



Geochemical factors controlling the mobilization of geogenic cadmium in soils developed on carbonate bedrocks in Southwest China

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ABSTRACT

Soils developed on carbonate bedrocks commonly contain high contents of geogenic cadmium (Cd). The bioavailability of Cd greatly varies among such soils and tends to be elevated in paddy soils compared to upland soils. However, the factors controlling the mobilization of geogenic Cd in paddy soils remain unclear. Therefore, this study aimed to reveal the processes and influencing factors of Cd mobilization in soils, by collecting upland soils and paddy soils from a carbonate region in Southwest China and analyzing the integrated soil properties and content, speciation and bioavailability of Cd. The results showed that the *in-situ* weathering of Cd-rich limestone (average of 0.66 mg/kg) resulted in the enrichment of Cd in overlying soils (4.75 to 13.2 mg/kg). Based on sequential extraction, ~43%, 18% and 17% of Cd in paddy soils was retained by Mn oxides, Fe oxides and the residual fraction, respectively. Hence, the transformation of Mn oxides drove the redistribution of Cd. In the upper layers, Cd released from Mn oxides was sequestered by soil organic matter and carbonate. Based on extraction using diethylene triamine pentaacetic acid (DTPA), paddy soils presented a higher Cd bioavailability (27%) than upland soils (18%). Furthermore, both the bioavailability and mobility of Cd gradually increased toward the surface in the profiles. The bioavailability of Cd was significantly correlated with the content of soil organic matter in these soils, indicating that soil organic matter was another crucial factor controlling Cd mobilization in paddy soils. The outcomes of this study provided new evidence for understanding the mobilization of Cd in soils and are helpful for developing pollution-control strategies to combat geogenic Cd in paddy soils in carbonate regions.

1. Introduction

The geogenic enrichment of cadmium (Cd) in soils developed on carbonate bedrocks, which account for 12% of the land area on the Earth, is a global environmental issue (Bellanca et al., 1996; Johnson et al., 1996; Quezada-Hinojosa et al., 2009; Temur et al., 2009; Rambeau et al., 2010; Yamasaki et al., 2013; Wen et al., 2020a; Xia et al., 2020; Yang et al., 2021c). This endogenous Cd depresses the environmental capacity of soils in carbonate regions and presents potential risks to crops (Quezada-Hinojosa et al., 2015a; Yang et al., 2021c). In Southwest China, ~70,000 km² of land has remarkably high Cd contents (>1.5 mg/kg), and ~90% of this Cd is related to carbonate rocks (Xia et al., 2022). The total Cd contents range from 0.068 to 16.91 mg/kg in carbonate

rock-derived paddy soils in Southwest China and even reach an average value of 8.59 mg/kg in certain areas (Yang et al., 2021a; Yang et al., 2021c). The enrichment of Cd in these paddy soils results in the accumulation of Cd in rice grains (Xia et al., 2020; Yang et al., 2021a; Yang et al., 2021c). As rice is the staple food for half of the world's population (Kögel-Knabner et al., 2010), Cd in paddy soils in carbonate regions deserves focused attention.

Paddy soils present higher Cd bioavailability than other soil types in carbonate regions. It has been reported that the average exchangeable Cd and 0.01 M CaCl₂-extractable Cd in paddy soils account for ~35% and ~9.6% of the total Cd, respectively, whereas the corresponding proportions were ~18% and ~0.1% in Cambisols, respectively (Wen et al., 2020a,b). Additionally, it is widely recognized that the Cd in

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pristine soils developed on carbonate rocks presents low mobility and availability at the early stage of weathering. For example, the exchangeable Cd was found to be negligible in limestone-derived soils from the Jura Mountains in Europe (Quezada-Hinojosa et al., 2009; 2015b). This geogenic Cd is prone to mobilization during the soil developing processes, as was demonstrated by the changes in Cd speciation observed in upland soil profiles (Bellanca et al., 1996; Quezada-Hinojosa et al., 2015b). However, the factors controlling the mobilization of geogenic Cd in paddy soils in carbonate regions remain unclear. In addition to the variance in pH, the Fe-Mn oxides that usually sequester large amounts of Cd in soils may play a key role considering the periodic redox fluctuations of paddy soils (Suda and Makino, 2016; Abgottsson et al., 2015; Wang et al., 2019).

Fe-Mn oxides are regarded as a crucial factor that control the fate of Cd in carbonate rock-derived soils (Bellanca et al., 1996; Quezada-Hinojosa et al., 2015b; Wen et al., 2020a; Yang et al., 2021a). For example, Bellanca et al. (1996) reported that ~50% of Cd resides in the Mn oxide-dominated reducible fraction in *terra rossa* soil in western Sicily. An investigation of soil profiles in the Jura Mountains showed that ~50% of Cd released from limestone was incorporated into Fe oxides (Quezada-Hinojosa et al. 2015b). Approximately 59% of Cd was found to reside in the reducible fraction in paddy soils sampled from a carbonate area in Southwest China (Yang et al., 2021a). However, redox oscillations, which commonly exist in redox-active soils such as rice paddies, may change the mineral phase and crystallinity of Fe-Mn oxides (Thompson et al., 2006; Vogelsang et al., 2016; Winkler et al., 2018). These changes can affect the speciation and mobility of the Cd sequestered by Fe-Mn oxides. Furthermore, the reductive dissolution of Fe-Mn oxides under anoxic conditions can release Cd into the soil solution (Tack et al., 2006; Weber et al., 2009; Abgottsson et al., 2015). Subsequently, this released Cd may be sequestered by other soil constituents, such as sulfides, organic matter, carbonates and clay minerals (Weber et al., 2009; Khaokaew et al., 2011; Gao et al., 2022), which alter the speciation and availability of Cd in paddy soils. However, it remains unclear whether and how Fe-Mn oxides influence the redistribution and mobilization of Cd in paddy soils developed on carbonate rocks.

In the present study, we hypothesized that the transformation of Fe-Mn oxides resulting from long-term redox fluctuations is a crucial factor controlling the mobilization of geogenic Cd in paddy soils. Therefore, surface soils and paddy soil profiles were collected from a rural area with a high geochemical Cd background in Southwest China. The soil properties, speciation and bioavailability of Cd were investigated to reveal the factors controlling the mobilization of Cd in paddy soils. The results of this study are expected to provide new perspectives for understanding the environmental behaviors of Cd in soil systems. This study also has

significance for the management of naturally occurring Cd-rich paddy soils in carbonate regions.

2. Materials and methods

2.1. Study area

The study area is located in northern Luodian County of Guizhou Province, Southwest China (Fig. 1). This region is a rural area without industrial or mining activities, and is a representative area with high geochemical background of Cd (Yang et al., 2021a, Xia et al., 2022). The land use types included upland soils and rice paddies. The geogenic unit in the study area is the Shangsi Formation of Carboniferous age, and the outcropping lithology is limestone (Yang et al., 2021a). The local climate belongs to the subtropical monsoon climate and features a mean annual precipitation of ~1335 mm and a mean temperature of ~20 °C.

2.2. Sample collection and preparation

In total, 10 bedrock samples, 37 surface soil samples (including 21 upland soil and 16 paddy soil samples) and 4 paddy soil profiles were collected from the study area. The sample collection and pretreatment processes were conducted according to the procedures described in the Technical Specification for Soil Environmental Monitoring (HJ/T 166-2004). The bedrock samples were collected at fresh outcrops along roadsides. Soil profiles were collected to study the changes in the speciation and bioavailability of Cd during soil developing processes. The profiles were dug to 60–80 cm depending on the sampling site. The soil samples were air dried and sieved to < 2 mm, crushed into fine powder (<0.075 mm) and then stored in plastic bags until further chemical analysis.

2.3. Analysis of soil physical–chemical properties

The soil physical–chemical properties were measured by methods detailed elsewhere (Bao, 2000). In brief, pH was measured by a calibrated pH electrode in a 1:2.5 soil/deionized water suspension. Soil carbonate (CaCO₃) was determined by the gas-volumetric method, and soil organic material (SOM) was measured by the Walkley-Black wet oxidation method. The effective cation exchange capacity (ECEC) was determined by the hexamminecobalt trichloride solution-spectrophotometric method suggested by the Chinese EPA (HJ 889-2017). Bulk mineralogy was determined by powder X-ray diffraction (XRD, Empyrean, Netherlands).

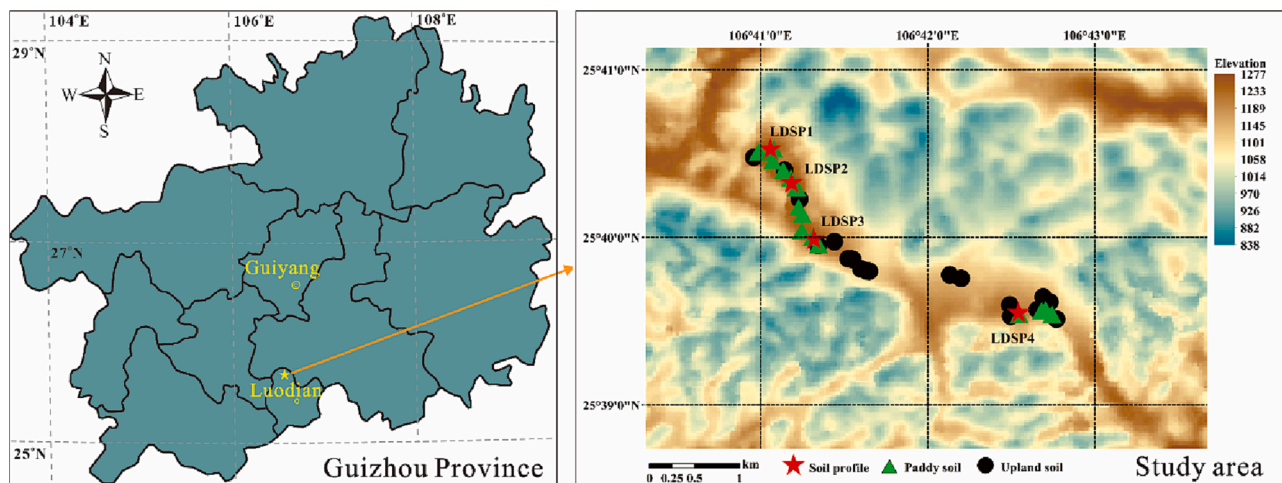


Fig. 1. Geographical location of the study area and soil sampling sites.

2.4. Elemental analysis

The major elements (SiO₂, Al₂O₃, Fe₂O₃, CaO, Na₂O, K₂O, MgO, P and Mn) in the bedrock samples were measured by X-ray fluorescence (XRF, Axios^{max}, Netherlands). For trace metals, approximately 30 mg powdered samples were digested in mixed acid (HNO₃ + HF + HClO₄) in an auto microwave digestion instrument (Auto Digiblock S60 UP) for 3.5 h. Trace metals in the digested solution were then measured by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700x, USA) in the State Key Laboratory of Environmental Geochemistry (SKLEG). Certified national reference material (GSS-5) was used to verify the accuracy of the digestion method, and the Cd recovery rates were between 90% and 110%.

The bedrock was treated with 1 mol/L HCl to remove carbonates and recover insoluble residues (Ji et al., 2004). Each insoluble residue was digested by the aforementioned method, and trace metals were measured by ICP-MS in SKLEG.

2.5. Chemical extraction

The bioavailable Cd in the soils was extracted by diethylene triamine pentaacetic acid (DTPA), which was designed for soils with a neutral pH according to the HJ/T 166-2004. In brief, ten grams of soil was extracted by 20 mL of DTPA solution (0.005 mol/L DTPA-0.01 mol/L CaCl₂-0.1 mol/L TEA) for 2 h at room temperature. After centrifugation and filtration, the Cd contents in the extracts were measured by ICP-MS. The bioavailability of Cd in soil was defined as the ratio of DTPA-extractable Cd to the total Cd contents in this study.

A slightly modified seven-step sequential chemical extraction method based on previous studies (Voegelin et al., 2008) was applied in this study to reveal the geochemical speciation of Cd in soils (Table 1). Cd and selected major elements (Ca, Fe and Mn) in the extracted solution were measured by ICP-MS and ICP-OES, respectively. A certified reference material for the speciation of trace metals in soils (GBW07445) was used to verify the extraction procedure. The Cd recovery rate of

Table 1
Sequential chemical extraction procedures applied in collected soils (modified from Voegelin et al., 2008).

Fraction	Extractant	Procedures	Targeted speciation
F1	1 mol/L NH ₄ NO ₃	Solid: solution = 1:25, T = 25 °C, t = 24 h	mobile fraction (water soluble, exchangeable, soluble metal-organic complexes)
F2	1 mol/L NH ₄ OAC (pH = 6.0)	Solid: solution = 1:25, T = 25 °C, t = 24 h	easily mobilizable fraction (specifically adsorbed, occluded near surfaces, CaCO ₃ -bound, weak metal-organic complexes)
F3	0.1 mol/L NH ₂ OH-HCl + 1 mol/L NH ₄ OAC (pH = 6.0)	Solid: solution = 1:25, T = 25 °C, t = 30 min	bound to Mn-oxides
F4	0.025 mol/L NH ₄ -EDTA (pH = 4.6)	Solid: solution = 1:25, T = 25 °C, t = 90 min	organically bound fraction
F5	0.2 mol/L (NH ₄) ₂ C ₂ O ₄ (pH = 3.25)	Solid: solution = 1:25, T = 25 °C, t = 2 h, dark	bound to weakly crystalline Fe-oxides
F6	0.1 mol/L ascorbic acid + 0.2 mol/L (NH ₄) ₂ C ₂ O ₄ (pH = 3.25)	Solid: solution = 1:25, T = 25 °C, t = 2 h, 96°C	bound to crystalline Fe-oxides
F7	HNO ₃ + HF + HClO ₄	Microwave assisted digestion	residual fraction

extraction was 99% to 111%.

2.6. Enrichment factor

The enrichment factor (EF) was used to reflect the degree of Cd enrichment in soils relative to the bedrock and was calculated according to the method of Reimann and de Caritat (2005):

$$EF = (C_{Cd}/C_{Al})_{soil}/(C_{Cd}/C_{Al})_{bedrock} \quad (1)$$

where C_{Cd} and C_{Al} are the total concentrations of Cd and Al in the soil samples and the average concentrations in bedrock, respectively. Al was selected as the reference element because of its terrestrial sources (Reimann and de Caritat, 2005).

2.7. Statistical analysis

The Pearson correlation coefficients were used to describe the linear correlation among different geochemical indices. The independent-samples T test was applied to compare the data between upland soil and paddy soil. Both methods were performed by IBM SPSS Statistics 23.0 (International Business Machines Corporation, USA).

3. Results

3.1. Cd in the bedrock

The geochemical composition of the bedrock was dominated by CaO (55.2%-58.9%) and LOI (41.1%-43.9%) (Table 2), consistent with the XRD results in which only calcite was detected (Fig. S1). The proportion of acid-insoluble residues in the bulk rocks was low (based on mass, ranging from 0.40 to 4.70 g/kg, with an average of 1.68 g/kg). These results suggested that the bedrock in the study area is pure limestone. The total Cd contents in the bulk bedrock ranged from 0.35 to 1.25 mg/kg, with an average value of 0.66 mg/kg. The total Cd in the insoluble residues ranged from 2.01 to 88.1 mg/kg, with an average value of 20.1 mg/kg. Approximately 86.5% to 99.5% of Cd (average of 96%) in the bedrock resided in acid-soluble carbonate minerals.

3.2. Soil properties

In the surface soils in the study area, the soil pH ranged from 5.79 to 7.59 (Table 3). The average pH values of the upland soils and the paddy soils were 6.62 and 6.97, respectively. The CaCO₃ contents in soils ranged from 0.81 to 56.8 g/kg. The lowest and highest CaCO₃ contents were both observed in the upland soils. The average values of CaCO₃ contents were similar between the paddy and upland soil groups. The ECEC value ranged from 2.61 to 31.8 cmol/kg, and the average value in the upland soils was slightly lower than that in the paddy soils. The SOM contents in the soil samples ranged from 24.5 to 73.6 g/kg, with an average value of 43.6 g/kg in the upland soils and 49.3 g/kg in the paddy soils. The physical-chemical properties of the soil profiles were within the established range for surface soils. The upper layers presented higher SOM contents and slightly lower pH values than the deeper layers, whereas no universal trend was observed for the ECEC value or CaCO₃ content along soil depth. As an exception, the 0–40 cm layer of LDSP3 presented a higher CaCO₃ content than the other profile samples.

3.3. Total and DTPA-extractable Cd in soils

The total Cd ranged from 4.75 to 13.2 mg/kg (average of 9.34 mg/kg) in the upland soils and from 6.00 to 12.3 mg/kg (average of 8.26 mg/kg) in the paddy soils. According to the soil environmental quality of China (GB15618-2018), the Cd contents in all collected soil samples exceeded the risk screening values and risk intervention values for soil contamination of agricultural land. Regarding the soil profiles, the Cd

Table 2

Major geochemical compositions and Cd concentrations of the bedrock samples in the study area, residue refers to the insoluble material in the treatment of 1 mol/L HCl.

Sample	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	MgO %	CaO %	Na ₂ O %	K ₂ O %	MnO %	P ₂ O ₅ %	TiO ₂ %	LOI %	Cd in bulk rocks mg/kg	mass of residues g/kg	Cd in residues mg/kg
LDP2008-4	0.01	0.03	0.05	0.22	55.8	0.22	0.02	0.013	0.007	0.014	43.9	0.47	0.72	88.1
LDP2010-6	0.43	0.04	0.04	0.22	55.4	0.13	0.02	0.013	0.006	0.010	43.6	0.35	1.80	8.64
LDP2011-4	0.21	0.11	0.01	0.38	55.2	0.18	0.07	0.012	0.008	0.009	43.7	1.25	4.70	2.01
LDP2013-5	0.01	0.01	0.03	0.22	58.4	0.16	0.03	0.013	0.007	0.000	41.1	0.59	1.50	12.0
LDP2016-5	1.56	0.01	0.04	0.23	58.9	0.16	0.03	0.015	0.003	0.005	43.7	0.76	1.20	3.31
LDP010	0.01	0.07	0.04	0.32	55.5	0.01	0.02	0.010	0.008	0.002	43.8	1.02	1.60	15.0
LDP016	0.01	0.04	0.05	0.26	55.7	0.14	0.03	0.014	0.004	0.008	43.8	0.36	2.80	4.69
LDP020	0.01	0.01	0.04	0.26	55.7	0.11	0.03	0.013	0.006	0.015	43.7	0.41	0.90	9.45
LDP024	0.08	0.06	0.04	0.21	55.6	0.24	0.03	0.013	0.011	0.003	43.7	0.59	1.20	21.2
LDP033	0.07	0.02	0.05	0.24	55.6	0.15	0.02	0.013	0.006	0.004	43.7	0.75	0.40	36.5
Average	0.24	0.04	0.04	0.26	56.2	0.15	0.03	0.013	0.007	0.007	43.5	0.66	1.68	20.1

Table 3

Major physical-chemical properties, contents of total and DTPA-extractable Cd, and extractability (ratio of DTPA-extractable Cd/total Cd) of the soil samples in the study area.

Sample	pH	ECEC cmol/kg	SOM g/kg	CaCO ₃ g/kg	Total Cd mg/kg	DTPA extractable Cd mg/kg	Extractability %
upland soil (n = 21)	Min	5.79	2.61	24.5	0.81	4.75	0.93
	Max	7.59	31.8	73.6	56.8	13.2	22.9
	Average	6.62	19.2	43.6	9.74	9.34	17.8
	S.D.	0.56	7.29	12.8	12.0	2.34	0.48
paddy soil (n = 16)	Min	6.09	13.1	36.4	2.89	6	17.4
	Max	7.55	28.2	58.2	26.4	12.3	36.9
	Average	6.97	22.4	49.3	8.4	8.26	26.9
	S.D.	0.44	3.96	6.93	5.92	1.77	0.75
LDSP1	0–20 cm	6.51	3.61	44.3	8.08	9.37	29.8
	20–25 cm	7.10	4.69	33.0	8.38	9.71	15.7
	25–35 cm	7.18	8.71	16.6	7.91	8.05	9.23
	35–45 cm	7.29	5.45	14.8	7.96	4.73	6.55
	45–55 cm	7.23	4.69	13.8	6.51	4.74	5.76
LDSP2	55–65 cm	7.19	4.36	24.6	7.37	5.45	8.99
	65–70 cm	7.44	2.52	9.74	7.62	6.87	3.89
	0–20 cm	7.14	3.25	43.1	12.5	8.02	23.2
	20–25 cm	7.39	11.2	36.3	17.4	7.72	18.9
	25–45 cm	7.17	2.52	18.3	13.9	6.40	3.80
LDSP3	45–60 cm	7.44	5.06	15.5	15.0	6.23	1.96
	0–20 cm	7.38	29.3	47.6	12.4	6.25	21.0
	20–40 cm	7.55	25.3	25.3	11.0	5.97	11.2
LDSP4	40–60 cm	7.14	5.44	22.8	9.02	6.25	6.40
	60–80 cm	7.15	5.44	25.9	9.80	5.79	6.29
	0–20 cm	7.06	2.18	38.8	10.8	7.56	23.5
	20–40 cm	7.25	5.81	25.8	10.2	7.76	12.2
LDSP4	40–60 cm	7.46	5.43	29.6	16.3	7.48	10.8
	60–80 cm	7.13	4.00	28.1	12.5	9.44	5.52

contents increased slightly with decreasing soil depth, and relatively higher Cd contents were observed in the upper layers of LDSP1 (Fig. 2a). The *EF* of Cd in soils relative the bedrock was as low as < 0.04, and the *EF* was higher in upper layers than the deeper layers (Fig. 2b).

The DTPA-extractable Cd in the upland soils ranged from 0.93 to 2.54 mg/kg, with an average of 1.65 mg/kg. These values were lower than those measured in the paddy soils (1.28–3.67 mg/kg, average of 2.25 mg/kg). The Cd extractability of DTPA in the upland soils ranged from 11.8% to 22.9% (average of 17.8%), which was significantly lower ($p < 0.01$) than that in the paddy soils (17.4%–36.9%, average of 26.9%). In the soil profiles, the Cd extractability of DTPA gradually increased toward the surface, and that in the upper layers was higher than that in the deeper layers (Table 3, Fig. 3).

3.4. Speciation of Cd, Fe and Mn in paddy soil profiles

Based on sequential extraction, the majority of Cd was bound to Mn oxides (F3), which ranged from 17.0% at 0–20 cm in LDSP3 to 64.2% at 65–75 cm in LDSP1 (Fig. 4). Fe oxides-associated Cd (F5 + F6) was also important in these soils, ranging from 12.0% to 28.0% (average of

16.5%), close to that in the residual fraction (F7). Mobile Cd (F1) was low except at 0–20 cm in LDSP1, where it accounted for 14.6%. Easily mobilizable Cd (F2) varied over a wide range of 2.88% to 43.0%. The other fractions varied in relatively narrower ranges. Regarding the vertical distribution of Cd speciation in these profiles, the easily mobilizable fraction gradually increased toward the surface, and was remarkably higher in the topsoil (~23.6%, 0–20 cm) than that in the subsoil (~8.44%, < 20 cm), while Cd bound to Mn oxides showed the opposite trend. Organically bound Cd (F4) was slightly higher in the upper layers than in the deeper layers except in LDSP3. The Fe oxides fractions (F5 + F6) were stable along the LDSP1, LDSP3 and LDSP4 profiles but were lower in the upper layers than in the deeper layers of LDSP2.

The sequential extraction procedure applied in this study targeted Mn oxides in F3, weakly crystalline Fe oxides in F5 and crystalline Fe oxides in F6. The three major pools of Fe descended in the following order: residual fraction (F7: 35.9%–61.6%, average of 53.3%) > crystalline Fe oxides (F6: 32.9%–56.2%, average of 40.8%) > weakly crystalline Fe oxides (F5: 2.78%–6.63%, average of 4.2%) (Fig. 5). The majority of Mn was extracted in F3, ranging from 43.0% to 84.3%, with

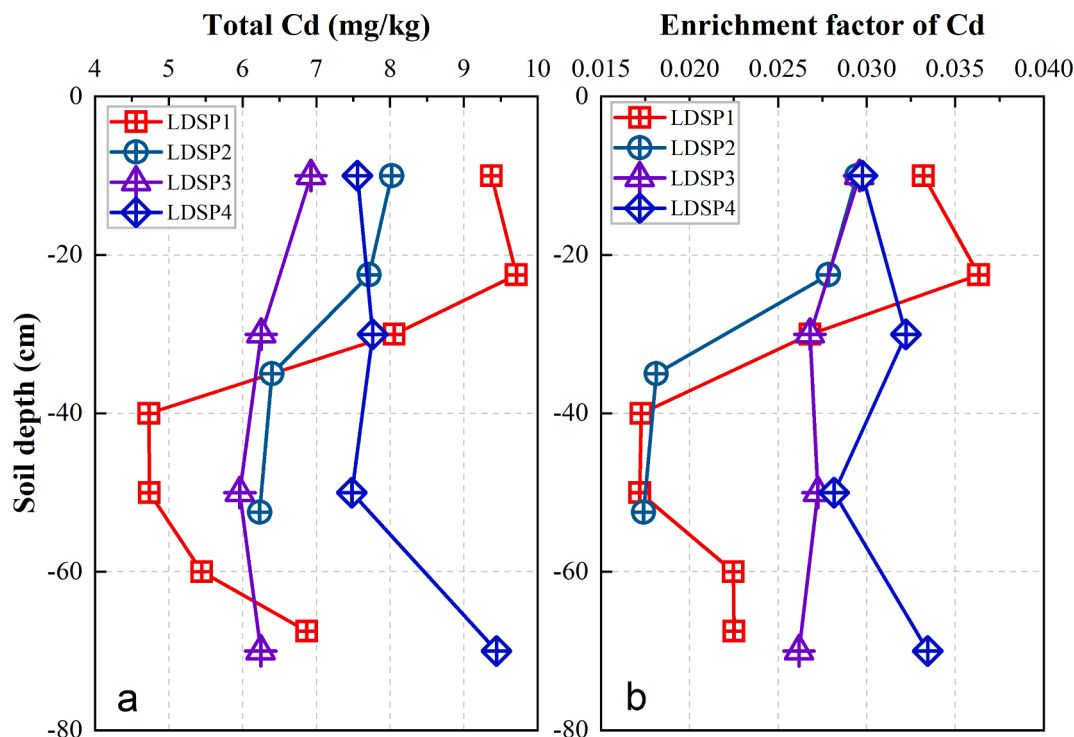


Fig. 2. Vertical distribution of (a) total Cd contents in the profiles and (b) enrichment factor of Cd in soils relative to the bedrock.

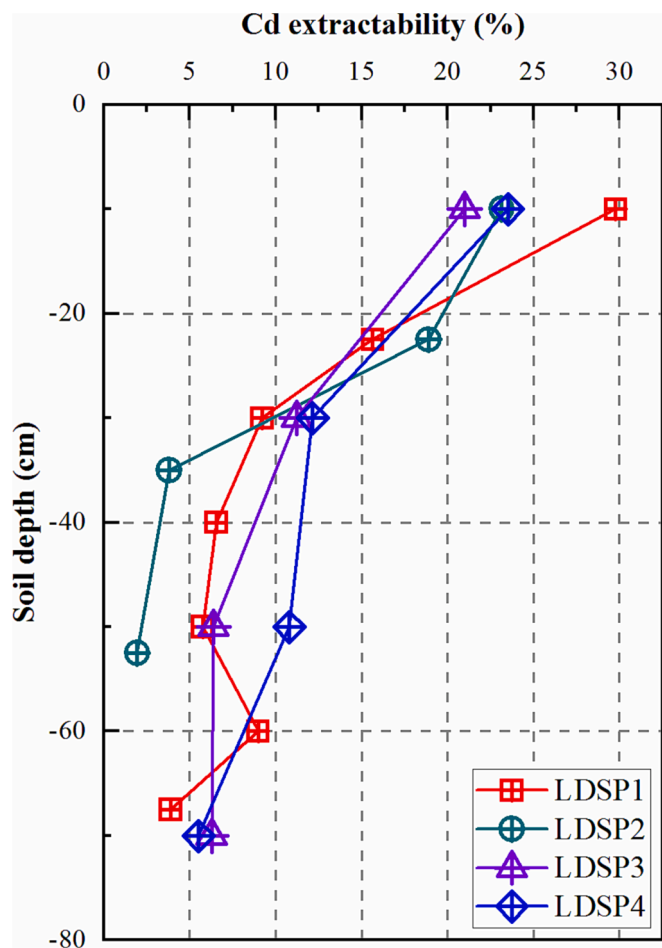


Fig. 3. Vertical variance in Cd extractability (ratio of DTPA-extractable Cd/total Cd, %).

an average value of 70.1%, followed by the residual fraction (F7: 7.17%–29.5%, average of 12.8%). There was no obvious universal trend representing the fractionation of Fe or Mn along the profiles.

4. Discussion

4.1. Dynamics of geogenic Cd in soils

The study area is a rural area without industrial or mining activities, and far away from arterial traffic. The anthropogenic input of Cd, therefore, should be limited. Previous studies have shown that carbonate-derived soils in Guizhou Province are mostly weathered *in situ* based on evidence from mineralogy and Si-Li isotopes (Wang et al., 1999; Ji et al., 2004, 2021). The significantly positive correlations between Fe₂O₃ and Al₂O₃ in bedrocks and paddy soil profiles ($R^2 = 0.983$, $p < 0.01$, Fig. S3) suggesting that soils in the study area were weathering *in situ*. Accordingly, the weathering of bedrock was considered to the primary reason for the abnormally high Cd contents measured in the soils. The high Cd contents in the collected limestone and their insoluble residues (Table 2) and high Cd contents in the deep soil layers (Table 3) reflected the high Cd baseline in the study area. The average value of our limestone was higher than the average value of carbonate rocks (0.035 mg/kg; Turekian and Wedepohl, 1961), and was comparable to the Cd contents measured in carbonate rocks from other areas with high geochemical background conditions, such as 0.03–4.91 mg/kg (average of 0.28 mg/kg) in carbonate rocks from the Jura Mountains of Swiss (Quezada-Hinojosa et al. 2009), 0.1–1.6 mg/kg (average of 0.4 mg/kg) in carbonate rocks from Konya, Turkey (Temur et al., 2009), and 0.09–1.54 mg/kg (average of 0.45 mg/kg) in carbonate rocks from Guangxi, China (Wen et al., 2020a). As a result, the total Cd in the soils in the study area was higher than the background Cd values measured in surface soils in Guizhou Province (0.46 mg/kg) and China (0.15 mg/kg) (Hou et al., 2020). The total Cd in soils in the study area was also higher than those reported in soils from other carbonate regions, such as soils from Guangxi in Southwest China (average of 4.94 mg/kg; Wen et al., 2020a) and soils from the Jura Mountain in Switzerland (average of 0.82 mg/kg; Quezada-Hinojosa et al. 2009).

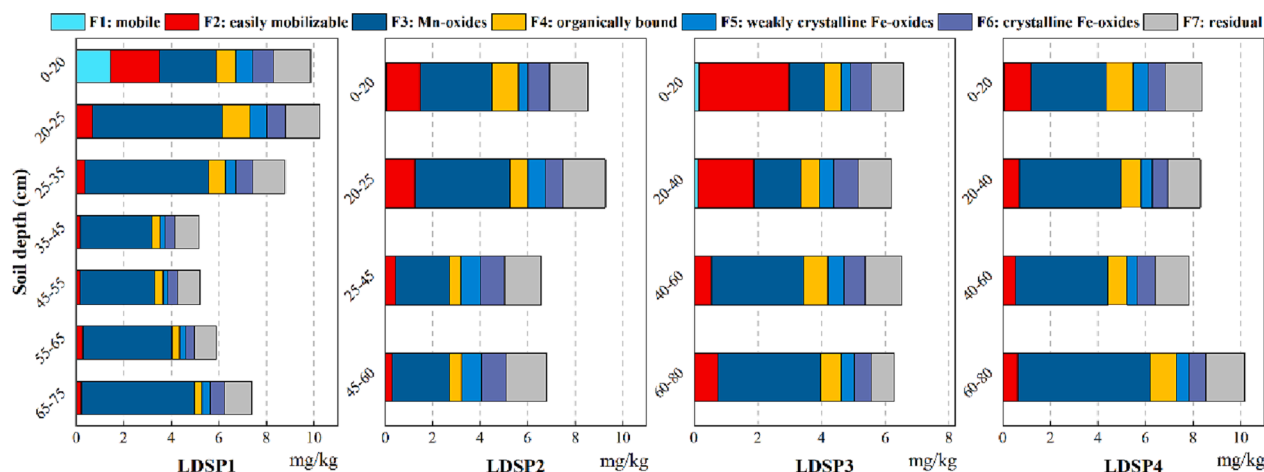


Fig. 4. Concentrations of Cd in different fractions derived by sequential extractions in the paddy soil profiles.

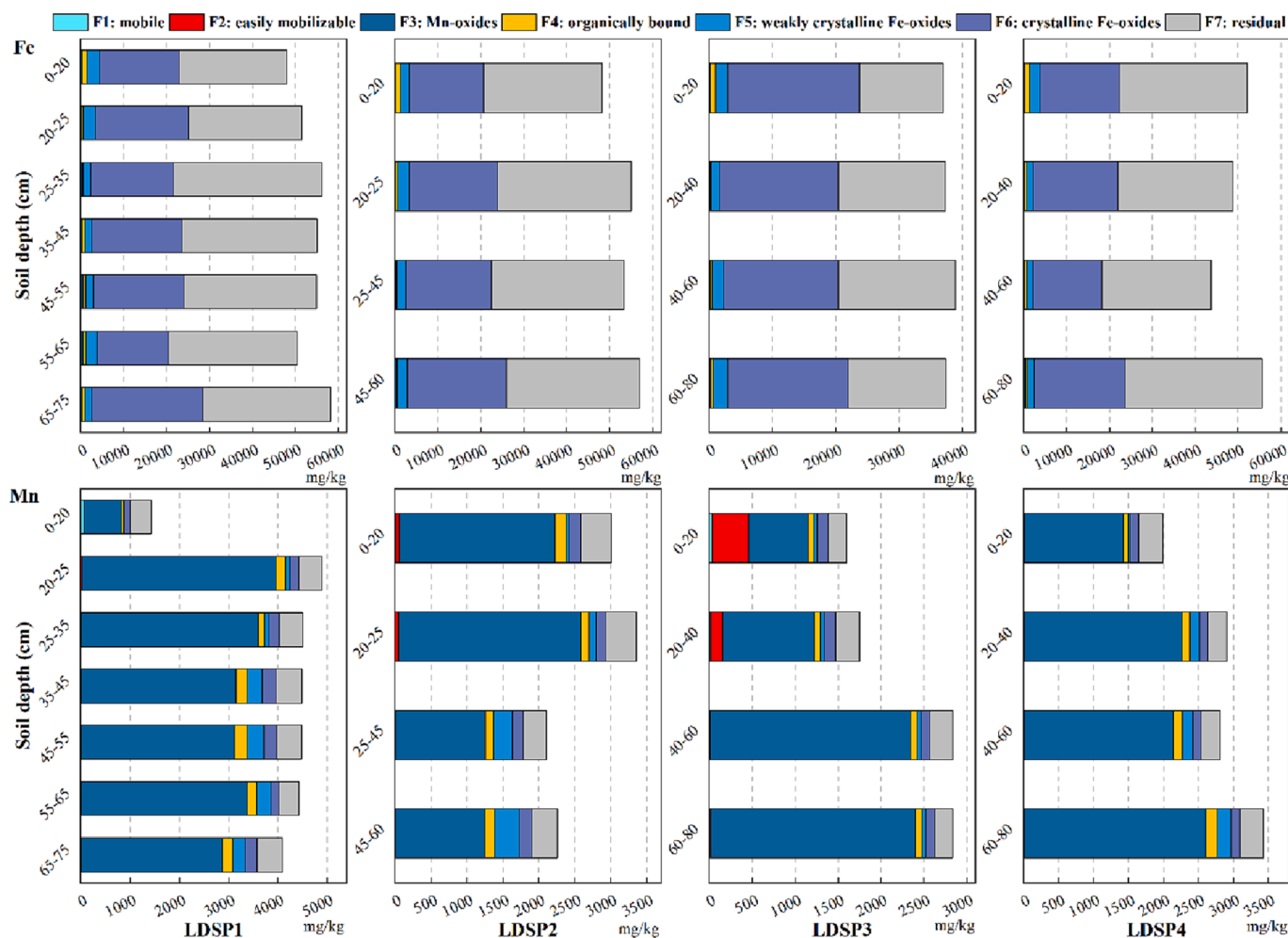


Fig. 5. Concentrations of Fe and Mn in different fractions derived by sequential extractions in the paddy soil profiles.

Approximately 96% of Cd in the bedrock of our study area was hosted in calcite. The low *EFs* of Cd in soils relative to bedrock ($EFs < 0.04$, Fig. 2) indicated that only ~2.6% of Cd from bedrock was retained in paddy soils from the study area and that most of the Cd from bedrock were leached during the dissolution of carbonates. This result was consistent with Yang et al., (2021b) which showed that 2% of Cd was retained in soils developed on carbonates in Southwest China. Relatively

higher Cd contents and *EFs* were observed in the upper layers of LDSP1 and LDSP2 (Table 3, Fig. 2). Given that the profiles were collected from agricultural lands and that phosphate fertilizer and manure are major sources of Cd in agricultural fields (McLaughlin et al., 1996; Bigalke et al., 2017; Rao et al., 2018), the application of fertilizer may introduce exogenous Cd into the surface soils. However, it was reported that the input flux of Cd from fertilizer was only 0.95 g/ha/y in karst area of

Guangxi in Southwest China (Li et al., 2022). Moreover, the inputs from 30 years of fertilization can only contribute an increase of ~ 0.5 mg/kg Cd to paddy soils (Rao et al., 2018). Thus, fertilization may not be a dominant factor controlling Cd enrichment in the surface layers considering their large variance in total Cd (Fig. 2). Additionally, atmospheric deposition is commonly regarded as an important source of Cd in soils (Liu et al., 2022). In the karst areas in Southwest China, the input flux of Cd from atmospheric deposition was estimated at 2.73 g/ha/y, higher than that from fertilizer (Li et al., 2022). The survey in a city close to the study area showed that Cd concentrations in the precipitation and dust fall and the corresponding annual total input amount (< 0.3 mg/m²) were low (Yang et al., 2016). Therefore, the effect of atmospheric deposition on Cd enrichment in the surface layers was probably limited. Alternatively, the “plant pump” mechanism may explain this phenomenon: plants can take up Cd from deeper layers and then return it into upper layers via plant debris (Goldschmidt 1937; Reimann et al., 2007; Imseng et al., 2018). Similarly, Imseng et al. (2018) found that a soil–plant Cd cycling model perfectly explained the higher total Cd contents and heavier Cd isotopes in the upper layers than in the deeper layers of agricultural soils. Moreover, the higher SOM content and higher proportion of organically bound Cd in the upper layers than that in the deeper layer of our profiles may further support soil–plant Cd cycling (Fig. 4, Table 3).

4.2. Changes in Cd speciation in paddy soils

Approximately 36% to 64% of Cd from bedrock was sequestered by Mn oxides in the deepest soil layer of the profiles (Fig. 4). This result was in accordance with a previous study in which $\sim 50\%$ of Cd was bound to poorly crystallized Mn oxides in *terra rossa* soils from Sicily (Bellanca et al., 1996). However, the Fe oxides (weakly crystalline and crystalline) bound Cd in the deepest layer of the profiles accounted for $\sim 17\%$ of total Cd, which was lower than that reported in previous studies (Quezada-Hinojosa et al. 2015b; Wen et al., 2020a). This discrepancy may be ascribed to two reasons. First, the approaches applied in previous studies did not separate Mn oxides from Fe oxides and therefore, the contribution of Mn oxides may have been masked. Second, partially crystalline Fe oxides were not extracted in F6, which targeted crystalline Fe oxides, but were included in the residual fraction, as was observed in a previous study (Palumbo et al., 2000) and in our results ($\sim 58\%$ of Fe in the residual fraction, Fig. 5).

It has been reported that Mn oxides have a greater adsorption ability for cations such as Cd than Fe oxides (Suda and Makino, 2016). In soils, Mn oxides are usually reported to be amorphous, such as birnessite, with high surface area and reactivity (Suda and Makino, 2016; Mo et al., 2021). Moreover, the edge sites and cation vacancy sites of birnessite provide a great Cd adsorption ability (Wang et al., 2012; van Genuchten and Peña, 2016). For example, at pH 4.5, the maximum Cd sorption amount ranged from 0.32 to 1.32 mmol/g for birnessite with different average oxidation states, and Cd was primarily adsorbed at vacancy sites (Wang et al., 2012). This amount is higher than the Cd adsorption capacities (< 0.2 mmol/kg) of goethite and hematite at the same pH (Liu et al., 2021). In the study area, the average Mn content (1627 mg/kg) in the bedrock was higher than the average value in carbonate rocks (1100 mg/kg, Turekian and Wedepohl, 1961), resulting in the Mn content (average of 2868 mg/kg in soil profiles) being remarkably higher than that measured in soils in Guizhou Province (1181 mg/kg) and China (552 mg/kg) (Hou et al., 2020). The co-enrichment of Cd and Mn in soils were also found in other carbonate regions in Southwest China (Wen et al., 2020a). Therefore, we proposed that poorly crystalline Mn oxides primarily govern the fate of Cd in paddy soils in the study area, and probably in carbonate-derived soils in Southwest China as well.

Indeed, coupled changes in Cd and Mn speciation were observed in the soil profiles, particularly in the upper layers. It is likely that some Mn oxides were transformed to other phases, such as carbonates, in surface soils, as evidenced by the increase in F2 (Fig. 5). As a result, Cd was

redistributed in the upper profile layers, as supported by the decrease in Mn oxides-bound Cd and increase in mobile and easily mobilizable Cd (Fig. 4). These results were likely related to the reductive dissolution of Mn oxides during the flooding period of paddy soils, during which the released Cd was sequestered by other soil constituents (Weber et al., 2009; Khaokaew et al., 2011; Gao et al., 2022). Among these constituents, soil organic matter may be an important factor because it usually presents negatively charged functional groups (e.g., carboxylic groups, phenolic groups and thiols) and is a major source of surface exchangeable sites for cations in soil (Bradl, 2004; Karlsson et al., 2007; Loganathan et al., 2012). Clay minerals such as kaolinite in our soils (Fig. S2) usually presented low Cd adsorption capacities at pH < 8 (Vasconcelos et al., 2008). This assumption was supported by the significant correlation between SOM and ECEC in our surface soils ($r = 0.726$, $p < 0.01$), and the positive correlation of total Cd vs ECEC ($r = 0.251$) and total Cd vs SOM ($r = 0.223$) (Table S1). The correlation coefficient between total Cd and SOM was even higher in the profiles ($r = 0.495$, $p < 0.05$). Additionally, carbonates are also regarded as the sinks of Cd in soils because Cd can not only form CdCO₃ under neutral pH but can also be incorporated into carbonates by coprecipitation/surface precipitation (Liu et al., 2017; Gao et al., 2022). The remarkably high Cd content measured in the easily mobilizable fraction observed in the 0–40 cm layers of LDSP3 (Fig. 4) may be related to the sequestration of carbonates because high CaCO₃ and calcite contents were observed in this layer but not in the other layers (Table 3, Fig. S2). On the other hand, the soil–plant Cd cycling contribute to the higher proportion of organically bound Cd in surface soils than sub-soils (Fig. 4). This fraction accounted for a low proportion because the decomposition of litters in soil. Collectively, increased proportion of Cd in mobile and easily mobilizable fractions in the upper layers of the profiles suggested an increased Cd mobility toward the surface in paddy soils.

4.3. Mobilization of geogenic Cd in paddy soils

In the study area, paddy soils presented a significantly higher Cd bioavailability ($\sim 27\%$) than upland soils ($\sim 18\%$) ($p < 0.01$; Table 3), and the Cd bioavailability gradually increased with decreasing depths in the paddy soil profiles (Fig. 3). Additionally, a remarkable increase in easily mobilizable Cd toward the surface was also observed in the profiles. These results indicated that geogenic Cd was mobilized in surface paddy soils, and confirmed the findings from previous studies (Rao et al., 2018; Wen et al., 2020a,b). DTPA usually targets soluble, exchangeable, adsorbed and organically bound metals, but carbonates are not included because of the neutral pH of the extractant (Lindsay and Norvell, 1969; Dai et al., 2004). In our soils, the sum of the soluble and exchangeable fractions of Cd was as low as $< 1\%$ (Fig. 4). Hence, the increased Cd availability in paddy soils was most likely related to the changes in specifically adsorbed and organically complexed Cd, because over 70% of Cd in these pools is isotopically labile (Ahnstrom and Parker, 2001). This supposition was supported by the significantly positive correlation between the Cd extractability and the proportion of easily mobilizable Cd ($p < 0.01$; Fig. 6a). The lower slope of LDSP3 (with high CaCO₃ in surface layers) compared to the other profiles may imply that the influence of carbonates on Cd availability was not as significant as other factors such as organic matter that can sequester Cd. This is reasonable given that Cd was adsorbed onto carbonate minerals by surface precipitation of the (CdCa)CO₃ solid solution with a calcite-type structure, and sorbed Cd was finally incorporated into the structure of carbonates (Prieto et al., 2003; Callagon et al., 2017).

It is noteworthy that the DTPA extractability of Cd was positively correlated with the SOM in surface soils ($r = 0.403$, $p < 0.05$). Furthermore, the Cd extractability was highly correlated with SOM in soil profiles ($r = 0.897$, $p < 0.01$, Fig. 6b). These results suggested that organic matter is a crucial factor controlling Cd mobilization in the sampled soils. On the one hand, solid organic matter is one of the most important factors retaining Cd in soils. Previous studies have proposed

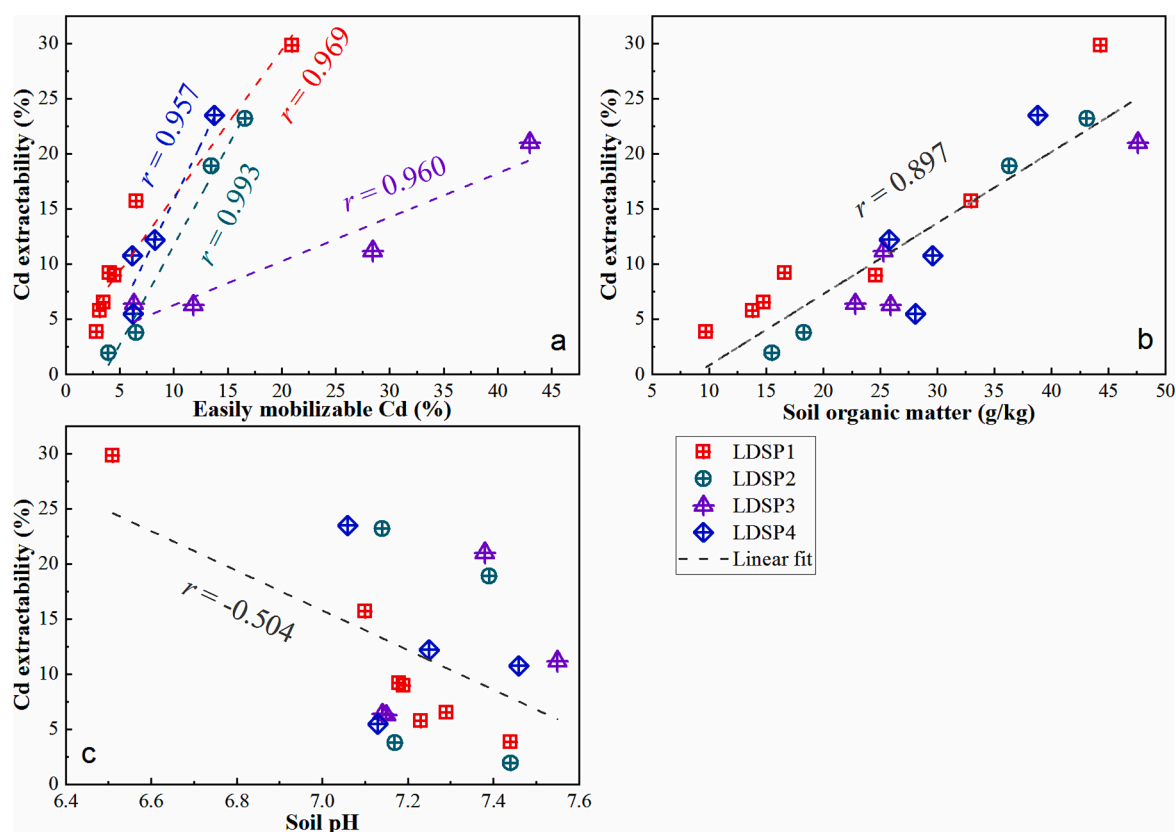


Fig. 6. Correlation between the Cd extractability (ratio of DTPA-extractable Cd/total Cd) and the easily mobilizable Cd (ratio of 1 mol/L NH_4OAC -extractable Cd/total Cd) (a), soil organic matter (b), and soil pH (c) in the paddy soil profiles.

that most Cd in soils is likely to form inner-sphere complexation with reduced sulfur groups (thiols, RS^-) under low Cd-loading conditions and that the contribution of carboxylic groups (RCOO^-) increase with increasing Cd loading (Karlsson et al., 2005, 2007). They also proposed that for soil with 1% organic carbon, the RS^- groups would be saturated at ~ 50 mg/kg Cd in soil, indicating that the SOM in our soils was sufficient for Cd adsorption. Therefore, the Cd released from the reductive dissolution of Mn oxides can be sequestered by solid organic matter, in which Cd presented a higher availability than that occluded by minerals. On the other hand, dissolved organic matter (DOM) was demonstrated to mobilize Cd in soils by forming Cd-DOM solution complexes and colloids and by ligand-assisted dissolution (Sauvé et al., 2000; Collins et al., 2003; Welikala et al., 2021). In a pot experiment, straw amendment in paddy soils was found to decrease the soil pH and increase the soluble Cd and DOC contents in soil solution, consequently enhancing the Cd availability (Bai et al., 2013). A recent study observed the increasing mobilization of colloidal Cd in soil amended with compost and peat, and the structural properties of DOM were found to influence the mobilization of Cd from soils (Welikala et al., 2021).

Furthermore, dissolution of CO_2 produced by root respiration, acid deposition, and organic acids originating from plant root exudates and the decomposition of litter can accelerate soil acidification and mobilize Cd in soils (Strobel et al., 2001; Li et al., 2010; Sun et al., 2019; Li et al., 2020). For instance, researchers have observed increased acid soluble fractions of Cd in soils cultivated with rice compared to rice-free treatment due to plant-induced acidification (Li et al., 2020). Moreover, an increased Cd content in rhizosphere solution was also observed in sand cultures with different insoluble Cd compounds ($\text{Cd}_3(\text{PO}_4)_2$, CdS, CdCO_3 and CdSe) in the same study. In our study area, a slight decrease in pH (<0.5 units) was observed in bulk soils from the surface layers of the profiles (Table 3). The negative correlation between the Cd extractability of DTPA and the soil pH in the profiles ($r = -0.504$, $p < 0.05$,

Fig. 6c) indicated the impacts of acidification on the mobilization of Cd in soils.

Additionally, some studies showed that freshly applied Cd through fertilizer and irrigation may affect the availability of Cd in soils. Bracher et al. (2021) investigated the fate of phosphorus fertilizer derived Cd in soil-fertilizer-wheat systems, and their results showed that $<2.3\%$ of these Cd was taken up by wheat whereas over 95% of the newly applied Cd remained in the soil and partitioned into the easily mobilizable and reducible fractions. Contrasting, another study found that most of the newly introduced soluble Cd in paddy soils was aged and partitioned into residual fraction after 56 days of incubation (Dong et al., 2021). In a factorial atmospheric exposure experiment, researchers found that the proportion of weak acid extractable Cd increased in the surface layers (0–2 cm) and decreased with depths (2–6 cm) in soil profiles exposed to high deposition rate after 1.5 years (Liu et al., 2022). However, in the study area, the small amount of Cd from fertilization and atmospheric deposition suggested that the effects of newly introduced Cd on Cd bioavailability may be limited.

Therefore, the effects of DOM and pH may explain the higher proportion of DTPA extractable Cd than easily mobilizable Cd (Fig. 6a). These results suggested that manure application and straw amendment in soils with naturally elevated Cd contents in carbonate regions must be performed with caution because these practices may mobilize geogenic Cd and thus increase the potential risks associated with Cd. Further studies are needed to reveal the extent to which organic amendment mobilized Cd in the studied soils.

5. Conclusion

This study investigated the dynamics, speciation transformation and mobilization of Cd in paddy soils in a carbonate area in Southwest China. In the study area, the weathering of Cd-rich limestone has

resulted in the remarkable enrichment of Cd in soils. In paddy soils, 43% of Cd was found to be bound to Mn oxides, followed by Fe oxides and residual fractions. Hence, Mn oxides was a dominant factor controlling the fate of Cd, and their transformation drove the redistribution of Cd. In the upper layers of the profiles, Cd released from Mn oxides was sequestered by soil organic matter and carbonate. Moreover, the bioavailability of Cd in paddy soils was 1.5 times higher than that in upland soils, and both the Cd mobility and Cd bioavailability gradually increased toward the surface in the profiles. Soil organic matter is another crucial factor controlling Cd mobilization in soils. These results imply the great significance of Mn oxides and organic matter on the fate of Cd in paddy soils derived from carbonate bedrocks. This work is also helpful for the management of soils with naturally elevated Cd contents in carbonate regions, in where the effects of amendment of manure and straw on the Cd mobilization need to be assessed.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2023.116606>.

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