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Original Research

Spatial Distribution and Migration of Cadmium in Contaminated Soils Associated with a Geochemical Anomaly: A Case Study in Southwestern China

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Abstract

The karst terrain of Guizhou in southwestern China is ecologically fragile, but has undergone severe heavy metal contamination. To assess such contamination, the spatial distribution of cadmium (Cd) within soils was studied in a lead (Pb)-zinc (Zn) smelting area, coal mining area, Pb-Zn mining area, sewage irrigation area, and an uncontaminated area. Cd concentrations were highest in topsoil, with the highest value of 23.36 mg/kg in the Pb-Zn mining area and lowest value of 0.46 mg/kg in the uncontaminated area. Cd content decreased from 0 to 0.8 m depth, then sharply increased, reflecting Cd precipitation within the contaminated soil profiles. Migration of Cd within the soil was affected by organic content in the Pb-Zn smelting area (R^2 = 0.99**), coal mining area (r = 0.72*), and Pb-Zn mining area (r = 0.73*). In contrast, Cd accumulated within a clay horizon in the uncontaminated area, where the correlation between Cd and specific surface area was 0.78**; Cd concentrations reached 2.11 mg/kg within this horizon. Reducible, oxidizable, and acid-exchangeable fractions accounted for 60-80% of total Cd in soils having pH values of 5.05-6.86. This indicates that Cd could easily transfer from soil to food or water, leading to human health and environmental risks.

Keywords: cadmium; soil; spatial distribution; fraction; migration mechanism

Introduction

Cadmium is both extremely toxic and ubiquitous in the natural environment, occurring in most soils, surface waters, and plant tissues. It is readily mobilized by human activities, such as mining [1]. Soils documented in this study featured total concentrations of Cd, Cu, Pb and Zn, exceeding the maximum levels permitted by law [2-3]. Their geogenic heavy metal content reflects geological sources [4]. Unlike organic contaminants, enrichment of heavy metals in soils has attracted a great deal of attention worldwide because they are

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non-biodegradable and have a long biological half-life for elimination from the body [5]. However, marked discrepancies in heavy metal contents between soils and their underlying bedrocks suggest that geochemical processes act on heavy metal distributions within soils [6]. High element concentrations in soils may be related to the occurrence of mineralization, unusual rock types (like serpentinites, black shales or alkaline intrusions), or caused by human activities [7]. The World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) recommend a maximum allowable ingestion for Cd in humans as 1 μg/kg per day [8]. Sewage irrigation, solid waste application as fertilizers, agricultural activities, mining, and atmospheric deposition cause abnormal increases in heavy metal contents in soils [9-12]. The storage of solid waste in landfills is one of the oldest and most universal methods all over the world, and heavy metals can be transported from the landfill to the environment as a serious threat [13]. Solid waste landfills are potential sources of soil, groundwater and plant pollution by heavy metals [14-15].

In the case of cadmium (Cd), the water-soluble and acid-exchangeable (easily mobilized) fractions are considered to be the most bioavailable; reducible and oxidation fractions are potentially bioavailable, while the residue fraction is not [16-18]. It is widely recognized that the spatial distribution of Cd is influenced by geology, soil, climate, vegetation, elevation, natural mineralization, and human activity. These processes affect geochemical variables at different spatial scales, ranging from microscale mineral compositions to macroscale geochemical provinces [19]. The mobility of heavy metals is determined by its chemical form, which reflects soil attributes, such as organic matter content, clay mineral content, soil particle size, Eh, and pH [20-26].

Karst areas of China are mainly distributed in carbonate outcropping areas (about 1.3×10^6 km^2), accounting for about 13.5% of the land area of China. Meanwhile, the global carbonate outcropping area is about 5.1×10^7 km^2, accounting for 34.2% of the land area of the world [27]. Karst geochemistry of regions with high background levels of heavy metals have received widespread attention around the world because they cover such vast areas. In environmental geochemistry, the term 'background' distinguishes natural concentrations of potentially toxic elements (e.g., Cd, As, Cr, Hg, Pb, and Zn) from anthropogenic contamination [28]. Because of their high geochemical background values, heavy metal pollution in vegetable-growing soils is of concern, with health risks related to contaminants entering the food chain [29]. Severe Cd pollution has been documented in mining areas, sewage irrigation areas, and other areas of Guizhou [30-31]. Clearly, it is important to understand the spatial distribution of Cd in this region in order to assist with environmental management and to minimize health risks in agricultural production.

Although the presence of Cd in the environment has been documented, information about Cd distribution in the soil profile is scarce. In this study, we investigated the Cd distribution in soil profiles having high geochemical backgrounds throughout this karst region in order to establish factors causing Cd migration in soil profiles and to assess its environmental and health risks.

Materials and Methods

Study Site

Guizhou, in southwestern China, lies on the plateau and has an average elevation of about 1100 m. It is situated within a moderate subtropical humid monsoon climate, with four distinctive seasons. Guizhou has a very well-developed karst topography, which is rich in mineral resources. However, mining activities have brought about serious heavy metal pollution in this region. Unfortunately, lack of surface water and use of sewage irrigation have aggravated this heavy metal pollution, making Cd one of the most commonly reported soil contaminants in Guizhou [32].

Sample Preparation and Analysis

Five areas throughout Guizhou were selected for study (Fig. 1). In particular, soil profiles were documented at the towns of Yemachuan (YMC), Bijie; Dawan (DW), Liupanshui; Bagu (BG), Duyun; plus Wudang (WD) and Qingyan (QY) districts of Guiyang. The sampling site at YMC has large tailing areas related to zinc smelting (1.57 mg/kg). DW is located within a coal-mining area; soils were sampled near No. 1 Zhongshan Mine from cultivated land with a background Cd concentration of 6.07 mg/kg. BG is located within a Pb-Zn mining area, having a high background Cd value of up to 23.36 mg/kg. This is typical for soils overlying Cd mineral deposits in Guizhou, especially in areas associated with diggings and tailings. WD is within farmland, which has been irrigated with a mixture of swine wastewater and sewage since the last century; the concentration of Cd at WD averages 0.78 mg/kg. QY is

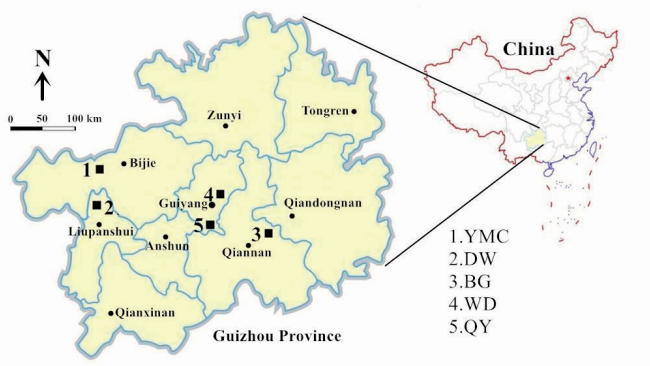

Fig. 1. Distribution of the study areas.

Table 1. Basic characteristics of topsoil at the five study areas.

Study areas (n)	Geological background	Soil type	Pollution source	Average total precipitation (mm)	Average temperature (ºC)	Organic matter (g/kg)		Cd (mg/kg)		pH	
						Concentration range	Mean±SD	Concentration range	Mean±SD	Concentration range	Mean±SD
YMC(7)	Permian limestone	Grey yellow soil	Indigenous zinc smelting	72.2	13.0	41.36 ~ 58.66	52.93±6.87	1.48 ~ 1.69	1.57±0.08	4.87 ~ 5.28	5.05±0.16
DW(8)	Permian limestone	Yellow soil	Zhongshan mine No.1	98.0	12.6	30.66 ~ 39.08	35.58±2.57	4.71 ~ 7.55	6.07±0.99	5.75 ~ 6.23	5.97±0.18
BG(16)	Sinian system	Brown limestone soil	Lead and zinc mine	117.2	16.3	23.72 ~ 79.59	38.64±15.69	1.61 ~ 162.40	23.36±41.19	6.35 ~ 7.12	6.76±0.21
WD(16)	Triassic limestone	Grey yellow soil	Sewage irrigation	89.4	14.6	32.83 ~ 80.73	53.55±12.86	0.37 ~ 1.72	0.78±0.44	6.43 ~ 7.27	6.86±0.29
QY(16)	Triassic limestone	Yellow podzolic soil	None	92.1	15.0	19.37 ~ 59.55	33.88±13.31	0.22 ~ 0.69	0.46±0.12	5.87 ~ 6.38	6.15±0.13

NB: Each value is the mean of four replicates ± standard deviation (SD).

the control site, showing no obvious signs of exogenous pollution. Cd concentrations at this site were around 0.46 mg/kg (Table 1).

Cultivated soil profiles were collected at each location, with samples collected every 20 cm from the top to a depth of 2.0 m. Surface soils were sampled from all sites. Pollution sources and basic soil properties of the topsoil at the five sampling sites are shown in Table 1.

The soil samples were transported to the laboratory, air dried at room temperature for a week, and sieved through 0.15- and 0.75-mm sieves. In addition to the total concentration of Cd and fractions of various forms of Cd, the specific surface area of soils (SSA), as well as organic carbon (OC), free iron oxide (FeOf) and free manganese oxide (MnOf) contents were determined for each sample.

Chemical Determinations

Soil subsamples of 0.10 g were accurately weighed and placed in Teflon crucibles. The total concentration of Cd in soils was determined by digestion with a mixture of HF-HNO_3-$HClO_4$ [33]. Operational forms of Cd in the soil were extracted using the three-stage Community Bureau of Reference (BCR) sequential extraction procedure [34-35]. In step 1 (to obtain the acid-extractable fraction), 0.5 g of dried soil was extracted for 16 h with 20 mL of 0.11 mol/L acetic acid in a polypropylene centrifuged tube at 20ºC. In step 2 (to obtain the reducible fraction), the washed residue from step 1 was extracted for 16 h with 20 mL $NH_2OH{\cdot}HCl$ (0.5 mol/L, adjusted to pH 2.0 with nitric acid) at 20°C. In step 3 (to obtain the oxidizable fraction), the washed residue from step 2 was twice treated with 5 mL H_2O_2 (8.8 mol/L, adjusted to pH 2.0 with nitric acid) at 85ºC in a water bath for 2 h. The volume of liquid was reduced to about 1 mL and 25 mL of ammonium acetate (1.0 mol/L adjusted to pH 2.0 with concentrated nitric acid) was added to the cooled moist residue and shaken for 16 h at 20ºC. In step 4 (to obtain the residual fraction), the residual fraction of Cd was measured using the same method as for total Cd. All Cd solutions were analyzed by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7700; Agilent Corp., Santa Clara, CA, USA).

A laser particle sizer (Malvern Mastersizer 2000; Malvern Instruments Ltd.; Malvern; UK) was used to measure particle size to determine the specific surface area of soils. $Na_2S_2O_4$-$Na_3C_6H_5O_7{\cdot}2H_2O$-$NaHCO_3$ (dithionite-citrate-bicarbonate; DCB) extraction was used to extract MnOf and FeOf. The potassium dichromate volumetric method was used to measure OC content.

Quality Control and Statistical Analyses

Blank controls and the national standard reference material GSV-2 were included in each batch of samples

analyzed as quality controls. Descriptive statistical analyses and plotting of figures were carried out using Origin 8.0 (OriginLab Corp., Northampton, MA, USA) and Excel 2013 (Microsoft Corp., Waltham, MA, USA). Each value represents the mean of four replicates ±standard deviation (SD). Correlation analysis was performed using IBM SPSS Statistics version 17.0 for windows (IBM, Armonk, NY, USA). Levels of statistical significance are shown as *p<0.05 and **p<0.01.

Results and Discussion

Total Cadmium Distribution in the Topsoil

Reflecting the high geochemical background values of Cd in the carbonate rocks of Guizhou, the average Cd concentration in the topsoil was 0.659 mg/kg, more than twice the national average value of 0.30 mg/kg [36]. All cultivated soils are contaminated with Cd in the study area, having concentrations that exceed levels of the standards for Soil Environmental Quality of China (GB15618-1995) (Table 1). This reflects Cd contamination from local metal mining and smelting areas, as well as other industrial activities. There was a strong spatial dependency in heavy metals concentration due to the dilution effects of precipitation [37]. Related to the underlying Cd ore deposit, concentrations at BG were highest, averaging 23.36 mg/kg, while the lowest value of 0.46 mg/kg was recorded in the uncontaminated area (QY)

Total Cadmium Distribution in the Soil Profile

The Cd distributions for all soil profiles are shown in Figs 2-6. YMC and DW were both polluted by mining activities, yielding concentrations of Cd at the surface of 1.73 mg/kg and 3.26 mg/kg, respectively. Concentrations of Cd decreased with depth in these profiles. At 100 cm below the surface, the Cd concentration at DW had a value of 1.11 mg/kg. Concentrations varied in different soil horizons within the BG profile, although all were severely polluted, reflecting natural Cd mineral occurrences and long-term mining activities [9]. The concentrations of Cd in the BG profile from 20 cm to 200 cm fluctuated between 4.29 and 32.97 mg/kg. At WD, concentrations also fluctuated between 0.16 and 0.63 mg/kg over this depth range. Surface concentrations of Cd at this site were only slightly higher than at the bottom of the profile. The soil profile at QY occurs in a low-lying paddy field, with a possible aquitard at its base. This profile represents a relatively clean background site. Cd concentration in the surface soil was 0.57 mg/kg, reflecting the high geochemical background value of the karst area [30]. Concentrations of Cd slightly decreased with increasing depth in the QY profile. At the bottom of the QY profile, Cd reached concentrations of 2.22 mg/kg.

Typically, Cd accumulated within the surface horizons and at the bottom of the soil profile. This suggests that ore mining and processing, producing large quantities of dust, waste gas, and waste residues of sewage, have led to the accumulation of heavy metals in the surface horizons of the soil profile [38-39]. As Miller and Friedman [40] found, the average speed of dispersion of heavy metals through the soil profile is about 0.5 cm/year, and in forest soils even up to 2 cm/year. Ecological Soil Screening Levels (Eco-SSLs) are concentrations of contaminants in soil that are protective of ecological receptors that commonly come into contact with and/or consume biota that live in or on soil (USEPA), and the concentrations of Cd to the standard of Eco-SSLs were 0.36 mg/kg for mammals and 32 mg/kg for plants [8]. Electronic waste recycling often creates secondary sources of Cd pollution and its potential threat to shallow groundwater [41]. All shallow groundwater pH was in the range 6.9-7.4, indicating that the shallow groundwater was neutral and the impact of soil acidification on the pH of shallow groundwater was limited [41]. As is known to all that the exchangeable Cd has high mobility and easy to entering the shallow groundwater. In the study area, Cd in the surface soil could migrate downward by leaching and as a threat to shallow groundwater, so it is urgently required to control Cd accumulation in order to reduce the risk of Cd leaching from topsoils and shallow groundwater contamination.

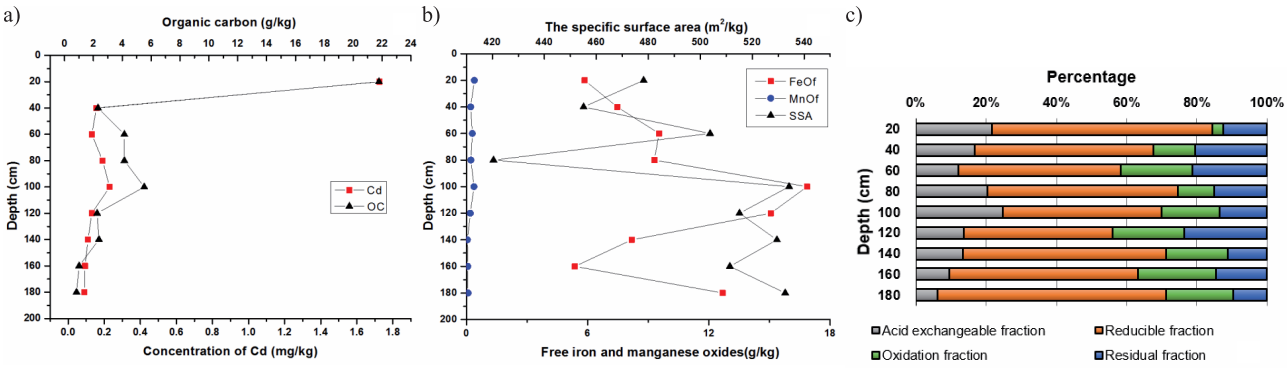

Fig. 2. Concentrations of Cd a), OC a), FeOf b), MnOf b) and SSA b), fraction distribution c) in YMC soil profile.

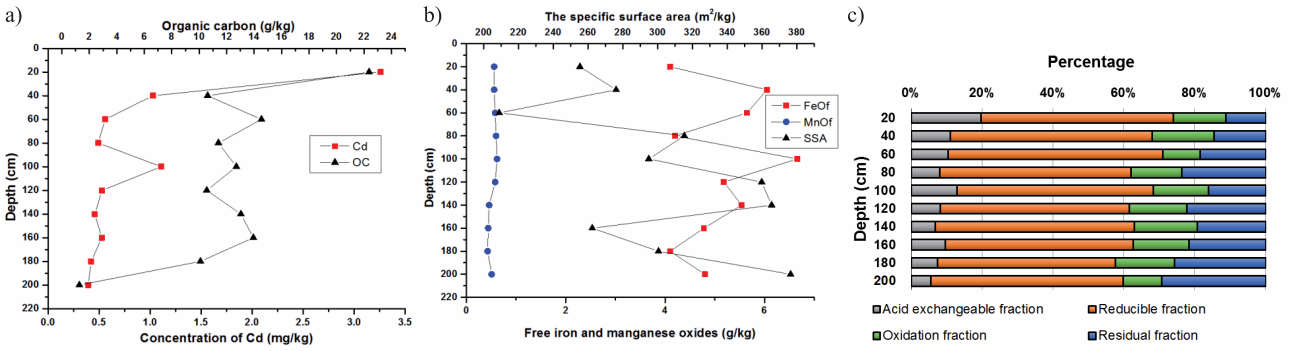

Fig. 3. Concentrations of Cd a), OC a), FeOf b), MnOf b) and SSA of soils b), fraction distribution c) in DW profile.

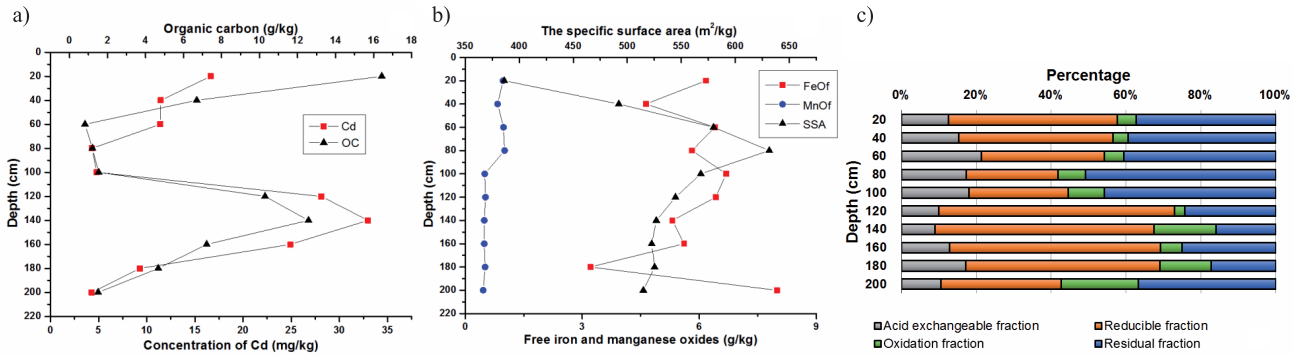

Fig. 4. Concentrations of Cd a), OC a), FeOf b), MnOf b) and SSA of soils b), fraction distribution c) in BG profile.

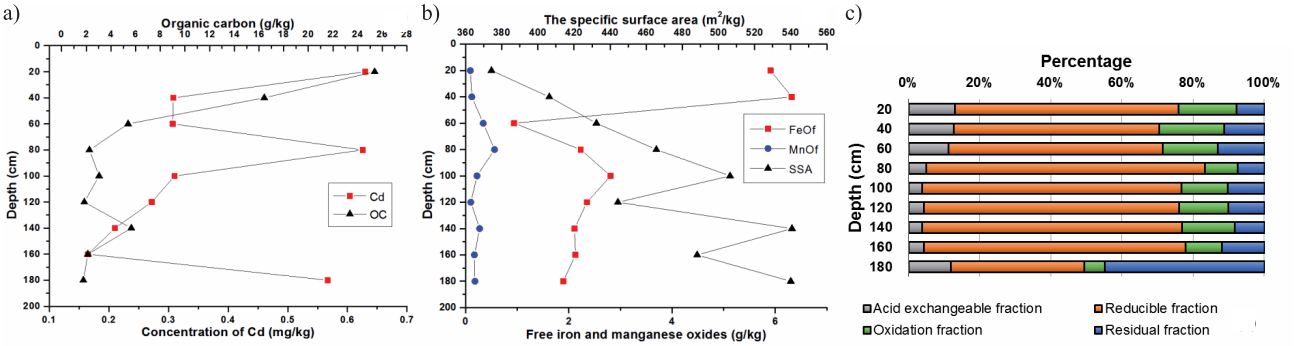

Fig. 5. Concentrations of Cd a), OC a), FeOf b), MnOf b) and SSA of soils b) fraction distribution c) in WD profile.

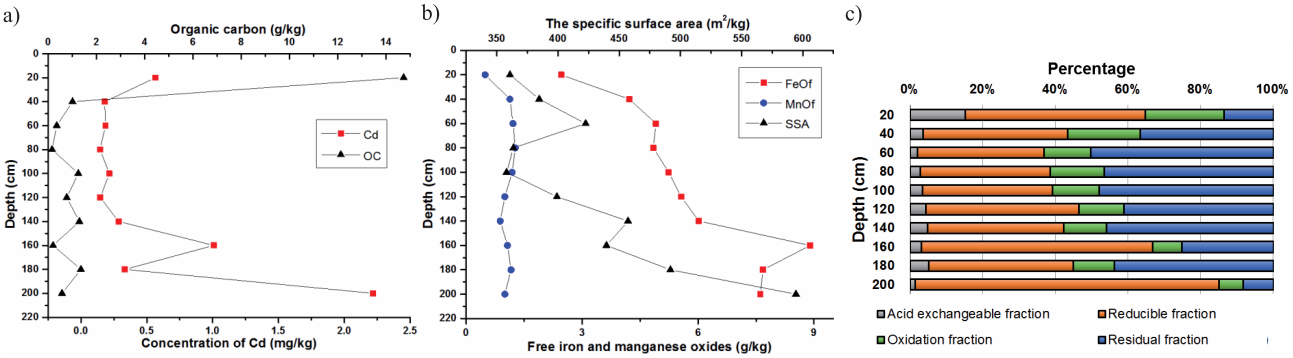

Fig. 6. Concentrations of Cd a), OC a), FeOf b), MnOf b) and SSA of soils b) fraction distribution c) in QY profile.

Cadmium Fractionation in the Soil Profile

The migration of Cd within soil profiles, its uptake by plants and toxicity to soil organisms all depend on its speciation in the soil solution [42]. Operational forms of Cd in different horizons of all profiles were determined by BCR sequential extraction (Figs 2-6).

In all soil profiles, the reducible fraction was the main form of Cd, consistent with conclusions of some scholars [35, 43-44]. The ratio between the reducible fraction and total Cd ranged from 24.5% to 83.6%. Generally, Cd occurred in different forms, with the reducible fraction (24.5-83.6%) > residual fraction (9.3-50.3%) > oxidizable fraction (2.7-21.8%) > acid-extractable fraction (1.3-24.7%). Acid-extractable and -oxidizable fractions were far smaller than fractions of the other two forms.

The concentrations of the reducible fraction of Cd were constant in soil profiles. However, Cd concentrations of other forms varied with increasing depth. In the QY and WD profiles, the Cd concentrations of acid-extractable and oxidizable fractions markedly decreased with increasing depth, while the residual fraction showed the reverse pattern. In the DW and YMC profiles, the acid-extractable fraction slightly decreased with depth, while the residual fraction increased. In contrast, the concentrations of Cd forms changed little in the BG profile.

Other heavy metals, except Pb and Cr, were mainly associated with non-residual fractions, indicating their high mobility and bioavailability [45]. Biochar can significantly enhance the pH and electrical conductivity of the soil, and it can promote the transformation of Cd from the acid-extractable fraction to the residual

Table 2. Correlations between Cd, FeOf, MnOf, OC and SSA in profiles (n) of different study areas.

Area (n)		Cd (mg/kg)	Free iron oxide (g/kg)	Free manganese oxide (g/kg)	The specific surface area (m^2/kg)	Organic carbon (g/kg)
YMC (9)	Cd (mg/kg)	1				
	Free iron oxide (g/kg)	-0.35	1			
	Free manganese oxide (g/kg)	0.6	0.2	1		
	The specific surface area (m^2/kg)	-0.22	0.44	-0.25	1	
	Organic carbon (g/kg)	0.99**	-0.29	0.70*	-0.23	1
DW (10)	Cd (mg/kg)	1				
	Free iron oxide (g/kg)	-0.18	1			
	Free manganese oxide (g/kg)	0.28	0.39	1		
	The specific surface area (m^2/kg)	-0.38	-0.07	-0.17	1	
	Organic carbon (g/kg)	0.72*	-0.09	0.16	-0.63*	1
BG (10)	Cd (mg/kg)	1				
	Free iron oxide (g/kg)	-0.15	1			
	Free manganese oxide (g/kg)	-0.31	-0.02	1		
	The specific surface area (m^2/kg)	-0.25	0.06	-0.01	1	
	Organic carbon ($g \cdot kg^{-1}$)	0.73*	-0.18	-0.01	-0.75**	1
WD (9)	Cd (mg/kg)	1				
	Free iron oxide (g/kg)	0.25	1			
	Free manganese oxide (g/kg)	0.27	-0.5	1		
	The specific surface area (m^2/kg)	-0.24	-0.65*	0.23	1	
	Organic carbon (g/kg)	0.34	0.87**	-0.42	-0.74*	1
QY (10)	Cd (mg/kg)	1				
	Free iron oxide (g/kg)	0.5	1			
	Free manganese oxide (g/kg)	-0.2	0.38	1		
	The specific surface area (m^2/kg)	0.78**	0.69*	0.03	1	
	Organic carbon (g/kg)	-0.01	-0.61*	-0.87**	-0.31	1

* denotes significant difference at $p<0.05$; ** denotes significant difference at $p<0.01$.

fraction [46]. The bacteria in the soil was reduced and the soil invertase activity was significantly increased after ryegrass and earthworms combined remediation, indicating that the combination of the rhizosphere of plants and earthworms can effectively repair the Cd-contaminated soil and improve soil biological activity [47]. Typically, Cd is activated as the ratio between the acid-extractable fraction and total Cd rises within the topsoil, related to biological activity. In lower horizons, weathering processes effectively perform natural remediation, and are likely responsible for the decrease in the acid-extractable fraction and the increase in the residual fraction of Cd with depth [48].

Cadmium Migration in the Soil Profile

It is widely recognized that the mobility of heavy metals is determined by organic matter, clay minerals, soil particle size, Eh, and pH [20-26]. Profiles of OC, SSA, FeOf and MnOf are shown in Figs 2-6.

The concentrations of OC in all five soil profiles fluctuated between 0.21 and 25.38 g/kg. Generally, OC concentrations decreased with depth. In contrast, the SSA of all profiles ranged from 208.9 to 631.4 m^2/kg, although it increased with depth in all soil profiles. The concentrations of both FeOf and MnOf were typically highest in the middle of the soil profile. Consistent with the research of Wu [41], the pH of soils had an almost inverse distribution trend with Cd in soils, indicating that soil acidification and Cd accumulation were synchronous.

Correlations among concentrations of Cd, OC, FeOf, MnOf, and SSA in samples (Table 2) revealed that: (1) the concentrations of Cd were significantly highly correlated with concentrations of OC in the YMC profile (0.99; $p \leq 0.01$), while concentrations of Cd were significantly correlated with concentrations of OC in both the BG and DW profiles (0.73, 0.72; $p \leq 0.05$); (2) the concentrations of Cd were significantly highly correlated with SSA in the QY profile (0.78; $p \leq 0.01$); and (3) concentrations of Cd had positive correlations with both FeOf and MnOf in both YMC and QY profiles. Driven by eluviation, Cd was enriched in soil layers with higher OC concentrations, affecting the mobility or bioavailability of heavy metals in the soil system [49]. The concentrations of Cd are highly correlated with organic C content [50], suggesting that in mining areas, OC has significant effects on the vertical distribution of Cd. It is urgently required to control Cd accumulation in order to reduce the risk of soil contamination by Cd.

Conclusions

The results of correlation analysis indicate that the concentration of Cd was significantly positively correlated with OC content and negatively correlated with SSA at these contaminated sites. Cd was mainly concentrated in the topsoil, coupled with loose and porous minerals. At WD, within a typical sewage irrigated area, the leaching of soil enhanced the activity of Cd, affecting its vertical distribution. Meanwhile, at the uncontaminated site (QY), Cd showed potential to accumulate. In this case, the SSA of the soil was the main factor affecting the vertical distribution of Cd. Within the five soil profiles, the reducible fraction was the dominant form of Cd, with subdominant residual fractions at most sites. Cd was activated, as the reducible fraction to the total Cd rose in the topsoil, related to biological activity. Such activation constitutes a threat to the environment and human health.

Migration mechanisms of Cd were mainly driven by eluviation, which were affected by OC in Pb-Zn mining and smelting areas. In contrast, Cd accumulated in clay horizons in uncontaminated areas. Eluviation caused Cd enrichment within the soil profile, related to higher concentrations of OC. Cd in the topsoil migrated downward via leaching processes, accumulating at the bottom of the profile, where it may pose a threat to shallow groundwaters. Although the concentrations of Cd in uncontaminated areas were not high, they should not be underestimated, given Cd's high mobility and potential to interact with groundwater. In the future, the accumulation of Cd in deep soil profiles overlying carbonate rocks of this region and mechanisms that influence its accumulation need to be addressed.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

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