



Enrichment and environmental availability of cadmium in agricultural soils developed on Cd-rich black shale in southwestern China

Yizhang Liu¹ · Zijie Chen² · Tangfu Xiao² · Zhengjie Zhu³ · Shuyu Jia⁴ · Jing Sun¹ · Zengping Ning¹ · Ting Gao¹ · Chengshuai Liu¹

Received: 21 July 2021 / Accepted: 5 December 2021 / Published online: 21 January 2022
© The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2021

Abstract

The enrichment of cadmium (Cd) in black shale-derived soils is of increasing concern due to its wide occurrence, high Cd concentrations, and potential risks. However, characteristics of enrichment and environmental availability of Cd in these soils are not well understood, which has restricted pollution control and land management. In this study, agricultural soils with elevated Cd concentrations resulting from weathering of Cd-bearing black shale in southwestern China were collected and analyzed. The results showed that Cd could be retained in soils through mechanical inheritance and/or associated with secondary minerals and organic materials. Cd concentrations in soils of the study area ranged between 0.83 and 21.6 mg/kg (average of 5.20 mg/kg), exceeding the risk screening value for agricultural land in China. The heterogeneity of Cd in these soils was highly related to geochemical composition of parent rock and other natural factors. The 0.01 M CaCl₂ and 0.05 M EDTA extraction showed that Cd in these soils had high environmental availability and potential risks. Mobile Cd pool (CaCl₂ extractable Cd, average: 0.24 mg/kg) accounted for 0.07–38.9% of the total Cd, depending on soil pH. Mobilizable Cd pool (EDTA extractable Cd, average: 2.18 mg/kg) accounted for 22.0–100%. These results showed the significance of geochemical background on enrichment of Cd in soils, documented high environmental availability of Cd in black shale-derived soils, and influence of soil pH.

Keywords Cadmium · Soil · Pollution · Geogenic source · Weathering · Retention

Introduction

Cadmium (Cd) is a notorious toxic trace element that is regarded as a global contaminant and carcinogen (Satarug et al. 2003). The enrichment of Cd in soils originating from anthropogenic and/or geogenic sources has been widely reported (Lund et al. 1981; Chen et al. 2015; Bigalke et al. 2017). The pollution is growing in almost every region, threatening global soil security and ecosystems (FAO 2018). Additionally, Cd could be transferred from polluted soils into food crops, resulting in crop loss and contamination, as well as human exposure through the food chain (Liu et al. 2015). The well-known Itai-Itai disease reported in Japan (Nogawa et al. 1983) demonstrated the serious adverse impact of soil Cd pollution on human health.

The majority of soil Cd pollution cases have been attributed to anthropogenic inputs, such as mining and smelting, sewage irrigation, fertilization, and industrial drainage (Nriagu and Pacyna, 1988; FAO 2018). Nevertheless, elevated Cd concentrations in soils resulting from geogenic

Responsible Editor: Kitae Baek

✉ Shuyu Jia
jiasy@njau.edu.cn

✉ Chengshuai Liu
liuchengshuai@vip.gyig.ac.cn

¹ State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

² School of Environmental Science and Engineering, Guangzhou University, Guangzhou 510006, China

³ College of Agriculture and Food Engineering, Baise University, Baise 533000, China

⁴ College of Resources and Environmental Sciences, Nanjing Agricultural University, Nanjing 210095, China

sources have been widely reported, such as in Korea (Lee et al. 1998), the USA (Lund et al. 1981), Europe (Quezada-Hinojosa et al. 2009; Rambeau et al. 2010), Africa (Nganje et al. 2020), and China (Duan et al. 2020; Wen et al. 2020a; Liu et al. 2021a, 2021b). Among these areas, southwestern China is probably the largest region with a high geochemical background of Cd, with at least 200,000 km² of land having a naturally high Cd concentration (Zhao et al. 2015; Xia et al. 2020).

Generally, the geogenic enrichment of Cd in soils is a result of weathering and pedogenic processes of Cd-rich parent rocks (e.g., Quezada-Hinojosa et al. 2009; Wen et al. 2020a; Liu et al. 2021b). During the weathering of carbonate rocks, a majority of primary carbonate (> 97%) and feldspar is dissolved and major elements such as Ca, K, Na, and Mg are leached, while Fe, Mn, and Al are remained and transformed into Fe–Mn oxides and clay minerals (Ji et al. 2004; Wen et al. 2020a). Cadmium released from parent materials could be re-adsorbed by these secondary minerals and added organic matter. These processes result in the enrichment of Cd in soils although Cd concentrations in many carbonate rocks are not high (e.g., 0.09–1.54 mg/kg; Wen et al. 2020a). However, black shales usually have much higher Cd concentrations than other rocks and it is susceptible to weathering due to their diagenetic environment (Parviainen and Loukola-Ruskeeniemi 2019). For example, black shales from Chongqing of China can contain up to 64.3 mg/kg of Cd (Cheng and Cheng, 2012), and Cd concentration in local soils can reach a maximum of 64.5 mg/kg (average of 9.36 mg/kg, Liu et al. 2021a, 2021b), much higher than that reported in carbonate regions (average of 1.49 mg/kg, Wen et al. 2020a). Furthermore, soils derived from black shales may inherit the geogenic organic matter, Fe oxides, and phyllosilicates, and presents high surface area (Richardson et al. 2022); together with the added organic matter from vegetation, these characteristics can favor the enrichment of trace metals such as Cd. Additionally, the acid drainage result from weathering of sulfides (e.g., pyrite) in black shale may acidify soil and increase the environmental availability of metals (Liu et al. 2017). Thus, environmental issues originating from the weathering of black shale are of increasing concern (Parviainen and Loukola-Ruskeeniemi 2019).

In recent years, Cd pollution in soils resulting from the weathering of black shale has been reported in many studies and most of them focused on total Cd concentrations (e.g., Duan et al. 2020; Liu et al. 2021b). The environmental availability of Cd in soils, which is important for the assessment of potential risks to the ecosystem (Gupta et al. 1996) and prediction of Cd concentration in food crops (Liu et al. 2018; Ma et al. 2020; Wen et al. 2020b), is still insufficient. This may hinder the effective land management and risk controlling strategies for soils with elevated Cd in black

shale regions. Moreover, the inherited clay minerals, geogenic organic matter, and Fe–Mn oxides may make black shale-derived soil present high adsorption capacity for Cd, while oxidic weathering of sulfides in black shale will induce soil acidification then increase availability of Cd. Based on these characteristics, we hypothesized that soils derived from black shales may present higher environmental availability and greater potential of Cd mobilization than soils developed on carbonate. Therefore, it is necessary to reveal the environmental availability of Cd in black shale-derived soils to provide referential results for similar regions.

In this study, agricultural soils derived from Cd-rich black shales in a mountainous area in southwestern China were studied to investigate the total, mobile, and mobilizable Cd utilizing mixed acid (HNO₃–HClO₄–HF–HCl) digestion, 0.01 M CaCl₂, and 0.05 M ethylene diamine tetraacetic acid (EDTA) extraction approaches, respectively. The main objectives of this study were to (1) investigate the enrichment of Cd in black shale derived soils and compare the results with soils developed on carbonate, (2) explore the environmental availability of Cd in soils and their controlling factors, and (3) uncover the underlying environmental implications of black shale weathering. The results are expected to provide a new understanding on the mobile and mobilizable pools of Cd in black shale-derived soils. Additionally, it is expected to determine the prospects for managing Cd pollution in areas with high geochemical background of Cd.

Materials and methods

Study area

The study area is located in northwestern Chengkou County, Chongqing City, southwestern China (Fig. S1). The study area is at an elevation of above 1000 m with a subtropical monsoon climate, with an average annual precipitation of 1261 mm and an average annual temperature of 13.8 °C, which depended on the altitude. The geological unit in the study area includes the Lujiaping Formation of early Cambrian age, which is composed of carbonaceous siltstone, carbonaceous calcareous siltstone, carbonaceous slate, and siliceous siltstone (Liu et al. 2021b). The upland soil is mostly composed of Luvisols and Cambisols (IUSS Working Group WRB, 2014), which are used for agricultural cultivation. No local mining or industrial activities were found in the study area. The enrichment of heavy metals in local soils has been documented as a result of geogenic sources related to the weathering of black shales (Cheng and Cheng 2012; Liu et al. 2021b).

Sampling and analysis

A total of 51 surface (0–20 cm) upland agricultural soil samples from representative locations (Fig. S1) were systematically collected in the study area in December 2015. Sample collection and pretreatment were conducted according to the procedures described in the Technical Specification for Soil Environmental Monitoring (HJ/T 166–2004). Concentrations of major (Ca, Fe, Al, Mn, and Mg) and trace elements (Cd, Zn, Cu, Pb, Cr, and Ni) were measured in the ALS Laboratory Group (Guangzhou, China) with ICP-MS and ICP-AES after total digestion with mixed acid ($\text{HNO}_3\text{--HClO}_4\text{--HF--HCl}$) on a hotplate (method code ME-MS61r). The detection limit for Cd utilizing ICP-MS was 0.02 mg/kg for solid samples. The accuracy of this digestion method was verified by $100 \pm 10\%$ recovery of three reference soil materials (GSS-3, GSS-5, and GBW(E)070,009). Soil pH was measured in a soil suspension with a solid-to-deionized water ratio of 1:2.5 (w/v) by a calibrated pH electrode. Total carbon (TC) and sulfur (TS) were determined by an elemental analyzer (Elementar, Germany) in the State Key Laboratory of Environmental Geochemistry (SKLEG). To acquire the content of total organic carbon (TOC), samples were pretreated with 0.1 M HCl and analyzed by an elemental analyzer. The contents of total inorganic carbon (TIC) were calculated via subtraction of TOC from TC, and TIC was regarded as not detected if the TOC was slightly higher than TC within errors. The effective cation exchange capacity (ECEC) was measured according to the methods proposed by Hendershot and Duquette (1986). Briefly, samples were extracted by 0.1 M BaCl_2 unbuffered solution with a solid to solution ratio of 1:30 (w/v), and then ECEC was calculated from the charge equivalents of Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Al^{3+} , Fe^{3+} , and Mn^{2+} . ECEC was also measured by the hexamminecobalt trichloride solution-spectrophotometric method as suggested by the Chinese EPA (HJ889-2017). The results of the two methods showed very close values; thus, only the results from the BaCl_2 method were reported in this study.

Single-step chemical extraction and analysis

To determine the mobile and mobilizable pools of Cd in the local soils, two commonly used single-step extraction approaches (CaCl_2 and EDTA) were conducted (Rivera et al. 2016; Ma et al. 2020). Briefly, for each extraction, 2 g of soil powder was weighed into a 50-mL centrifuge tube, and then 20 mL 0.01 M CaCl_2 or 0.05 M EDTA (pH = 7) were pipetted into the tube. The suspensions were shaken in a horizontal shaker for 2 h at room temperature. At the end of the extraction, the suspensions were centrifuged at 5000 rpm for 10 min. The supernatants were filtered through a 0.45- μm filter membrane, acidified by HNO_3 , and then analyzed

by ICP-MS (Agilent 7700 \times , USA) in the SKLEG. Blank controls were used to confirm no Cd contamination from the experimental procedures.

Data processing and calculation

Origin 9.0 (OriginLab Corporation, USA) was used for figure production and linear fitting of the collected data. Statistical analysis was performed by IBM SPSS Statistics 23.0 (International Business Machines Corporation, USA). The level of Cd pollution in the soils was assessed based on various indexes, including the pollution factor (P_i), geoaccumulation index (I_{geo}), and enrichment factor (EF), each of which can be categorized into different pollution classes.

Pollution factor

The pollution index, which is commonly used to reveal the soils with metals exceeding the risk screening value, was calculated according to the Technical Specification for Soil Environmental Monitoring (HJ/T 166–2004):

$$P_i = C_i/C_s \quad (1)$$

where C_i is the measured concentration of Cd and C_s is the screening value of Cd, which is 0.3 mg/kg for soil pH ≤ 7.5 and 0.6 mg/kg for soil pH > 7.5 for upland fields (GB 15, 618–2018).

Geoaccumulation index

The geoaccumulation index (I_{geo}), which has been used to evaluate the pollution level of heavy metals in naturally occurring polluted soils in previous studies (Liu et al. 2015; Duan et al. 2020), was calculated according to Müller (1969):

$$I_{\text{geo}} = \log_2(C_i/1.5B_i) \quad (2)$$

where C_i is the measured total concentration of Cd, B_i is the background value of Cd in soils, and 1.5 is a correction coefficient for natural fluctuation and anthropogenic influences (Wei and Yang 2010; Liu et al. 2015). The screening of background values for Cd in the study area is a challenge due to the unique geochemical background and spatial variance of concentrations. Therefore, the average concentration of Cd (0.293 mg/kg) in 9739 surface soil samples (0–20 cm) from Chongqing city (Hou et al. 2020) was used in this study. I_{geo} was categorized into seven levels according to Müller (1969): uncontaminated ($I_{\text{geo}} \leq 0$), uncontaminated to moderately contaminated ($0 < I_{\text{geo}} \leq 1$), moderately contaminated ($1 < I_{\text{geo}} \leq 2$), moderately to heavily contaminated ($2 < I_{\text{geo}} \leq 3$), heavily contaminated ($3 < I_{\text{geo}} \leq 4$), heavily to

extremely contaminated ($4 < I_{\text{geo}} \leq 5$), and extremely contaminated ($I_{\text{geo}} > 5$).

Enrichment factor

The enrichment factor (EF) can be used to evaluate the anthropogenic and/or biogenic disturbance of trace metals relative to the initial background (Sucharova et al. 2012). Although heterogeneous geochemical composition and biogeochemical processes may interfere the application of EF in source distinguishing (Reimann and de Caritat 2005), it is still a useful index to reveal the enrichment of Cd in soils when local background was used for calculation to constrain uncertainty. In this study, EF was calculated for comparison with P_i and I_{geo} . Titanium (Ti) was chosen as the reference element due to its immobile nature during weathering processes (Reimann and de Caritat 2005). The EF was calculated as:

$$EF = (\text{Cd/Ti})_{\text{sample}} / (\text{Cd/Ti})_{\text{background}} \quad (3)$$

The average concentrations of Cd (0.293 mg/kg) and Ti (0.456%) in the surface soils (0–20 cm) of Chongqing city (Hou et al. 2020) were selected as reference values to evaluate the enrichment of Cd in local soils.

Environmental availability

Environmental availability of heavy metals in soils includes the actual available pool dissolved in soil solution (mobile fraction) and the potential available fraction that is easily released (mobilizable fraction) (Kim et al. 2015). Generally, CaCl_2 extraction targets the mobile fraction of metals

in soil, which is mostly soluble and available for plant uptake (Voegelin et al. 2008; Rivera et al. 2016; Ma et al. 2020). The EDTA extraction probes the mobilizable fraction, including water-soluble, exchangeable, organic-bound Cd, and may also include the carbonate fraction (McLaughlin et al. 2000; Anju and Banerjee 2011; Rivera et al. 2016). In this study, the mobile and mobilizable fractions of Cd and their impacting factors were discussed.

Results and discussion

Soil properties and Cd concentrations

The physical–chemical parameters and concentrations of selected major elements are listed in Table 1. Soils had heterogeneous geochemical compositions, with pH values ranging from 4.43 to 7.59, and show a significantly positive correlation with Ca concentration ($r = 0.550$, $p < 0.01$). The soils were categorized as acidic soils ($\text{pH} \leq 6.5$, $N = 41$) or neutral soils ($\text{pH} > 6.5$, $N = 10$) for discussion. TIC ranged from below the detection limit to 3.02%, and the average TIC of neutral soils (0.95%) was higher than that of acidic soils (0.39%). TOC ranged from 0.41 to 3.93%, with an average value (1.70%) higher than the average of surface soils from Chongqing (0.95%, Hou et al. 2020) but lower than that of Chinese surface soils (2.48%, Liang et al. 2019). ECEC had a large range, from 3.98 to 16.0 cmol/kg, with a higher average value in the neutral group (12.3 cmol/kg) than in the acidic group (8.47 cmol/kg), and displayed a significantly positive relationship with pH ($r = 0.594$, $p < 0.01$), suggesting the importance of variable charges. The collected soil samples had similar concentrations of Mg and Fe, slightly

Table 1 The physical–chemical parameters and concentrations of major elements of the collected soils

Soils	Statistics	pH	TS	TIC	TOC	ECEC	Al	Ca	Mg	Fe	Mn
		/	%	%	%	cmol/kg	%	%	%	%	mg/kg
All soil ($N = 51$)	Min	4.43	0.02	n.d	0.41	3.98	3.32	0.18	0.52	1.85	148
	Max	7.59	0.27	3.02	3.93	16.0	7.5	6.79	1.49	4.12	943
	Average	5.97	0.07	0.51	1.70	9.22	5.45	0.80	0.86	2.91	344
	Median	5.94	0.06	0.34	1.66	8.82	5.35	0.45	0.85	2.83	309
	SD	0.70	0.06	0.85	0.62	3.18	0.80	1.33	0.21	0.53	172
Acidic soil ($\text{pH} \leq 6.5$, $N = 41$)	Min	4.43	0.02	n.d	0.41	3.98	4.39	0.18	0.52	1.85	148
	Max	6.42	0.27	1.02	3.93	16.0	6.94	1.07	1.49	4.03	769
	Average	5.71	0.08	0.39	1.74	8.47	5.52	0.45	0.85	2.91	304
Neutral soil ($\text{pH} > 6.5$, $N = 10$)	Min	6.65	0.02	n.d	0.78	8.82	3.32	0.31	0.57	1.85	287
	Max	7.59	0.23	3.02	2.83	15.9	7.50	6.79	1.45	4.12	943
	Average	7.03	0.07	0.95	1.55	12.3	5.19	2.26	0.90	2.88	507
Chinese soil ^a	Average	/	/	/	/	/	6.62	1.54	0.78	2.94	583
Chongqing soil ^b	Average	/	/	/	0.95	/	7.61	1.23	1.07	3.60	579

^aWei et al., 1991

^bHou et al., 2020

higher Al, and lower Ca and Mn relative to the Chinese soil background (Wei et al. 1991).

The total concentrations of Cd (Cd_{Tot}) ranged from 0.83 to 21.6 mg/kg, with an average of 5.20 mg/kg (Table 2). Cd_{Tot} in these soils was significantly higher than the background value of Chinese soil and the average of world soils, which were 0.097 mg/kg and 0.40 mg/kg, respectively (Wei et al. 1991; Adriano 2001). The average Cd_{Tot} in our soils was significantly higher than that in natural soils derived from gray shale at Appalachian Mountains ($Cd_{Tot} < 1$ mg/kg in most of samples, Richardson et al. 2022), and that in surface soils developed on black shale in Nigeria (Cd_{Tot} : 0.03–0.56 mg/kg, Nganje et al. 2020) and Guangxi of China (Cd_{Tot} : 0.12–5.46 mg/kg, Duan et al. 2020). But it is comparable to residual soils developed on shale in Santa Monica Mountains of California (average of 7.5 mg/kg, Lund et al. 1981). This is most likely to be the results of different Cd concentrations in parent rocks. The Cd_{Tot} in acidic soils (0.83 to 21.6 mg/kg, average of 5.71 mg/kg) had wider range and higher average than that in neutral soils (1.22 to 8.82 mg/kg, average of 3.09 mg/kg; Fig. 1). The extremely acidic soils contained relatively low Cd_{Tot} , which could be attributed to low sorption of Cd on soil minerals at low pH (Loganathan et al. 2012; Huang et al. 2020). Although a higher pH would favor the stabilization of metals, our results showed that some samples with high pH had relatively lower Cd concentrations. This may have been influenced by the limitation of surface sites and competitive adsorption. As shown in Fig. S2 and Table S1, other heavy metals (e.g., Zn, Cu, Cr, and Ni) had high concentrations (average of Zn, Cu, Cr, and Ni was 457 mg/kg, 91.8 mg/kg, 151 mg/kg, and 85.7 mg/kg, respectively), and they were positively correlated with Cd. The sorption edge of Cd is lower than that of other metals (e.g., Zn, Cu, and Co) in soil minerals (Loganathan et al. 2012), and the affinity of soils for Cd is

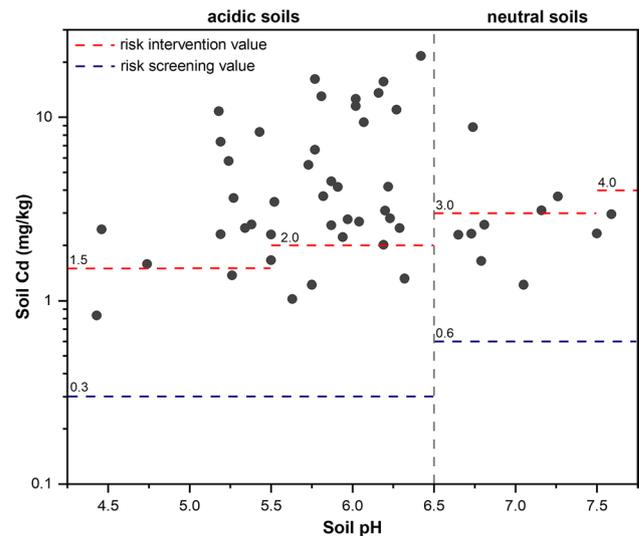


Fig. 1 The soil Cd concentration in acidic and neutral soils

lower than that of some metals (e.g., Pb and Cu, Morera et al. 2001).

Compared with the risk control standard for soil contamination of agricultural land in China (GB 15, 618–2018), all collected samples exceeded the risk screening value for upland soils, which was 0.3 mg/kg for soil with $pH \leq 7.5$ and 0.6 mg/kg for soil with $pH > 7.5$. The pollution factor P_i ranged from 2.77 to 72 with an average of 17.2; 68.6% of the samples exceeded the risk intervention value, which was 1.5 mg/kg for soil with $pH \leq 5.5$, 2.0 mg/kg for $5.5 < pH \leq 6.5$, 3.0 mg/kg for $6.5 < pH \leq 7.5$ and 4.0 mg/kg for soil with $pH > 7.5$ (Fig. 1). I_{geo} ranged from 0.92 to 5.62 with an average of 3.08. According to the categorization, 15.7% of the collected samples were moderately contaminated, 23.5% of them were heavily contaminated, and

Table 2 Total and extractable Cd in soils from the study area

Soil	Statics	Total Cd	CaCl ₂ extractable Cd	CaCl ₂ extractability	EDTA extractable Cd	EDTA extractability
		mg/kg	mg/kg	%	mg/kg	%
All soil (N=51)	Min	0.83	0.001	0.07	0.26	22.0
	Max	21.6	1.28	38.9	8.82	115
	Average	5.20	0.24	5.94	2.18	47.8
	Median	2.96	0.12	1.60	3.75	43.5
	SD	4.73	0.25	7.54	1.69	19.8
Acidic soil (pH ≤ 6.5, N=41)	Min	0.83	0.007	0.15	0.26	22.0
	Max	21.6	1.28	38.9	8.82	115
	Average	5.71	0.28	7.12	2.37	48.9
Neutral soil (pH > 6.5, N=10)	Min	1.22	0.001	0.07	0.34	25.4
	Max	8.82	0.11	3.96	3.94	70.0
	Average	3.09	0.03	1.09	1.40	43.5

5.9% of them were extremely contaminated. No mining or industrial activities were observed in the study area during field investigation. Previous geochemical survey (personal communication) in this area showed that the average input flux of Cd through atmospheric deposition is $2.49 \text{ g/hm}^2\text{-a}$, much lower than that in urban area of Chongqing City ($10.09 \text{ g/hm}^2\text{-a}$), suggested that Cd contamination originate from atmosphere could be excluded. Phosphate fertilizer is a potential Cd source in agricultural soils, but it usually resulted in slight enrichment and uniform distribution of Cd in soils (Bigalke et al. 2017); this was not observed in soil of the study area. In the rural area without obvious anthropogenic pollution, parent material dominated concentrations of heavy metals in soils (Lund et al. 1981; Zinn et al. 2020). Heterogeneous Cd concentrations ($0.44\text{--}64.3 \text{ mg/kg}$, Cheng and Cheng 2012; Liu et al. 2021b) in parent rocks of the study area explained the wide range and high Cd_{Tot} in local soils. Therefore, soil Cd contamination in the study area was attributed to geogenic enrichment of Cd. The results of these risk assessments indicate that these soils have potential risks to the eco-environmental system and that the consumption of food crops cultivated in these soils may have adverse impacts on human health. Therefore, stringent control strategies are necessary for most agricultural fields in the study area.

Retention of Cd in black shale–derived soils

The geogenic Cd from parent rocks, at least a large fraction of it, was retained in weathered soils and resulted in geogenic enrichment in the study area. The *EF* in the collected soils ranged from 3.19 to 100, with an average of 23.0; average *EFs* were 25.4 and 13.2 in acidic and neutral soils, respectively. The fate of metals during weathering is dependent on the host minerals, stability of secondary phases, and association between metals and secondary minerals (Tuttle

et al. 2009). In black shale, Cd might be hosted in sulfides (pyrite and sphalerite), adsorbed by clay minerals such as illite, combined with Fe oxides and carbonate (Lavgren et al. 2009; Tuttle et al. 2009; Liu et al. 2021a). Among these, clay minerals and Fe oxides could be mechanically inherited by the weathered soils via clastic particles, then Cd in these fractions was retained in soils (Tuttle et al. 2009; Ling et al. 2018; Richardson et al. 2022). In contrast, sulfides and carbonates is reactive during weathering, and Cd is likely to be released into solution. In this case, Cd may deplete in the weathered materials, such as lower Cd concentration in weathered zone compared to fresh rock observed in Devonian and Mississippian black shale (Tuttle et al. 2009; Perkins and Mason 2015). However, dissolved Cd also could be associated with secondary minerals (e.g., Fe–Mn oxides and phyllosilicates commonly observed in weathering profile of black shale) under circumneutral condition (Tuttle et al. 2009; Peng et al. 2014). Because pyrite could transform into Fe (hydr)oxides during weathering (Prommer et al. 2018), which is an important scavenger for Cd in soils at pH close to neutral. The acidic conditions resulting from pyrite oxidation could favor the transformation of muscovite and feldspar into secondary phyllosilicates (Ling et al. 2018) that provide surface sites for Cd adsorption. These geochemical processes would favor the retention of Cd in soils. Under neutral pH, dissolved Cd may even react with certain anions (e.g., CO_3^{2-} and PO_4^{3-}) and precipitate directly in soils (Kabata-Pendias and Pendias 2001; Xia et al. 2020). Additionally, oxidized kerogen in black shale and modern plant litter in weathered soils may also favor the retention of Cd (Tuttle et al. 2009; Derkowski and Marynowski 2018).

Based on correlation analysis (Fig. 2), the concentrations of Fe and Al were positively correlated ($r = 0.702$), Cd and Al were negatively correlated ($r = -0.402$), and Ca and Al were negatively correlated ($r = -0.455$, not shown

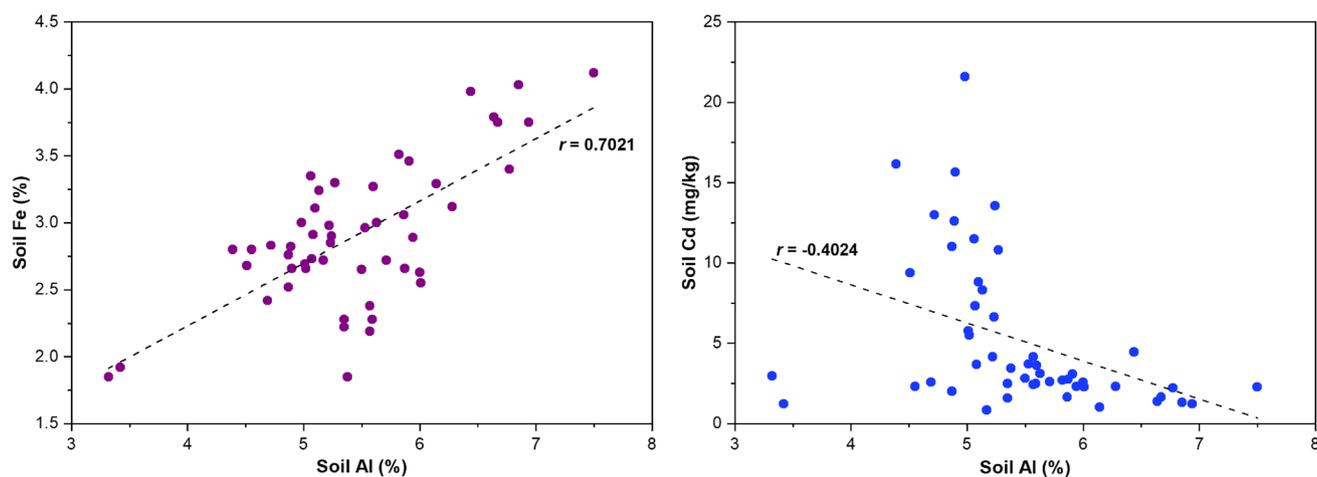


Fig. 2 The relationship between Cd and Fe and Al (**a** total Fe vs total Al; **b** total Cd vs total Al)

in Fig. 2). The relationships between Al, Ca, and Fe in the soils were reasonable because during weathering, Fe and Al remain in the residual fraction due to their immobile nature, whereas Ca is prone to release at an early stage (Ling et al. 2015; Wen et al. 2020a). However, the negative correlation between Cd and Al was unexpected, because positive relationship between Cd and Al_2O_3 was observed in carbonate derived soils (Wen et al. 2020a; Xia et al. 2020). This result may indicate that Cd in black shale-derived soils was prone to deplete during long-term weathering due to the acidic environment caused by oxidizing of sulfide, although elevated Cd was observed in these soils. Further research on profile is needed to quantify the retention and loss of Cd during weathering and to recognize the dominated process contribute to Cd enrichment in these soils.

Spatial heterogeneity of geogenic Cd in soils

The data from this study and those reported in previous studies (summarized in Table 3) were combined to reveal the characteristics of geogenic Cd in black shale- and carbonate-derived soils. Generally, sedimentary rocks with elevated Cd are mainly composed of carbonate and black shale, although strata differ. Cd_{Tot} in carbonate rocks is generally lower than 5 mg/kg, whereas those in black shale can be up to 104 mg/kg. Therefore, Cd_{Tot} in black shale-derived soils reaches a much higher value than that in soils derived from carbonate rocks. A regional survey from southwestern China showed that the average Cd_{Tot} in 308 terra rossa samples was 1.49 mg/kg (Wen et al. 2020a), which was much lower than the results of this study (5.20 mg/kg). In fact, Cd_{Tot} in these soils derived from black shale was even higher than that in some anthropogenically contaminated soils. For example, Cd_{Tot} in the soils in the industrial area of Zhejiang Province

ranged from 0.11 to 2.57 mg/kg (Ma et al. 2020), and Cd_{Tot} in acid mine drainage-contaminated paddy soils ranged from 0.22 to 1.6 mg/kg (Yu et al. 2016).

Cd_{Tot} in these soils showed significant spatial heterogeneity. The minimum and maximum values of Cd_{Tot} differed by two orders of magnitude in this study, and similar results have also been reported in other regions with naturally occurring Cd enrichment (Table 3). This is different from anthropogenic pollution. Cd_{Tot} in many anthropogenically polluted soils, particularly from nonpoint sources, tends to change in a narrow range. For example, Cd_{Tot} in agricultural soils in Switzerland, where the major source of Cd was fertilizer, had a median of 0.10 mg/kg with a variation lower than 1 mg/kg (Bigalke et al. 2017), and Cd_{Tot} in soils affected by acid mine drainage ranged from 1.02 to 3.82 mg/kg (Liao et al. 2016). In addition, there is no obvious trend at the scale of a small basin (Liu et al. 2021b) but highly depends on the lithology and soil maturity at a large regional scale (Wen et al. 2020a). However, for some point sources (e.g., mining and smelting), the soil Cd concentration generally has a “hot spot” and diffuses toward one or several directions (Wei et al. 2009). The spatial heterogeneity of Cd_{Tot} in these soils is most likely to be controlled by the following factor. First, the heterogeneity of Cd in parent rocks plays a vital role. Cd_{Tot} in rocks differs in different strata and even has high heterogeneity in different layers of the same stratum. For instance, Cd_{Tot} in lower Cambrian black shales collected in the study area ranged from 0.13 to 64.3 mg/kg (Cheng and Cheng 2012), and Cd_{Tot} ranged from 0.16 to 74.21 mg/kg in black shale from the lower Cambrian Niutitang Formation (Deng et al. 2015). This effect may be magnified in the mountainous area in southwestern China because multiple strata may crop out at different altitudes (Liu et al. 2013). Additionally, as discussed above, the variance of Cd-bearing

Table 3 Summary of reported rocks and soils with elevated Cd

Region	Stratum	Lithology	Rock Cd (mg/kg)	Soil Cd (mg/kg)	References
France	Jurassic	Carbonate	0.08–0.52	0.28–2.86 (1.24)	Rambeau et al. 2010
Switzerland	Jurassic	Carbonate	0.03–4.91	0.33–2.00 (0.82)	Quezada-Hinojosa et al. 2009
Guangxi, China	Carboniferous, Permian, etc	Carbonate	0.09–1.54	0.12–17.9 (1.49 ± 2.08)	Wen et al. 2020a
Japan	Triassic, Permian	Carbonate	0.17–2.41	–	Aizawa and Akaiwa 1992
Jamaica	Late-Miocene or Pliocene	Phosphorites	771–6200	142–771 (638)	Garrett et al. 2008
California, USA		Shale	0.85–33	0.59–22 (8)	Lund et al. 1981
America	Devonian	Black shale	2–48	–	Perkins and Mason 2015
Korea	Precambrian or Palaeozoic	Black shale	0.4–36	0.2–20.1 (0.93)	Lee et al. 1998
Chongqing, China	Permian	Black shale	0.37–21	0.42–42 (7.1)	Liu et al. 2013
Chongqing, China	Cambrian	Black shale	0.44–64.3	0.44–64.5 (9.36)	Cheng and Cheng 2012; Liu et al. 2021a, 2021b
Guangxi, China	Carboniferous, Devonian	Black shale	0.13–17.9	Average of 0.96	Duan et al. 2020
Zhejiang, China	Ordovician, Cambrian	Black shale	0.06–104	0.07–13.03 (0.81)	Zhao et al. 2018
Hunan, China	Cambrian	Black shale	0.16–74.2	–	Deng et al. 2015

fractions and mineral assembly in parent rocks may also contribute to the heterogeneity, because the fate of Cd differs during weathering. Second, because geogenic Cd enters into soils during the initial weathering stage, other natural factors that impact weathering and soil development will induce the spatial heterogeneity of Cd in soils, such as soil maturity resulting from different climates (Quezada-Hinojosa et al. 2009; Wen et al. 2020a) and variations in topography (Xia et al. 2020; Liu et al. 2021b). In the study area, residual soils from the sloping sites had higher Cd_{Tot} than soils from flat sites (Liu et al. 2021b). Cadmium is likely to be depleted in soils with high maturity (Fig. 2). Furthermore, the geochemical fraction of Cd in soils may also be influenced by these natural factors; for example, the percentage of Cd in the carbonate fraction increases in Cambisols with a weaker degree of weathering and higher Ca pools (Quezada-Hinojosa et al. 2015; Wen et al. 2020a), and the proportion of mobile Cd is higher in soils from alluvium than in those from upland eluvium (Xia et al. 2020).

Environmental availability of Cd in soil and the controlling factors

The $CaCl_2$ extractable pool represents the actually available Cd, which is mostly soluble and available for plant uptake (Rivera et al. 2016; Ma et al. 2020), with important environmental significance. The concentration of $CaCl_2$ extractable Cd (mobile Cd) ranged from 0.001 to 1.28 mg/kg (average of 0.24 mg/kg), with an average of 0.28 mg/kg in acidic soils and 0.03 mg/kg in neutral soils (Table 2). This result is comparable to the black shale-derived soils in Zhejiang Province of China (Zhao et al. 2018), where 0.01 M $CaCl_2$ extractable Cd ranges from 0.003 to 1.75 mg/kg (average of 0.22 mg/kg). Average extractability of Cd accounted for 7.12% of Cd_{Tot} in acidic soils, which was significantly higher than that in neutral soils (1.09%), with a maximum percentage of 38.9% in acidic soils. Extractability of our soils was lower than the soils reported by Zhao et al. (2018), which showed extractability ranging from 0.33 to 37.2% (average of 15.86%). However, the extractability of Cd in these black shale-derived soils was significantly higher than that in soils developed on carbonate. A previous study on soils from karst region in Guangxi of China showed that the median of 0.01 M $CaCl_2$ extractability was 1.9% for Cd ($N=278$, Wen et al. 2020b). It was significantly lower than most of our soils, but comparable to the results of neutral soils in this study. Low exchangeable fraction of Cd in carbonate-derived soils was also observed in other studies (Quezada-Hinojosa et al. 2015; Xia et al. 2020). Additionally, our results were obviously higher than those reported by Rivera et al. (2016) in which geogenically polluted soils had $CaCl_2$ extractability less than 5% and an average below 2%. These results indicated high availability of Cd in black shale-derived soils

(particularly acidic soils) compared to soils derived from carbonate. The high Cd_{Tot} and extractability would produce more available Cd for plant than that in carbonate-derived soils; this of course will result in elevated concentration of Cd in crops, particularly for the leafy vegetables which tend to accumulate Cd.

The Fig. 3a, b, and c show that the concentration of extracts was positively related to Cd_{Tot} ($r=0.604$) but negatively related to soil pH ($r=-0.349$) and ECEC ($r=-0.454$). However, the relationship was slightly changed when extractability ($Cd_{CaCl_2}\%$) was applied in the fitting, and the Pearson's coefficients were -0.209 for $Cd_{CaCl_2}\%$ vs Cd_{Tot} , -0.631 for $Cd_{CaCl_2}\%$ vs pH, and -0.647 for $Cd_{CaCl_2}\%$ vs ECEC. The mobile pool includes water-soluble and nonspecifically adsorbed Cd (Rivera et al. 2016); thus, a lower pH would favor the release of Cd from solids into solution in soils, which was documented by this study (Fig. 3b) and previous studies (e.g., Pueyo et al. 2004; Kim et al. 2015; Liu et al. 2018), indicating the important role of pH on mobile Cd. However, the negative correlation with ECEC was inconsistent with a previous study in which a positive correlation coefficient was reported (Pueyo et al. 2004). Usually, a higher CEC indicates more sites for metal adsorption, and nonspecifically absorbed metals could be exchanged by cations. The difference between CEC and ECEC is likely to be an important reason. The ECEC was highly associated with soil pH in this study, which indicates that ECEC increased with increasing pH, but mobile Cd decreased with increasing pH. These results suggested that pH was probably the dominant factor controlling mobile Cd, subsequently influencing the uptake of Cd by rice and vegetables (Liu et al. 2018; Wen et al. 2020b). In conclusion, the high availability of Cd and low pH was likely to be the most important reason for the elevated Cd concentrations in vegetables observed in black shale region in previous studies (Lee et al. 1998; Liu et al. 2015).

The EDTA extractable Cd (mobilizable Cd) ranged from 0.26 to 8.82 mg/kg, with an average of 2.37 mg/kg in acidic soils and 1.40 mg/kg in neutral soils. This pool accounted for 22.0 to 100% (115% within error) of Cd_{Tot} . Although the concentration of EDTA-extractable Cd was strongly correlated with total Cd ($r=0.865$, Fig. 3d), the extractability showed a negative correlation with total Cd ($r=-0.335$, not shown in Fig. 3). The EDTA extractable Cd concentrations and extractability showed very weak correlations with pH ($r=-0.034$) and ECEC ($r=0.162$) (Fig. 3e, f). The mobilizable pool includes water-soluble, exchangeable, organic-bound Cd and may also include the carbonate fraction but will not attack the aluminosilicates and crystalline iron oxides in short-term reactions (Anju and Banerjee 2011; Ma et al. 2020), accounting for the actual mobile and potentially mobile pool of Cd in soil. The weak correlation with pH and ECEC was likely the result of comprehensive

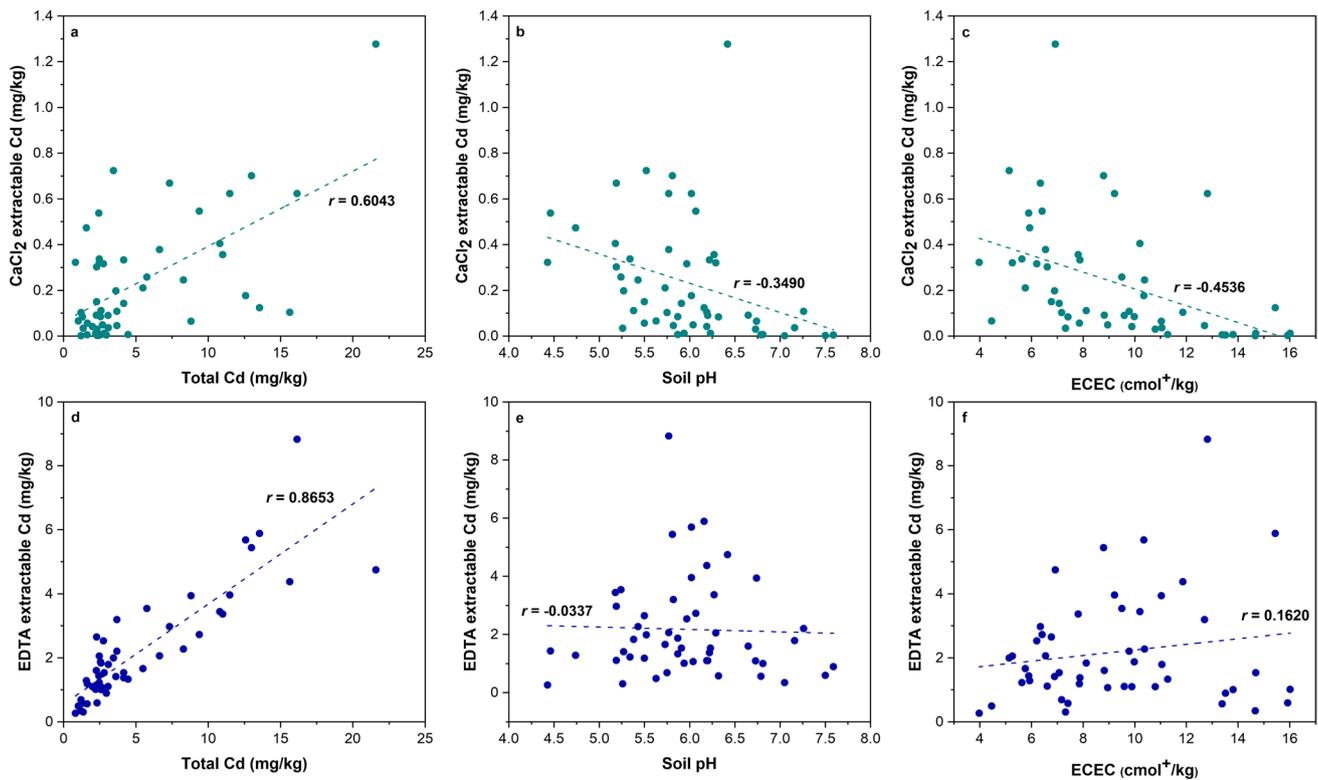


Fig. 3 The relationship between extractable Cd and major soil parameters (a CaCl_2 extractable Cd vs total Cd; b CaCl_2 extractable Cd vs soil pH; c CaCl_2 extractable Cd vs ECEC; d EDTA extractable Cd vs total Cd; e EDTA extractable Cd vs soil pH; f EDTA extractable Cd vs ECEC)

controlling factors, such as soil carbonate and organic matter, because these fractions contribute to extractable Cd. These results were consistent with geochemical partitioning, which showed that exchangeable and carbonate fractions dominated Cd in soils (Liu et al. 2021b). The results indicated a large pool of mobilizable Cd (average of 47.8%) in the local soils, which could be released into soil solution when the soil acidified, ionic strength changed, and organic matter decomposed.

The ratio of CaCl_2 to EDTA extractable Cd in the collected soils ranged from 0.0029 to 1.22 (average of 0.13), suggesting that approximately 13% of Cd in the mobilizable pool was labile and could be taken up by plants, which indicates that there is a large potential pool (0–8.2 mg/kg, average of 1.98 mg/kg) of mobile Cd in these soils. The ratio showed a negative correlation with pH ($r = -0.694$, Fig. 4), suggesting that the lability of mobilizable Cd decreased with increasing pH. At extreme acidity (pH < 4.5), approximately 40% and 100% were labile, indicating a very high lability in acidic soils. Additionally, these results also partly explain the relatively low concentration of Cd in acidic soils (Fig. 1). The high lability of Cd in geogenically contaminated soils was comparable to or even higher than that of anthropogenic contamination. This phenomenon deserves more attention because some studies have proposed that the lability of Cd

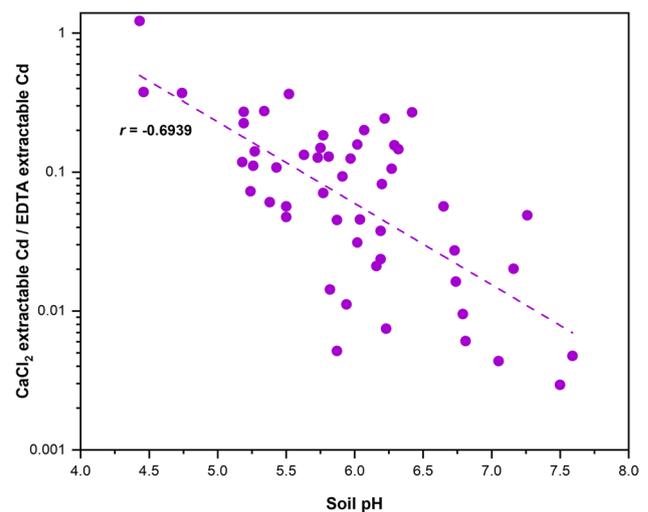


Fig. 4 The ratio of CaCl_2 extractable Cd to EDTA extractable Cd versus soil pH

from geogenic sources is lower than that from anthropogenic sources (Chlopecka 1996; Alexakis et al. 2019). But this may not be the case in black shale–derived soils in our study area and the others. Furthermore, the acid generated

during weathering of black shale may lead to soil acidification, which would increase the lability of Cd.

Conclusion and implications

The enrichment, environmental availability of Cd and the controlling factors in soils developed on Cd-rich black shales in southwestern China were studied. The results showed that Cd has enriched in these soils (0.83–21.6 mg/kg, average of 5.20 mg/kg), exceeding the risk screening value for Chinese agricultural soils and presenting a serious pollution situation. Physical inheritance and association with secondary phases may contribute to the geogenic enrichment of Cd in local soils. The geogenic Cd in soils showed obvious heterogeneity, particularly in soils derived from black shale, which was likely to be dominated by natural factors such as the geochemical composition of the parent rock and topography. High environmental availability of Cd was observed in the studied soils. Mobile Cd accounted for 5.94% (0.07–38.9%) of Cd in soils and was controlled by soil pH. Mobilizable Cd accounted for 47.8% (22.0–100%) in the studied soils and was controlled by multiple factors (e.g., carbonate, organic matter, and clay minerals in the soils). The lability of Cd decreased with increasing pH, and a large potential pool of mobile Cd existed in the soils.

In southwestern China, black shale with an extensive outcrop area (Yu et al. 2012) has developed many mineral deposits of nonferrous metals (Fan et al. 2004). Therefore, the natural weathering and mining activities of these rocks have a significant contribution to the geogenic enrichment of Cd in surface soils, in addition to weathering of carbonate rocks. The results of this study indicated that Cd in black shale-derived soils has high environmental availability, particularly in acidic soils. Soil acidification resulting from black shale weathering, soil development, and intensive cultivation may aggravate the situation by significantly increasing lability. This study proposed the significance of understanding the regional geochemical background and natural factors that control the enrichment and availability of Cd in soils, and provided a perspective for pollution control and land management in areas with high geochemical background of Cd.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11356-021-18008-x>.

Acknowledgements Liang Ma and Haiyan Chen are acknowledged for their help with laboratory work.

Author contribution Yizhang Liu: investigation, methodology, writing, and visualization. Zijie Chen: investigation. Tangfu Xiao: supervision, funding acquisition. Zhengjie Zhu: investigation. Shuyu Jia: review and editing. Jing Sun: data discussion, editing. Zengping Ning:

investigation, Ting Gao: investigation. Chengshuai Liu: review and editing, supervision, funding acquisition.

Funding This work was funded by the National Natural Science Foundation of China (41773142, U1612442, and 42025705), the Science and Technology Foundation of Guizhou Province ([2018]1177 and [2017]1195), the Youth Innovation Promotion Association of the Chinese Academy of Sciences (2021399), and the Bureau of Human Resources and Social Security of Guizhou Province ([2020]10).

Data availability The datasets used or analyzed in the current study are available from the corresponding author on reasonable request.

Declarations

Ethical approval Not applicable.

Consent to participate Not applicable.

Consent to publish Not applicable.

Competing interests The authors declare no competing interests.

References

- Adriano DC (2001) Trace elements in terrestrial environments: biogeochemistry, bioavailability, and risk of metals. 2nd Edition. Vol. 1. Springer, New York
- Aizawa S, Akaiwa H (1992) Cadmium contents of Triassic and Permian limestones in central Japan. *Chem Geol* 98:103–110
- Alexakis D, Gamvroula D, Theofili E (2019) Environmental availability of potentially toxic elements in an agricultural Mediterranean site. *Environ Eng Geosci*. XXV:169–178
- Anju M, Banerjee DK (2011) Associations of cadmium, zinc, and lead in soils from a lead and zinc mining area as studied by single and sequential extractions. *Environ Monit Assess* 176:67–85
- Bigalke M, Ulrich A, Rehmus A, Keller A (2017) Accumulation of cadmium and uranium in arable soils in Switzerland. *Environ Pollut* 221:85–93
- Chen HY, Teng YG, Lu SJ, Wang YY, Wang JS (2015) Contamination features and health risk of soil heavy metals in China. *Sci Total Environ* 512–513:143–153
- Cheng J, Cheng LJ (2012) The concentrations of heavy metals in the lower Cambrian black rock series in Chengkou District, Chongqing and their environmental effects. *Earth and Environment* 40(1):93–99 ((in Chinese with English abstract))
- Chlopecka A (1996) Assessment of form of Cd, Zn and Pb in contaminated calcareous and gleyed soils in Southwest Poland. *Sci Total Environ* 188:253–262
- Deng YN, Guo QJ, Zhu MY, Zhang JM (2015) Trace element geochemistry characteristics of Niutitang Formation from Lower Cambrian Black Rock Series in Western Hunan. *Bulletin of Mineralogy, Petrology and Geochemistry* 34:410–418 ((in Chinese with English abstract))
- Derkowski A, Marynowski L (2018) Binding of heavy metals by oxidized keroen in (palaeo)weathered black shales. *Chem Geol* 493:441–450
- Duan YR, Yang ZF, Yu T, Yang Q, Liu X, Ji WB, Jiang HY, Zhuo XX, Wu TS, Qin JX, Wang L (2020) Geogenic cadmium pollution in multi-medians caused by black shales in Luzhai, Guangxi. *Environ Pollut*. 260:113905

- Fan DL, Zhang T, Ye J (2004) Black shale and related mineral deposits in China. Science Press, Beijing
- Food and Agriculture Organization of the United Nations (FAO) (2018) Soil pollution: a hidden reality. Rome.
- Garrett RG, Porter ARD, Hunt PA, Lalor GC (2008) The presence of anomalous trace element levels in present day Jamaican soils and the geochemistry of Late-Miocene or Pliocene phosphorites. *Appl Geochem* 23:822–834
- GB 15618–2018. Soil environmental quality risk control standard for soil contamination of agricultural land. Ministry of Ecology and Environment of the People's Republic of China
- Gupta SK, Vollmer MK, Krebs R (1996) The importance of mobile, mobilisable and pseudo total heavy metal fractions in soil for three-level risk assessment and risk management. *Sci Total Environ* 178:11–20
- Hendershot WH, Duquette M (1986) A simple barium chloride method for determining cation exchange capacity and exchangeable cations. *Soil Sci Soc Am J* 50:605–608
- HJ 889–2017. Soil quality–determination of cation exchange capacity (CEC) –hexaminecobalt trichloride solution–spectrophotometric method. Ministry of Ecology and Environment of the People's Republic of China
- HJ/T 166–2004 (2004) The technical specification for soil environmental monitoring. Ministry of Ecology and Environment of the People's Republic of China
- Hou QY, Yang ZF, Yu T, Xia XQ, Cheng HX, Zhou GH (2020) Soil geochemical dataset of China. Geological Publishing House, Beijing
- Huang HH, Wang J, Yao RN, Bostick BC, Prommer H, Liu XD, Sun J (2020) Effects of divalent heavy metal cations on the synthesis and characteristics of magnetite. *Chem Geol* 547:119669
- IUSS Working Group, W.R.B., 2006. World reference base for soil resources 2014, update 2015 International soil classification system for naming soils and creating legends for soil maps. *World Soil Resources Reports* 106. FAO, Rome
- Ji HB, Wang SJ, Ouyang ZY, Zhang S, Sun CX, Liu XM, Zhou DQ (2004) Geochemistry of red residua underlying dolomites in karst terrains of Yunnan-Guizhou Plateau: I. The formation of the Pingba profile. *Chem Geol* 203:1–27
- Kabata-Pendias A, Pendias H (2001) Trace element in soil and plants, 3rd edn. CRC Press, Boca Raton, USA
- Kim RY, Yoon JK, Kim TS, Yang JE, Owens G, Kim KR (2015) Bioavailability of heavy metals in soils: definitions and practical implementation—a critical review. *Environ Geochem Health* 37:1041–1061
- Lavergren U, Astrom ME, Bergback B, Holmstrom H (2009) Mobility of trace elements in black shale assessed by leaching tests and sequential chemical extraction. *Geochem: Explor Env, A* 9:71–79
- Lee JS, Chon HT, Kim KW (1998) Migration and dispersion of trace elements in the rock-soil-plant system in areas underlain by black shales and slates of the Okchon Zone, Korea. *J Geochem Explor* 65:61–78
- Liang ZZ, Chen SC, Yang YY, Zhao RY, Shi Z, Rossel RAV (2019) Baseline map of soil organic matter in China and its associated uncertainty. *Geoderma* 335:47–56
- Liao JB, Wen ZW, Ru X, Chen JD, Wu HZ, Wei CY (2016) Distribution and migration of heavy metals in soil and crops affected by acid mine drainage: public health implications in Guangdong Province, China. *Ecotox Environ Safe* 124:460–469
- Ling S, Wu X, Zhao S, Liao X (2018) Evolution of porosity and clay mineralogy associated with chemical weathering of black shale: a case study of Lower Cambrian black shale in Chongqing, China. *J Geochem Explor* 188:326–339
- Ling SX, Wu XY, Ren Y, Sun CW, Liao X, Li XN, Zhu BL (2015) Geochemistry of trace and rare earth elements during weathering of black shale profiles in Northeast Chongqing, Southwestern China: their mobilization, redistribution, and fractionation. *Chem Erde* 75:403–417
- Liu CS, Chang CY, Fei YH, Li FB, Wang Q, Zhai GS, Lei J (2018) Cadmium accumulation in edible flowering cabbages in the Pearl River Delta, China: critical soil factors and enrichment models. *Environ Pollut* 233:880–888
- Liu YZ, Chen ZJ, Ye TP, Zhu ZJ, Ning ZP, Xiao TF (2021a) Occurrences of toxic elements in upper Permian black shales at Wushan area and their environmental implication. *Bulletin of Mineralogy, Petrology and Geochemistry* 40(4):938–945
- Liu YZ, Xiao TF, Baveye P, Zhu JM, Ning ZP, Li HJ (2015) Potential health risk in areas with high naturally-occurring cadmium background in southwestern China. *Ecotoxicol Environ Saf* 112:122–131
- Liu YZ, Xiao TF, Ning ZP, Li HJ, Tang J, Zhou GZ (2013) High cadmium concentrations in soil in the Three Gorges region: geogenic source and potential bioavailability. *Appl Geochem* 37:149–156
- Liu YZ, Xiao TF, Perkins RB, Zhu JM, Zhu ZJ, Xiong Y, Ning ZP (2017) Geogenic cadmium pollution and potential health risks, with emphasis on black shale. *J Geochem Explor* 176:42–49
- Liu YZ, Xiao TF, Zhu ZJ, Ma L, Li H, Ning ZP (2021b) Geogenic pollution, fractionation and potential risks of Cd and Zn in soils from a mountainous region underlain by black shale. *Sci Total Environ* 760:143426
- Loganathan P, Vigneswaran S, Kandasamy J, Naidu R (2012) Cadmium sorption and desorption in soils: a review. *Critical Reviews in Environ Sci Technol* 42:489–533
- Lund LJ, Betty EE, Page AL, Elliott RA (1981) Occurrence of naturally high cadmium levels in soils and its accumulation by vegetation. *J Environ Qual* 10:551–556
- Ma Q, Zhao WF, Guan DX, Teng HH, Ji JF, Ma LQ (2020) Comparing CaCl₂, EDTA and DGT methods to predict Cd and Ni accumulation in rice grains from contaminated soils. *Environ Pollut* 260:114042
- McLaughlin MJ, Hamon RE, McLaren RG, Speir TW, Rogers S (2000) Review: a bioavailability-based rationale for controlling metal and metalloids contamination of agricultural land in Australia and New Zealand. *Aust J Soil Res* 38:1037–1086
- Morera MT, Echeverría JC, Mazkiarán C, Garrido JJ (2001) Isotherms and sequential extraction procedures for evaluating sorption and distribution of heavy metals in soils. *Environ Pollut* 113:135–144
- Müller G (1969) Index of geo-accumulation in sediments of the Rhine River. *GeoJournal* 2:108–118
- Nganje TN, Edet A, Cuthbert S, Adamu CI, Hursthouse AS (2020) The concentration, distribution and health risk from potentially toxic elements in the soil - plant - water system developed on black shales in SE Nigeria. *J Afr Earth Sci* 165:103806
- Nogawa K, Yamada Y, Honda R, Ishizaki M, Tsuritani I, Kawano S, Kato T (1983) The relationship between Itai-Itai disease among inhabitants of the Jinzu River basin and cadmium in rice. *Toxicol Lett* 17:263–266
- Nriagu JO, Pacyna JM (1988) Quantitative assessment of worldwide contamination of air, water and soils by trace elements. *Nature* 333:135–139
- Parviainen A, Luokola-Ruskeeniemi K (2019) Environmental impact of mineralized black shales. *Earth-Sci Rev* 192:65–90
- Peng B, Rate A, Song Z, Yu C, Tang X, Xie S, Tu X, Tan C (2014) Geochemistry of major and trace elements and Pb–Sr isotopes of a weathering profile developed on the Lower Cambrian black shales in central Hunan, China. *Appl Geochem* 51:191–203
- Perkins RB, Mason CE (2015) The relative mobility of trace elements from short-term weathering of a black shale. *Appl Geochem* 56:67–79
- Prommer H, Sun J, Helm L, Rathi B, Siade AJ, Morris R (2018) Deoxygenation prevents arsenic mobilization during deepwell

- injection into sulfide-bearing aquifers. *Environ Sci Technol* 52(53):13801–13810
- Pueyo M, López-Sánchez JF, Rauret G (2004) Assessment of CaCl_2 , NaNO_3 and NH_4NO_3 extraction procedures for the study of Cd, Cu, Pb and Zn extractability in contaminated soils. *Anal Chim Acta* 504:217–226
- Quezada-Hinojosa RP, Föllmi KB, Verrecchia E, Adatte T, Matera V (2015) Speciation and multivariable analyses of geogenic cadmium in soils at Le Gurnigel, Swiss Jura Mountains. *CATENA* 125:10–32
- Quezada-Hinojosa RP, Matera V, Adatte T, Rambeau C, Föllmi KB (2009) Cadmium distribution in soils covering Jurassic oolitic limestone with high Cd contents in the Swiss Jura. *Geoderma* 150:287–301
- Rambeau CMC, Baize D, Saby N, Matera V, Adatte T, Föllmi KB (2010) High cadmium concentrations in Jurassic limestone as the cause for elevated cadmium levels in deriving soils: a case study in Lower Burgundy, France. *Environ Earth Sci* 61:1573–1585
- Reimann C, de Caritat P (2005) Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factor. *Sci Total Environ* 337:91–107
- Richardson JB, Mischenko IC, Mackowiak TJ, Perdrial N (2022) Trace metals and metalloids and Ga/Al ratios in grey shale weathering profiles along a climate gradient and in batch reactors. *Geoderma* 405:115431
- Rivera MB, Giráldez MI, Fernández-Caliani JC (2016) Assessing the environmental availability of heavy metals in geogenically contaminated soils of the Sierra de Aracena Natural Park (SW Spain). Is there a health risk? *Sci Total Environ* 560–561:254–265
- Satarug S, Baker JR, Urbenjapol S, Haswell-Elkins M, Reilly PEB, Williams DJ, Moore MR (2003) A global perspective on cadmium pollution and toxicity in nonoccupationally exposed population. *Toxicol Lett* 137:65–83
- Sucharovà J, Suchara I, Hola M, Marikova S, Reimann C, Boyd R, Filzmoser P, Englmaier P (2012) Top-/bottom-soil ratios and enrichment factors: what do they really show? *Appl Geochem* 27:138–145
- Tuttle MLW, Breit GN, Goldhaber MB (2009) Weathering of the New Albany Shale, Kentucky: II. Redistribution of minor and trace elements. *Appl Geochem* 24:1565–1578
- Voegelin A, Tokpa G, Jacquat O, Barmettler K, Kretzschmar R (2008) Zinc fractionation in contaminated soils by sequential and single extractions: Influence of Soil Properties and Zinc Content. *J Environ Qual* 37:1190–1200
- Wei BG, Yang LS (2010) A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. *Microchem J* 94:99–107
- Wei CY, Wang C, Yang LS (2009) Characterizing spatial distribution and sources of heavy metals in the soils from mining-smelting activities in Shuikoushan, Hunan Province, China. *J Environ Sci* 21:1230–1236
- Wei FS, Chen JS, Wu YY, Zheng CJ (1991) Study on the background contents on 61 elements of soils in China. *Environ Sci* 12(4):12–19 (in Chinese with English abstract)
- Wen YB, Li W, Yang ZF, Zhang QZ, Ji JF (2020) Enrichment and source identification of Cd and other heavy metals in soils with high geochemical background in the karst region. Southwestern China. *Chemosphere* 245:125620
- Wen YB, Li W, Yang ZF, Zhu XX, Guan DX, Song YX, Guo C, Ji JF (2020) Evaluation of various approaches to predict cadmium bioavailability to rice grown in soils with high geochemical background in the karst region. Southwestern China. *Environ Pollut* 258:113645
- Xia XQ, Ji JF, Yang ZF, Han HJ, Huang CL, Li Y, Zhang W (2020) Cadmium risk in the soil-plant system caused by weathering of carbonate bedrock. *Chemosphere* 254:126799
- Yu CX, Peng B, Peltola P, Tang XY, Xie SR (2012) Effect of weathering on abundance and release of potentially toxic elements in soils developed on Lower Cambrian black shales, P.R. China *Environ Geochem Health* 34:375–390
- Yu HY, Liu CP, Zhu JS, Li FB, Deng DM, Wang Q (2016) Cadmium availability in rice paddy fields from a mining area: The effects of soil properties highlighting iron fractions and pH value. *Environ Pollut* 209:38–45
- Zhao FJ, Ma YB, Zhu YG, Tang Z, McGrath SP (2015) Soil contamination in China: current status and mitigation strategies. *Environ Sci Technol* 49:750–759
- Zhao WF, Song YX, Guan DX, Ma Q, Guo C, Wen YB, Ji JF (2018) Pollution status and bioavailability of heavy metals in soils of a typical black shale area. *J AgroEnviron Sci* 37(7):1332–1341 (in Chinese with English abstract)
- Zinn YL, Faria JAd, Araujo MAD, Skorupa ALA (2020) Soil parent material is the main control on heavy metal concentrations in tropical highlands of Brazil. *Catena* 185:104319

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.