for tracing bio-geochemical cycling of Cd in soil systems. For example, Imseng et al. (2018) conducted a detailed investigation of Cd isotopes in soils and related environmental samples. Their study found that weathering of parent materials shifts Cd isotope compositions in bulk soil to lighter signals, and soil-plant cycling pumps heavy Cd isotopes from subsoil into topsoil, which provides valid information for the redistribution of Cd in their soils. Similarly, Cd isotopes could be a novel tool to investigate the environmental processes of endogenous Cd in soils with naturally elevated Cd concentrations.

In the present study, we proposed that the isotope compositions of Cd will respond to environmental processes (e.g., migration, enrichment and redistribution) of endogenous Cd in the soil profile if the anthropogenic input of Cd can be neglected. To test this hypothesis, the total concentration, speciation and isotope composition of Cd in two soil profiles with high geochemical background were investigated. In all, we expected to establish a linkage between Cd isotope fractionation and its environmental processes in the soil systems.

## 2. Materials and methods

### 2.1. Sample collection and preparation

Soil profiles were collected at Jianping area (109°55′–109°58′E, 31°01′–31°03′N), a rural area with a high geochemical background of Cd located in Wushan County, southwest China. The detailed geological and geographical background of this area has been described in our previous studies (Tang et al., 2009; Liu et al., 2013). Briefly, this area is a typical mountainous region with strata from the Silurian to Triassic period, mainly composed of carbonate rocks, carbonaceous mudstone and siltstone. The local climate features an average annual precipitation of 1052 mm and a mean temperature of 18 °C. Based on the spatial distribution of Cd reported in our previous investigation (Liu et al., 2013), two Cd-rich soil profiles developed on Permian carbonaceous siltstone were collected in April 2016. Profile 1 (depth of 120 cm, JPP1–1 to JPP1–12) was collected in a natural forest that located in an accumulation zone without obvious human disturbance, and it was dug to parent material (carbonaceous siltstone, JPP1–1). Profile 2 (depth of 60 cm, JPP3–1 to JPP3–6) was collected on a flat farmland located along a ridge. Subsamples from different layers were collected at an interval of 10 cm. Sample collection and pretreatment were conducted according to the procedures described in the Technical Specification for Soil Environmental Monitoring (HJ/T 166–2004). The soil samples were air dried and sieved into <2 mm grains, crushed by using an agate mortar into fine powder (< 0.075 mm, > 200 mesh) and then stored in plastic bags until further analysis.

### 2.2. Analysis of soil physical-chemical properties

The measurement of soil physical-chemical properties was based on the methods described in Bao (2000). Briefly, soil pH was measured with a calibrated pH electrode (PB-10 Sartorius, Germany) in a 1:2.5 soil/DI water suspension, and soil carbonate ( $\text{CaCO}_3$ ) was determined by the volumetric method. Soil organic carbon (SOC) was determined by an elemental analyzer (Elementar, Germany) at the State Key Laboratory of Environmental Geochemistry (SKLEG) as described in a previous study (Liu et al., 2022). The effective cation exchange capacity (CEC) was determined by the hexamminecobalt trichloride solution-spectrophotometric method suggested by the Chinese EPA (HJ 889–2017). The XRD data were collected at the Stanford Synchrotron Radiation Lightsource according to the method described in a previous study (Hayes et al., 2014).

### 2.3. Elemental analysis

Trace metals in soil samples were analyzed at the ALS Laboratory Group (Guangzhou, China). In brief, powdered samples were digested in mixed acid ( $\text{HCl} + \text{HNO}_3 + \text{HF} + \text{HClO}_4$ ) on a hotplate, and trace metals in the digestates were measured by ICP–MS. Certified references (GSS-3 and GSS-5) were used to verify the accuracy of the digestion method, and the recovery rates were between 90 % and 110 % for trace metals.

## 2.4. Single and sequential extraction

Unbuffered neutral salt solution was used to extract the mobile pool of Cd in the local soils (Ma et al., 2020). In brief, mobile Cd was extracted by 0.01 M CaCl<sub>2</sub> at a solid to solution ratio of 1:10 and then horizontally shaken for 2 h at room temperature. Then the suspensions were centrifuged at 5000 rpm for 10 min, filtered through 0.45 μm filter membranes, and acidified by HNO<sub>3</sub>. Cd concentration of the suspension was analyzed by ICP-MS (Agilent 7700 ×, USA) at SKLEG.

Sequential chemical extraction was applied to determine the speciation of Cd in soils. Based on the method suggested by Technical Specification for Soil Environmental Monitoring in China (HJ/T 166-2004), soil Cd was partitioned into 5 fractions: exchangeable fraction (F1, extracted by 1 mol/L MgCl<sub>2</sub> at pH = 7 for 1 h), carbonate fraction (F2, extracted by 1 mol/L NaAc at pH = 5 for 8 h), reducible fraction (F3, extracted by 0.04 mol/L NH<sub>2</sub>OH·HCl in acetic acid at 96 °C for 4 h), oxidizable fraction (F4, extracted by 30 % H<sub>2</sub>O<sub>2</sub> + HNO<sub>3</sub> at 85 °C for 5 h), and residual fraction (F5, digested by mixed acid solution). The average recovery of the approach for the samples was 91 ± 4.5 % for Cd.

## 2.5. Cd isotope measurement

The Cd stable isotopes were measured at the Isotope Geochemistry Laboratory of China University of Geosciences, Beijing. The detailed procedures of chemical purification and analytical protocols were described in Tan et al. (2020). Briefly, samples were digested by HNO<sub>3</sub> + HF at 185 ± 5 °C for 36–48 h in PTFE vials that were sealed in bombs and finally dissolved in 1 mL of 2 M HNO<sub>3</sub>. Chromatographic separation of Cd was conducted in a class 100 hood. The digested samples were mixed with a <sup>111</sup>Cd—<sup>113</sup>Cd double spike to achieve a ratio of sample/spike ratio ~ 2 before purification. The spiked samples were dissolved in 2 mL of 2 M HCl for anion column chromatography. The mini columns were packed with AGMP-1 M resin (100–200 mesh), cleaned with acids (HNO<sub>3</sub>, HCl-HF, HCl) and conditioned with 2 M HCl before sample loading. Gradually diluted HCl (2 M, 1 M, 0.3 M, 0.06 M, and 0.012 M) was added to remove the matrix and interfacial elements. Finally, 20 mL 0.0012 M HCl was added to elute Cd. The same column procedure was repeated to further purify Cd from residual Sn. After purification, Cd samples were dissolved in 2 % HNO<sub>3</sub> for isotope measurement.

The Cd isotopes were measured by a Neptune Plus multi-collector ICP-MS (MC-ICP-MS, Thermo Scientific, USA). Purified samples were introduced into plasma through an Aridus II desolvator equipped with an autosampler. Measurements were conducted in static mode using 9 Faraday cups for 3 blocks. The NIST 3108 solution was bracketed every 3–5

samples. The Cd isotope values were reported as δ<sup>114/110</sup>Cd relative to the NIST-3108 solution, which is calculated as:

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

The geological reference material (NIST 2711a) was processed together with the samples and yielded an average δ<sup>114/110</sup>Cd of 0.526 ± 0.017 ‰, which is consistent with a previous study (Tan et al., 2020; Gao et al., 2021).

## 3. Results

### 3.1. Soil properties

The dominated primary minerals in the studied soils were quartz, rutile, feldspar and mica (Table S1), similar to the primary minerals observed in soils of temperate regions underlain by black shale and carbonates where the soil was moderately developed (Ji et al., 2004; Ling et al., 2016). Secondary minerals such as goethite were formed during weathering. Dolomite was only observed in the 70–80 cm layer of profile 1. Clay minerals in soils were composed of montmorillonite and illite, with vermiculite in some layers. These clay minerals may originate from the weathering of mica and feldspar (Weil and Brady, 2017).

Soil profiles are acidic with pH values ranging from 4.75 to 6.73 (Fig. 1). Soil pH increased toward the bottom, particularly for profile 2, in which pH in the 0–20 cm layer was significantly lower than that in the 30–60 cm layer. However, pH in the upper layers of profile 1 was slightly higher than that in deeper layers. The concentration of CaCO<sub>3</sub> in soil profiles ranged from 4.83 % to 8.38 %. Furthermore, the concentration of CaCO<sub>3</sub> changed in a narrow range in profile 1 and decreased toward the surface in profile 2. Soil organic carbon (SOC) in profiles ranged between 0.72 % and 2.10 %, and it gradually increased with decreasing depth, with higher SOC in surface soil than deep soil. ECEC varied between 5.67 and 13.61 cmol/kg and gradually increased from the bottom to surface in profile 1, but showed no obvious trend in profile 2.

### 3.2. Vertical distribution of Cd in soil profiles

Cadmium concentrations (Cd<sub>Tot</sub>) in both soil profiles ranged from 0.63 mg/kg to 36.8 mg/kg (Table S1, Fig. 2a), comparable to the reported Cd concentrations in soils covering the study area (0.12–42 mg/kg; Liu et al., 2013). However, Cd<sub>Tot</sub> was much higher than the average of surface soil in Chongqing (0.293 mg/kg, Hou et al., 2020) and the background value of Chinese soil (0.097 mg/kg, Wei et al., 1991). In profile 1,

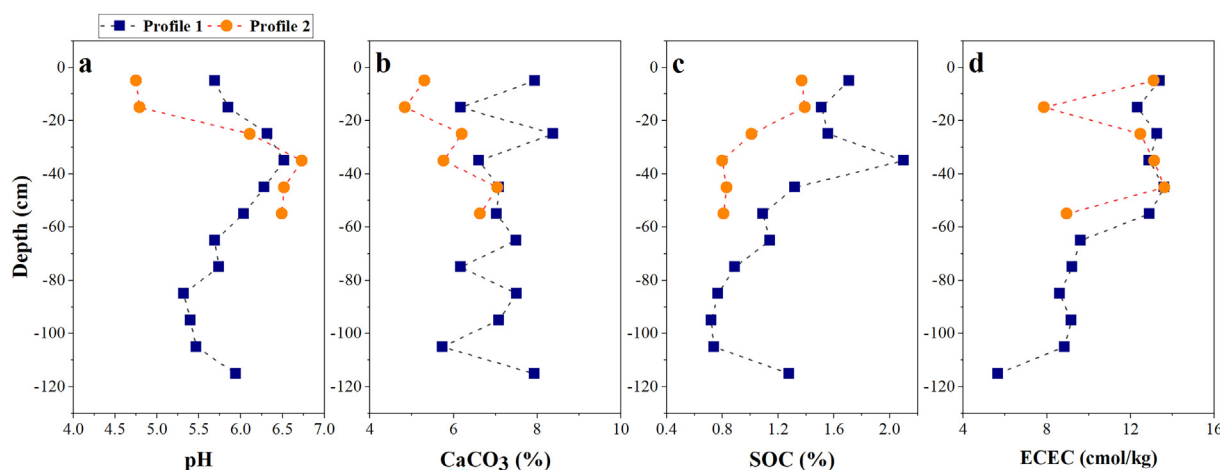


Fig. 1. Vertical distribution of soil parameters (a: pH; b: CaCO<sub>3</sub>; c: SOC; d: ECEC) in soil profiles.

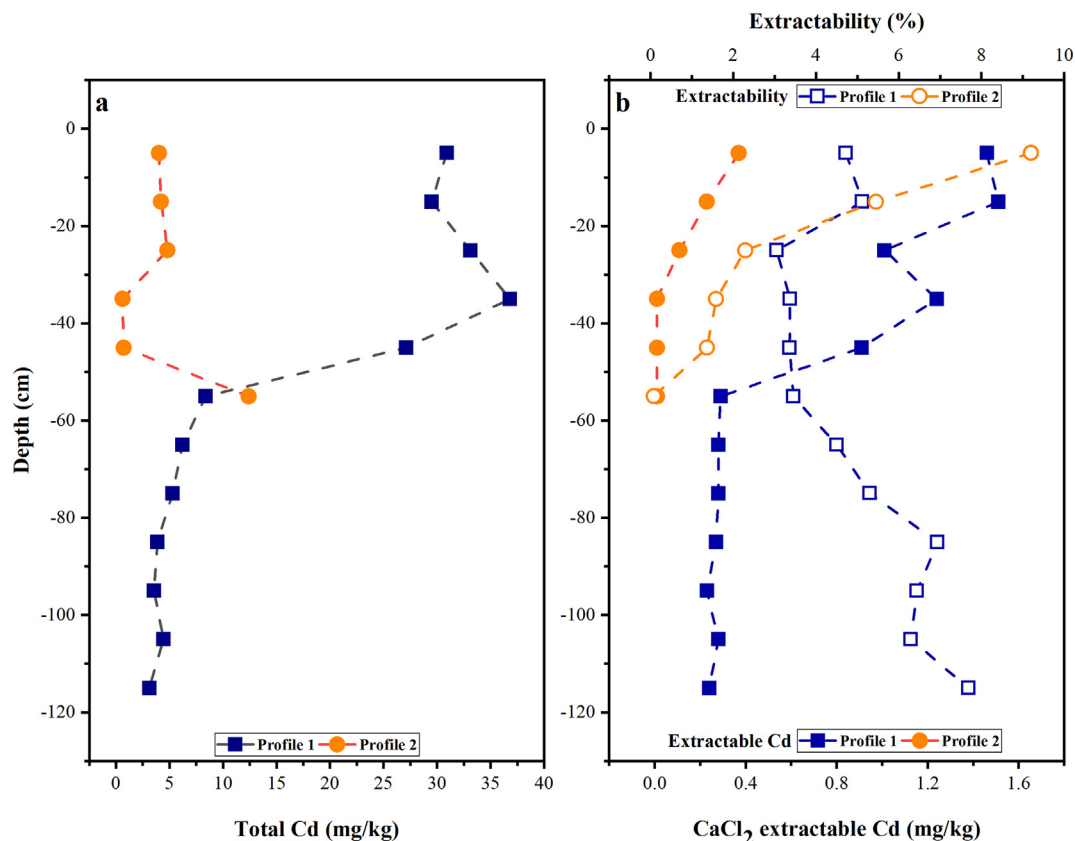


Fig. 2. Vertical distribution of total Cd (a), the concentration (filled symbol) and extractability (open symbol) of 0.01 M  $\text{CaCl}_2$  extractable Cd (b) in the soil profiles.

$\text{Cd}_{\text{Tot}}$  continuously increased toward the surface. Two distinct ranges of Cd were observed, with higher  $\text{Cd}_{\text{Tot}}$  in the upper layers (0–50 cm, 12.4–36.8 mg/kg, average of 28.3 mg/kg) than in the deeper layers (50–120 cm, 3.12–8.39 mg/kg, average of 4.99 mg/kg). In profile 2, the variation in  $\text{Cd}_{\text{Tot}}$  in different layers was small, with upper layers (0–30 cm) sharing very close values and the deepest layer having the highest Cd.

The  $\text{CaCl}_2$  extractable Cd ( $\text{Cd}_{\text{Ext}}$ ) ranged from 0.23 mg/kg to 1.51 mg/kg in profile 1 and from 0.01 to 0.23 mg/kg in profile 2 (Table S1, Fig. 2b). In profile 1, the upper layers presented much higher  $\text{Cd}_{\text{Ext}}$  than the deeper layers, similar to the distribution of  $\text{Cd}_{\text{Tot}}$ . In profile 2,  $\text{Cd}_{\text{Ext}}$  was constant from 60 cm to 40 cm and then gradually increased toward surface. However, extractability displayed a different trend when compared to  $\text{Cd}_{\text{Ext}}$  and  $\text{Cd}_{\text{Tot}}$ . Extractability gradually increased from 60 cm to 10 cm in profile 2, whereas it gradually decreased from 120 cm to 60 cm and then remained constant until 20 cm in profile 1. Extractability of Cd was negatively correlated with soil pH ( $r^2 = 0.737$ ).

### 3.3. Cd isotope compositions in soil profiles

Significant fractionation of Cd isotope composition was observed in these soils, with  $\delta^{114/110}\text{Cd}$  ranging from  $-0.325$  ‰ to  $0.075$  ‰, and most of samples presented negative  $\delta^{114/110}\text{Cd}$  (Table S1 and Fig. 3). In profile 1, a constant  $\delta^{114/110}\text{Cd}$  ( $-0.087$  ‰ to  $-0.056$  ‰) in the 0–50 cm layers and a lower  $\delta^{114/110}\text{Cd}$  ( $-0.325$  ‰ to  $-0.224$  ‰) in the deeper layers (50 to 120 cm) were observed. In profile 2,  $\delta^{114/110}\text{Cd}$  first increased from  $-0.047$  ‰ to  $0.075$  ‰ and then decreased to  $-0.146$  ‰ with decreasing depth.

### 3.4. Speciation of Cd in soil profiles

To investigate the redistribution of Cd in soil profiles, a sequential chemical extraction was conducted. For profile 1, Cd in different layers was dominated by exchangeable fraction (39 % to 61 %), except for

JPP1–1 (parent materials), which was dominated by a carbonate fraction (38 %) (Table S2 and Fig. 4). Residual fraction continuously decreased from 110 cm to 40 cm and then remained constant at surface. Exchangeable fraction continuously increased from 120 cm to 50 cm, and then no obvious changes were observed from 50 cm to surface. Reducible and oxidizable fractions along the profiles were remained at  $\sim 14$  % and  $\sim 5$  %, respectively. For profile 2, exchangeable fraction also dominated except for the deepest layer, which was dominated by residual fraction. The 0–30 cm layers had similar geochemical speciation. However, for the 30–60 cm

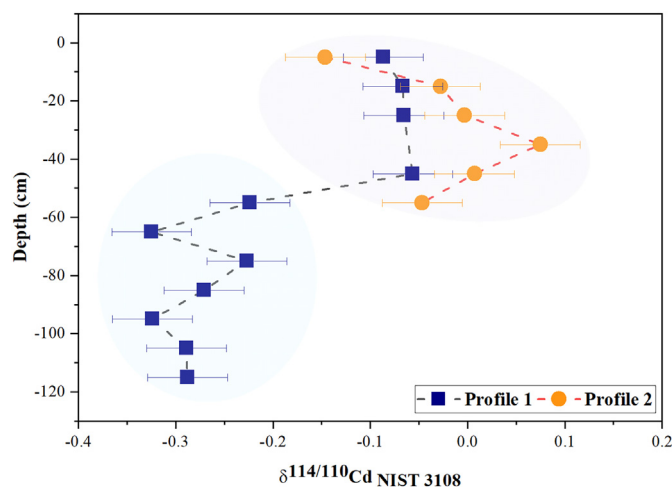


Fig. 3. Cadmium isotope compositions in different layers of profiles. Error bars represent 2SD uncertainties calculated from repeat measurements or the maximum 2SD uncertainties of the batch.



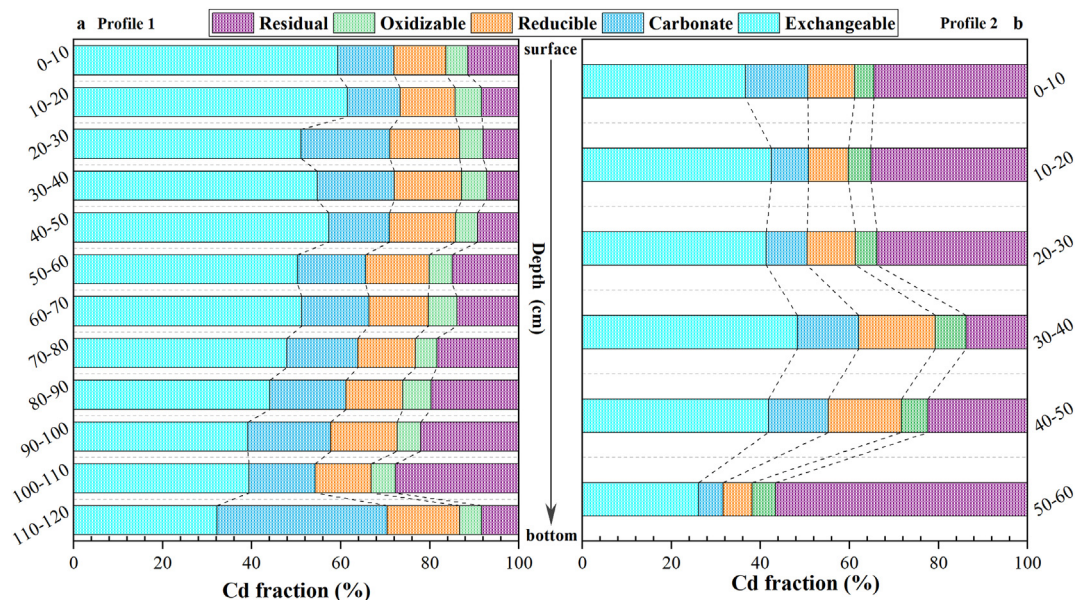


Fig. 4. Distribution of Cd speciation in the studied profiles (a: profile 1 from a forest at accumulation zone; b: profile 2 from a farmland at ridge).

layers, exchangeable and carbonate fractions increased with decreasing depth, while residual fraction having opposite trend.

#### 4. Discussion

##### 4.1. Dynamics and redistribution of Cd in soil profiles

##### 4.1.1. Dynamics of Cd

The study area is a rural area without industrial activities. High  $Cd_{Tot}$  (0.22–21 mg/kg) was observed in bedrocks of the study area, particularly in mudstone and siltstone (average of 4.6 mg/kg; Liu et al., 2013). The high geochemical background results in enrichment of Cd in local soils, with an average  $Cd_{Tot}$  of 2 mg/kg in natural soils (Liu et al., 2013). This is also supported by high  $Cd_{Tot}$  in deep soils and parent materials of the studied profiles (up to 12.4 mg/kg, Table S1). Dynamics of Cd in soil profiles are controlled by natural processes in rock–soil–plant systems (Kabala and Singh, 2001), if anthropogenic inputs are negligible. Weathering of parent rocks continually supplies geogenic Cd for soils, which maintains these soils with high concentrations of  $Cd_{Tot}$  as evidenced by high  $Cd_{Tot}$  in deep layers of our profiles (Fig. 2). Pedogenesis, such as eluviation and illuviation, usually induces downward movement of Cd

(Quezada-Hinojosa et al., 2015), which probably explains the enrichment of Cd at 30–40 cm in profile 1 due to high pH in this layer (Figs. 1, 2). For surface soil, biological activities may substantially influence dynamics of Cd through uptake and recycling of Cd, stimulating dissolution/desorption by root exudates (LeFevre et al., 2013; Imseng et al., 2018). Low pH and high SOC were observed in surface soils of the two profiles (Fig. 1), but  $Cd_{Tot}$  in the 0–30 cm layers is very close in profile 2 and only slightly changed in profile 1. Considering the counteracting effects of uptake and recycling, biological activities may not substantially alter total concentrations of Cd in soil profiles with such extremely high  $Cd_{Tot}$  (Table S1). Additionally, cultivation may mask the effects of biological activities, such as the uniform  $Cd_{Tot}$  in profile 2 that collected from farmland.

However, these processes could not explain the greatly distinct  $Cd_{Tot}$  observed in the upper (0–50 cm) and deeper (50–120 cm) layers of profile 1. Considering the mountainous topography of the study area and that profile 1 was collected from an accumulation zone, we speculate that soil erosion and deposition in mountainous regions (Quezada-Hinojosa et al., 2015; Song et al., 2019) may contribute to the great variance in  $Cd_{Tot}$ . Therefore, the relationships of Ta vs Nb and Zr/Hf vs Th/Sc, which can be used to distinguish material sources of soils (Peng et al., 2014; Song et al., 2019; Fang et al., 2019) were plotted in Fig. 5. The results showed

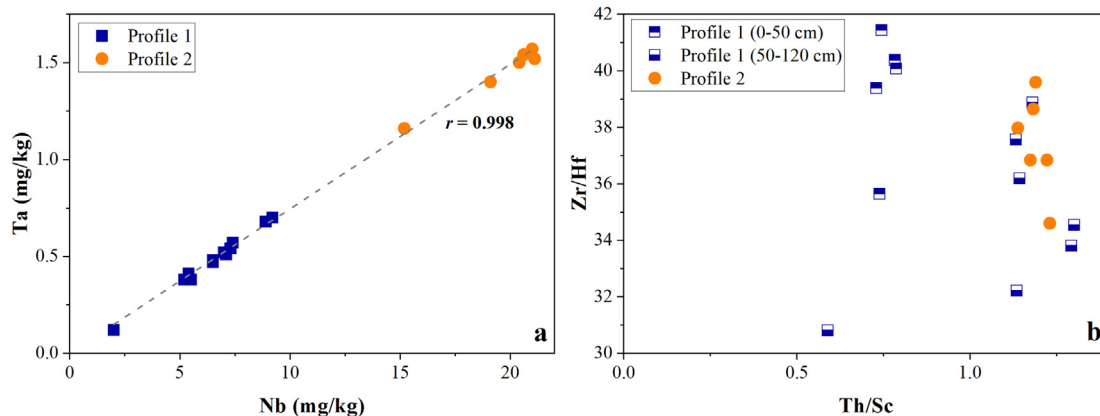


Fig. 5. Relationship between Ta vs Nb (a) and Zr/Hf vs Th/Sc (b) of soil profiles.

that concentrations of Ta in these soils were significantly correlated with Nb ( $r = 0.998$ , Fig. 5a), which may indicate that the parent materials of these soils are well-mixed sedimentary rocks. Relationship between Zr/Hf and Th/Sc (Fig. 5b) was further discussed to constrain the material sources. The upper layers (0–50 cm) and deeper layers (50–120 cm) of profile 1 presented significantly different Th/Sc and large variance in Zr/Hf, suggesting that this profile may be disturbed by materials from the upslope. The results were in contrast with profile 2, in which constant Th/Sc and small variation in Zr/Hf indicate the common origin of soils. These results indicated that regional soil erosion and deposition is most likely to be the key factor that contribute to the large variance in  $Cd_{Tot}$  of profile 1. Additionally, this may also explain the slightly higher pH and SOC (Fig. 1) in the upper layers (pH: 5.69–6.52; SOC: 1.32–2.10 %) than in the deep layers (pH: 5.32–6.04; SOC: 0.72–1.28 %).

#### 4.1.2. Redistribution of Cd

The dynamics of Cd in soil profiles are usually accompanied by redistribution among different phases, due to a series of reactions (e.g., dissolution-precipitation, adsorption-desorption, biological activities). Speciation results clearly showed the redistribution of Cd in the studied profiles (Fig. 4). In profile 1, exchangeable (32 %) and carbonate (38 %) fractions dominated in the deepest layer (JPP1–1, parent material) although no clay minerals and carbonates were detected by XRD (Fig. 4a). Carbonate fraction was dramatically decreased in overlying soils, suggesting dissolution of carbonate during weathering. Then Cd was mainly redistributed between F1 and F5, with exchangeable fraction increased from 39 % (100–110 cm) to ~60 % in surface soils (0–20 cm), while residual fraction decreased from 28 % to ~10 % in surface layers (Table S2, Fig. 4a). Similar results were also observed in the deeper layers of profile 2, in which Cd in F1 increased from 26 % (50–60 cm) to 48 % (30–40 cm) and Cd in F5 decreased from 57 % to 14 % (Fig. 4b). First, dissolution of primary minerals (e.g., carbonates and feldspar) and formation of secondary minerals, particularly Fe oxides and clay minerals that provide surface sites, may redistribute Cd into F1. For instance, transformation of minerals is most likely to shift the ECEC increases from 8.95 cmol/kg (50–60 cm) to ~13 cmol/kg (30–50 cm) in profile 2 because soil pH and SOC in these layers is uniform (Table S1). Second, biological activity is another important factor that may induce the redistribution of Cd. Solid organic matter can provide surface adsorption sites for Cd (Loganathan et al., 2012), which was evidenced by the positive relationship between  $Cd_{Tot}$  and SOC ( $r^2 = 0.782$ ), Cd and ECEC ( $r^2 = 0.675$ ) in profile 1. Additionally, acidification of surface soils resulting from decomposition of organic matter and acid exudates from roots may lead to dissolution of Cd in the F2. F3 only slightly changed in profile 1 but obviously changed in profile 2. Fe oxides are usually stable during oxidizing weathering and pedogenic processes (Jacquat et al., 2009; Richardson et al., 2022). Low Cd in F3 of the deepest layer in profile 2 is likely to be the result of reducing dissolution of Fe oxides because of the shallow groundwater level (~70–80 cm) of this site observed in field investigation. These results suggested that Cd is gradually redistributed into mobile fractions due to weathering of minerals and biological activities.

#### 4.2. Cd isotope fractionation in soil profiles

As an emerging geochemical tool, Cd isotopes present great potential to constrain the sources and biogeochemical processes of Cd in soil systems. The Cd isotope composition ( $\delta^{114/110}Cd$ ) of our samples was compared with published isotope data in typical rocks, native and polluted soils, and soils from different regions (Fig. 6). The parent materials (JPP1–1, carbonaceous siltstone) of profile 1 presented a  $\delta^{114/110}Cd$  of  $-0.288$  ‰, lower than the reported silicate rocks ( $-0.052$  ‰ to  $0.027$  ‰, Schmitt et al., 2009) and black shales ( $0.08$  ‰ to  $0.24$  ‰, Georgiev et al., 2015), but within the ranges of carbonates that vary in a wide range ( $-0.53$  ‰ to  $0.64$  ‰, Zhang et al., 2018). The  $\delta^{114/110}Cd$  of our soils varied over a wide range ( $-0.325$  ‰ to  $0.075$  ‰), which is lighter than the soils influenced by phosphate fertilizer and heavier than that polluted by smelting dust (Fig. 6). Similar result was also reported in a recent study,

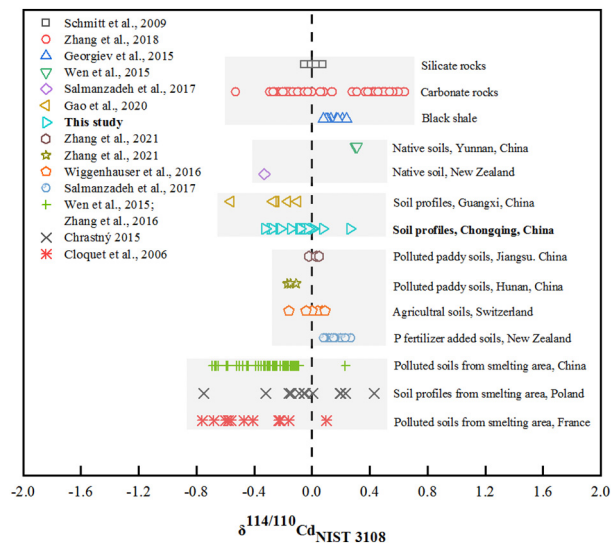


Fig. 6. Cadmium isotope compositions in different rocks, native and polluted soils and soil profiles. Data based on Cloquet et al. (2006), Schmitt et al. (2009), Chrastny et al. (2015), Georgiev et al. (2015), Wen et al. (2015), Wigganhauser et al. (2016), Zhang et al. (2016), Salmanzadeh et al. (2017), Zhang et al. (2018), Gao et al. (2020) and Zhang et al. (2021).

in which significant fractionation of Cd isotopes ( $\delta^{114/110}Cd$ :  $-0.562$  ‰ to  $-0.099$  ‰) was observed in soil profiles developed from carbonate in Guangxi, China (Fig. 6, Gao et al., 2021). As discussed above, Cd from anthropogenic sources can be neglected at our study sites (Liu et al., 2013). Thus, the fractionation of Cd isotopes ( $\Delta^{114/110}Cd = 0.400$  ‰) is most likely to be the result of bio-geochemical processes during weathering and soil formation and may also be influenced by soil erosion and deposition.

Regional soil erosion and deposition was regarded as the key factor that contributes to the large variance in  $Cd_{Tot}$  of profile 1 (Fig. 5). Similarly, contrasting isotope compositions in profile 1 (upper layers:  $-0.087$  ‰ to  $-0.056$  ‰; deeper layers:  $-0.325$  ‰ to  $-0.224$  ‰, Fig. 3) were also observed. The  $\delta^{114/110}Cd$  in the upper layers was close to a surface soil sample developed from carbonate in the study area ( $-0.082$  ‰, not shown in Table S1). These results indicated that soils derived from different parent materials may having distinct Cd isotope fingerprints (e.g., Zhang et al., 2016; Zhu et al., 2018; Imseng et al., 2019). For example, native soils derived from terrestrial clastic rocks in Yunnan Province of China ( $0.30$  ‰, Wen et al., 2015) and developed from greywacke loess in New Zealand ( $-0.31$  ‰, Salmanzadeh et al., 2017) show totally distinct isotope compositions. These results may suggest that the Cd isotope fingerprint can be a potential index to trace the regional physical migration of soil.

In deep layers with limited biological disturbance, subtle Cd isotope fractionation was observed in profile 1, i.e., Cd isotope composition was slightly increased toward surface (Fig. 3). This is inconsistent with a previous study that showed weathering shifted soil Cd isotope compositions to lighter values because of preferential leaching of isotopically heavy Cd (Imseng et al., 2018). This discrepancy may be related to the redistribution of Cd between different fractions induced by mineral transformation (Gao et al., 2022). Although lighter Cd isotopes are preferentially enriched in Fe (oxy)hydroxides ( $\Delta^{114/110}Cd_{solid-solution} \sim -0.50$  ‰; Yan et al., 2021) and Mn oxyhydroxide ( $\Delta^{114/110}Cd_{solid-solution} = -0.12$  ‰ at low ionic strength; Wasylenki et al., 2014) via adsorption, and in calcite via coprecipitation (Xie et al., 2021), the fractionation factors varied in a large range. However, this assumption needs to be addressed in the future due to the limited information of Cd isotopes in soil profiles and in different fractions of soils. Additionally, obvious Cd isotope fractionation was observed in profile 2, in which  $\delta^{114/110}Cd$  was first shifted to a heavier value and then to a lighter value toward surface (Fig. 3). Experimental and field studies have proven that leachate or solution tends to enrich in

heavier Cd (Imseng et al., 2018; Zhang et al., 2018), and plants cultivated in soils present a heavier Cd isotope composition than those in bulk soils (Wiggenhauser et al., 2016; Imseng et al., 2018; Zhou et al., 2020). Therefore, leaching of Cd out from soil and/or downward movement within profile will result in Cd isotopes being depleted in surface soils. On the other hand, continuous uptake of Cd in solution by food crops probably results in Cd isotope compositions in bulk agricultural soils being lighter (Fig. 3), and it may also extract heavier Cd from subsoil into topsoil (Imseng et al., 2018). A similar result was not observed in the surface layers of profile 1, which may be the result of soil–plant Cd cycling. Profile 1 was collected from a natural forest, in which litter from vegetation will return to soil and form soil–plant cycling of Cd. Thus, the Cd isotope compositions in these layers were very close. These results indicated that biological activities are key factors that influence Cd isotope fractionation in soils. However, this effect may differ in soils with different land–use types, such as the forest and farmland reported in this study, and further research is needed to verify it.

## 5. Conclusions

This study investigated the dynamics, redistribution and isotope fractionation of Cd in two soil profiles from a rural area with high geochemical background, southwest China. The Cd concentrations in the studied soil profiles are significantly higher than those in the local soil and Chinese background. Soil erosion and deposition substantially influenced the vertical distribution of total Cd in soils from the accumulation zone. Accordingly, distinct Cd isotope compositions in different layers ( $\delta^{114/110}\text{Cd}$ :  $-0.087\%$  to  $-0.066\%$  vs  $-0.325\%$  to  $-0.056\%$ ) were observed in different layers. Mineral transformation, pedogenesis and biological activities controlled the dynamics and redistribution of Cd in the studied profiles. Cd is primarily redistributed among exchangeable, carbonate and residual fractions. The mobility of Cd increased during weathering processes, with  $\sim 40\%$  to  $60\%$  residing in exchangeable fraction in the surface layers. Biological activity is a vital factor that drives Cd isotope fractionation in soils, resulting in depletion of heavy Cd isotopes in surface layers of the studied profiles. Contrasting fractionation effects were observed in soil profiles from forest and farmland due to the variance in soil–plant cycling of Cd. The results of this study highlighted that Cd isotopes could be a great tool to investigate the migration and biogeochemical cycling of Cd in soil systems.

## CRedit authorship contribution statement

**Yizhang Liu**: ideas, original draft, conceptualization; **Tangfu Xiao**: funding acquisition; review, supervision; **Jian-Ming Zhu**: methodology; **Ting Gao**: methodology, editing; **Yan Xiong**: field investigation, **Zhengjie Zhu**: field investigation; **Zengping Ning**: editing, methodology; **Chengshuai Liu**: review, editing, supervision.

## 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.2022.158447>.

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