



Geogenic pollution, fractionation and potential risks of Cd and Zn in soils from a mountainous region underlain by black shale

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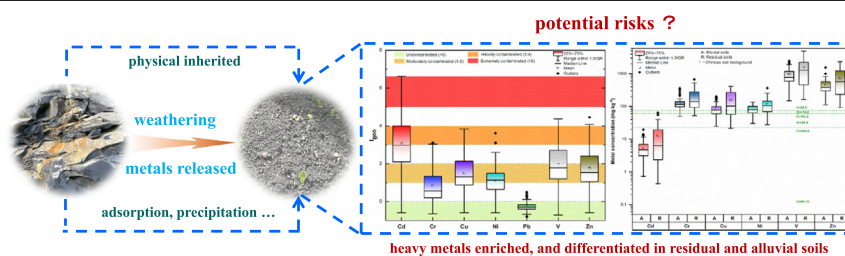
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HIGHLIGHTS

- Geogenic enrichment, differentiation and potential risks of heavy metals in soils derived from black shale were studied.
- Heavy metals were redistributed and retained in soil constituents during pedogenic processes.
- Cadmium and Zn were fractionated in soils and posed obviously different geochemical speciation.
- Cadmium is a highly concerned pollutant with potential risks to eco-environmental systems.
- The heavy metals in soils displayed topography dependent distribution.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated the pollution, fractionation and potential risks of heavy metals in soils from a mountainous area with black shale outcropping, with emphasis on Cd and Zn. Elevated concentrations of heavy metals in black shales reflected high geochemical baseline in the study area. Metals released from oxidative weathering were redistributed and retained during pedogenic processes, leading to enrichment of Cd, Cu, Cr, Ni, V and Zn in soils. As a highly concerned metal pollutant, the content of Cd in all collected samples ($N = 112$, Cd: 0.44–16.1 mg/kg) exceeded the risk screening value for Chinese agricultural land. Metals in local soils were retained through adsorption onto soil constituents clay minerals and Fe–Mn oxides and/or precipitation within secondary minerals. Based on sequential extraction, Cd and Zn fractionated in soils, with Cd mainly occurring in the mobile fraction (47.9% to 78.7%) as adsorbed, Fe–Mn oxides and carbonate associated phases, whereas residual fraction (67.1%) dominated for Zn, followed by Fe–Mn oxides coagulation (17.9%). Metals in residual soils from slopping location were highly related to metals in the parent rocks distributed more heterogeneously than metals in alluvial soils from flat location. High levels of heavy metal pollution in soils posed potential risks to the local eco-environmental systems and community, and Cd was highly concerned due to its high mobility. Cultivation in alluvial soils from valleys poses less risk than in residual soils, but appropriate approaches to reduce the risk in local soils is still necessary. The findings from this study provide basic knowledge and insight for risk control and targeted management of soils with geogenic heavy metal pollution in black shale outcropped mountainous areas.

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1. Introduction

Because soil is of prime importance for the production of food and maintenance of human beings, soil pollution could have serious adverse impacts on the eco-environmental system and human health. Soils may be polluted with different chemicals in which heavy metals are of high concern (FAO, 2018). Taking China as an example, report showed that 16.1% of the monitored Chinese soil samples were categorized as polluted, and the primary contaminant is heavy metals; in particular, 7.0% of the monitored soil samples were polluted with Cd (MEP and MLR, 2014), although these results were partly due to the stringent soil standards for food safety (Zhao et al., 2015). Heavy metals in soils mainly originate from anthropogenic inputs (Liu et al., 2017; Bostick et al., 2018; FAO, 2018). The enrichment of heavy metals in soils can also be naturally occurring, which has attracted increasing concern recently (Parviainen and Luokola-Ruskeeniemi, 2019; Duan et al., 2020; Nganje et al., 2020; Xia et al., 2020). The impacted region from naturally occurring heavy metals pollution could be at a regional scale, for example, the Cd anomaly area resulted from carbonate weathering is more than 200,000 km² in China (Xia et al., 2020) and geogenic weathering was also regarded as an important source of the Cd anomaly enrichment in Yangtze River catchment (Cheng et al., 2005). Importantly, geogenic inputs of heavy metals in soil may seriously influence the quality of soil, water and agricultural crops, and even posing high health risks to the local community in some regions (Lee et al., 1998; Peng et al., 2004; Liu et al., 2013, 2015, 2017; Xu et al., 2013; Kubier et al., 2019; Parviainen and Luokola-Ruskeeniemi, 2019; Duan et al., 2020).

Generally, anthropogenic sources could be regarded as exogenous sources, from which heavy metals are mobilized into soils over a relatively short-time scale (usually decades). In contrast, the geogenic inputs of heavy metals into soils are endogenous sources, from which the metals are inherited from parent rocks through long-term geochemical processes of weathering and pedogenesis. Therefore, the characteristics (e.g., distribution, speciation, mobility and potential risks) of soil polluted by naturally occurring metals may differ from those affected by anthropogenic pollution. For example, the enrichment, geochemical fractions and dynamics of Cd in soils derived from carbonate rocks were found to be controlled by compositions of parent rocks and soils, weathering and pedogenic factors, such as mineral dissolution-precipitation, adsorption and topography (Ling et al., 2015; Quezada-Hinojosa et al., 2009; Wen et al., 2020a; Xia et al., 2020). Previous studies documented that metals in anthropogenic contaminated soils were more mobile than in natural soils with background levels, which may be influenced by the form of anthropogenic inputs, and metal partitioning also differs between different soil types (Chlopecka, 1996).

Southwestern China is a large region with anomalously elevated heavy metals in soils, particularly Cd (Zhao et al., 2015; Luo and Teng, 2018). Many studies have investigated the geogenic enrichment of heavy metals in soil derived from carbonate rocks (Luo et al., 2009; Wen et al., 2020a, 2020b). However, black shales, which form under anoxic conditions and are usually enriched in trace metals, with extensive outcropping areas in Southwest China, could also be regarded as an important natural source of heavy metals in soil (Liu et al., 2015, 2017; Yu et al., 2012; Duan et al., 2020). Importantly, the Southern China Black Shale Region extends more than a thousand of kilometers from east to west and hosts many nonferrous metal minerals and developed mineral deposits (Mao et al., 2002; Fan et al., 2004; Yu et al., 2012), which were intensively mined to support industrial production. These mining activities would expose more black shales to the surface, accelerate oxidative weathering and finally diffused heavy metals into the local environment (Peng et al., 2004; Liu et al., 2017). In addition, the geogenic inputs from black shale weathering may also explain the geochemically abnormal distribution of heavy metals in Southwest China (Liu et al., 2017). Therefore, the dispersion of toxic metals into environment and potential risks to the local community deserve attention. Furthermore, approximately 33% of mountainous land in China is located in the southwest

(Gong, 2014), for instance, mountainous areas account for 76% of the total land in the Chongqing Municipality, and 92.5% in Guizhou Province (Tu et al., 2018), resulting in limited arable soils. The enrichment of heavy metals, stringent environmental policies, limited available arable soils, and demand for local agricultural activities have created complicated conflicts in these areas. Understanding the distribution, geochemical speciation and potential risks of heavy metals in soils in these areas is necessary for the targeted strategies on land use management and risk control, because many strategies for anthropogenic pollution are likely not appropriate to be applied in regions with naturally occurring enrichment of heavy metals.

In this study, a representative mountainous area with black shale outcropping was investigated, where the soils were highly related to weathering of black shales. The main objectives were to investigate the geochemical background, the enrichment and pollution levels of Cd, Zn and other metals in local soils, to reveal the geochemical fractionation of Cd and Zn, and the differentiation of heavy metals (focus on Cd and Zn) in soils from different locations, and finally to evaluate the potential risks of selected metals in soils. The results provide insights into the remediation and management of soil heavy metal pollution in the study area and other areas with high geochemical background of toxic metals, particularly in mountainous areas with outcrops of black shales.

2. Materials and methods

2.1. Study area

The study area is a rural area located in northern Chengkou County, Chongqing City, Southwest China (Fig. 1), presenting mountainous topography. The subtropical continental monsoon climate is warm and humid with an average annual precipitation of ~1261 mm. The average annual temperature is 13.8 °C, with the highest temperature in July and lowest temperature in January. The local rock outcrops are composed of Lower Cambrian (Lujiaoping Formation) black shales, mainly carbonaceous siltstone, carbonaceous calcareous siltstone, carbonaceous slate stone, and siliceous siltstone. There are no local industrial or mining activities, and the local residents cultivated food crops in soils for daily consumption. A previous geological survey showed that black shale and soils were enriched in heavy metals, particularly Cd (Cheng and Cheng, 2012).

2.2. Sample collection and analysis

A total of 12 outcropped fresh rocks and rock debris from soils were collected in the study area in August 2017. The black shale samples are composed of carbonaceous siltstone and slate stone, carbonaceous calcareous siltstone, with high organic carbon and sulfur, and displayed a black color. The rock samples were ground into powder <0.075 mm and stored in plastic Ziploc bags until further geochemical analysis.

In two adjacent small catchments underlain by black shales, sampling sites of arable soils were arranged along the brooks and covered all available soil parcels, soil samples were categorized as residual and alluvial soil depend on topographic locations. In this study, "residual soils" represent the surface arable soil samples from the slopping locations, where the slope mostly ranged from 20 to 30 degree, and these soils were mostly developed from residual materials of parent rock weathering, with no or slight transportation. "Alluvial soils" represent samples from the valley floor along the brooks, where the topography of sampling location is flat, and these soils were mostly formed from the colluvial and/or alluvial materials. The sampling sites of the two groups almost corresponded to each other so that the data are comparable. "Natural soil" in this study means samples from undisturbed forest or soils weathered in situ from black shale, and also includes samples from the slope washing materials without any anthropogenic disturbance observed. A total of 112 surface (< 20 cm) soil samples were systematically collected using a stainless shovel. Three to five subsamples were

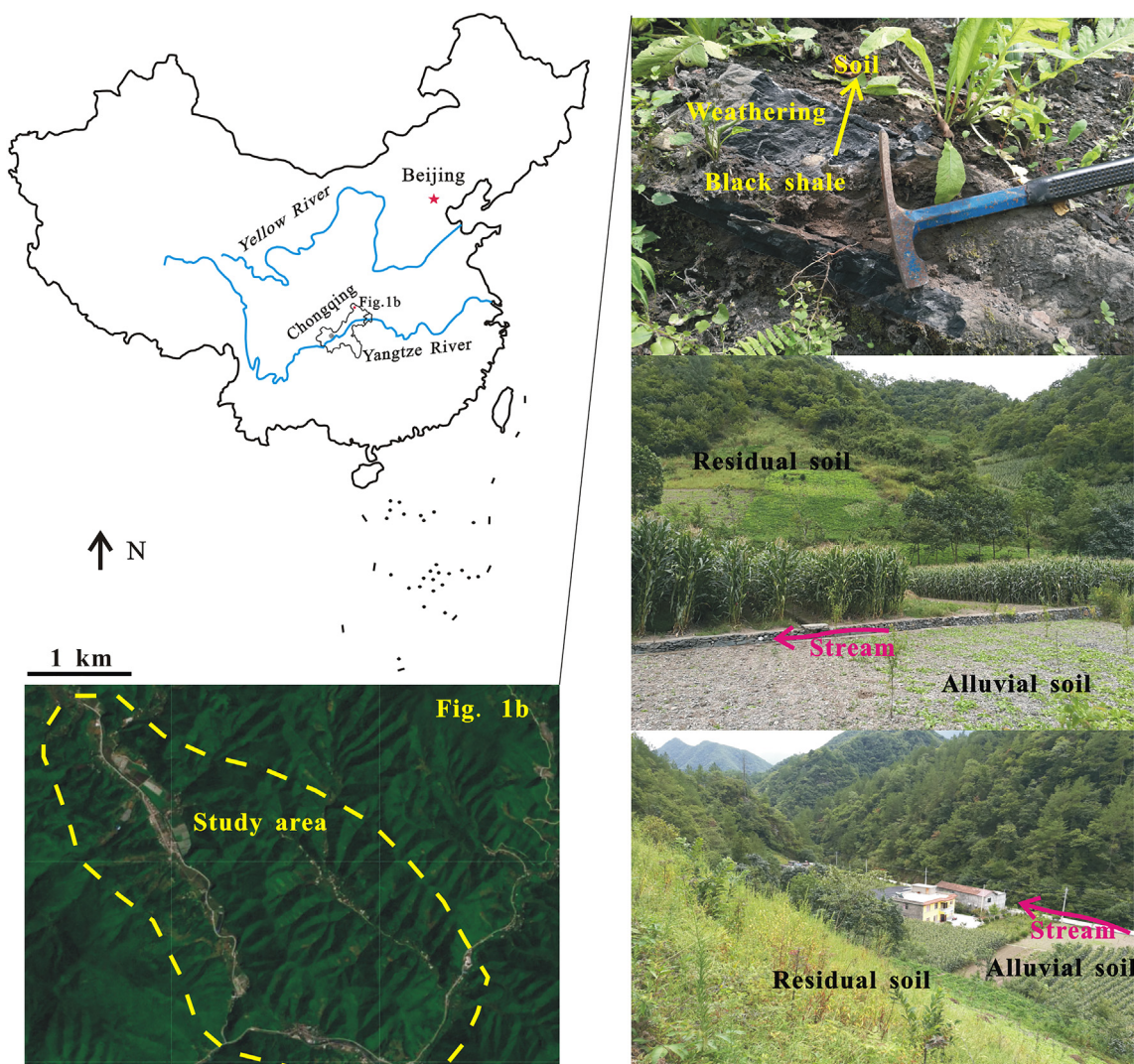


Fig. 1. Location and background of the study area.

collected in an area of approximately 5 m² to compose a composite sample at each sampling site. All soil samples were air dried indoors; sieved into <2 mm grains, crushed into fine powder (< 0.075 mm), and then stored in plastic bags until further geochemical analysis.

Soil pH and organic matter were measured according to the methods in Bao (2000). Briefly, the pH was measured with a calibrated pH electrode (PB-10 Sartorius, Germany) in a 1:2.5 soil/water suspension, and organic matter was determined by the Walkley-Black wet oxidation method. The effective cation exchange capacity was determined by the hexamminecobalt trichloride solution-spectrophotometric method suggested by the Chinese EPA (HJ889-2017). X-ray diffraction (XRD) analysis of rock samples was performed at the Stanford Synchrotron Radiation Lightsource on beam line 11-3 with the help of Chorover's Environmental Biogeochemistry Group (The University of Arizona).

Major and trace elements in solid samples were analyzed in the ALS Laboratory Group (Guangzhou, China). In brief, powdered samples were digested in mixed acid (HCl + HNO₃ + HF + HClO₄), and then elements in the digestates were measured by ICP-MS and ICP-AES. Certified references (GSS-3, GSS-5, GSR-6) were used to verify the accuracy of the digestion method, and the recovery rates were between 90% and 110% for all trace metals. The geochemical fractionations of heavy metals were determined following the procedure of the Technical Specification for Soil Environmental Monitoring (HJ/T 166-2004), which was fractionated into 5 fractions, i.e., exchangeable fraction (1 mol/L MgCl₂,

pH = 7, 1 h), carbonate fraction (1 mol/L NaAc, pH = 5, 8 h), Fe—Mn oxides fraction (0.04 mol/L, NH₂OH HCl in acetic acid, 96 °C, 4 h), organic fraction (30% H₂O₂ + HNO₃, 85 °C, 5 h), and residual fraction (mixed acid digestion). Heavy metals in each extract were measured by ICP-MS. Average recovery for samples was 85.8 ± 7.5% for Cd and 91.2 ± 8.4% for Zn. Our preliminary work showed that although total concentrations of Cr and Ni were also high, they mostly existed in residual fractions with subtle changes, so the data on Cd and Zn were the focus of this study.

2.3. Pollution index

The pollution accumulation index (P_{ai}) was calculated via measured concentration of each element divided by its background value (described in next section), and single pollution index (P_i) was calculated by measured concentration of heavy metal divided by the screening value (GB 15618-2018), according to The Technical Specification for Soil Environmental Monitoring (HJ/T 166-2004).

2.4. Geo-accumulation index

The study area presents high geochemical background of heavy metals, the geo-accumulation index (I_{geo}, Müller, 1969) may not be the best but is still proved to be a reasonable approach to reveal the

contamination level, based on previous studies (Liu et al., 2015; Duan et al., 2020; Nganje et al., 2020). It was calculated as:

$$I_{\text{geo}} = \log_2 (C_i/1.5B_i) \quad (1)$$

where C_i is the measured concentrations of the heavy metal in soils, B_i is the local geochemical background value of the heavy metal in soils, and 1.5 is a correction coefficient that helps analyze the natural fluctuation and anthropogenic influences (Wei and Yang, 2010; Liu et al., 2015). The local background values for heavy metals are not available. Nevertheless, over 100 soil samples were collected in the study area, carried enough information of heavy metal concentrations in local soils. Therefore, samples with the lower contents of Cd and other heavy metals were selected to estimate the local background values (0.44 mg/kg of Cd, 52 mg/kg of Cr, 21.7 mg/kg of Cu, 27.8 mg/kg of Ni, 20.0 mg/kg of Pb, 162 mg/kg of V, 93 mg/kg of Zn), which were quite close to the Chinese soil background values (Wei et al., 1991) for Cr, Cu, Pb and Ni but with slightly higher values for Cd, V and Zn. The latter higher values are consistent with the geochemical occurrence of heavy metals in local soils. According to Müller (1969), I_{geo} was categorized into different levels, i.e., uncontaminated (≤ 0), uncontaminated to moderately contaminated (0–1), moderately contaminated (1–2), moderately to heavily contaminated (2–3), heavily contaminated (3–4), heavily to extremely contaminated (4–5), and extremely contaminated (≥ 5).

2.5. Ecological risk assessment

The ecological risk factor (E_r) was used to illustrate the resulting potential ecological risks of heavy metals, calculated according to the method of Håkanson (1980):

$$E_r = \frac{C_i}{B_i} T_i \quad (2)$$

where C_i is the measured concentration of the element in soils, B_i is the geochemical background value in soils, which was the same as that used for the calculation of I_{geo} , and T_i is the toxic factor, which was assumed to be 30 for Cd; 2 for Cr; 5 for Cu, Ni and Pb; and 1 for Zn (Håkanson, 1980; Tian et al., 2017). The ecological risk was classified as low potential ecological risk ($E_r < 40$), moderate potential ecological risk ($40 \leq E_r < 80$), considerable potential ecological risk ($80 \leq E_r < 160$), high potential ecological risk ($160 \leq E_r < 320$), and very high potential ecological risk ($E_r \geq 320$) (Håkanson, 1980).

2.6. Statistic and graphic processing

Basic statistical analysis was performed by IBM SPSS Statistics 23.0 (International Business Machines Corporation, USA). Figures were produced with CorelDRAW X2 (Corel Corporation, Canada) and Origin 9.0 (OriginLab Corporation, USA).

3. Results and discussion

3.1. Heavy metals in black shale

The elemental and mineralogical compositions of the local rock samples are listed in Table 1. The results showed the heterogeneous chemical compositions of rocks from the study area. The major minerals included quartz, albite, barite and muscovite, while the minor minerals included pyrite, calcite and dolomite. The results of the bulk mineralogy were consistent with the results of elemental composition. For example, carbonate minerals were detected in samples with high Ca and Mg, and pyrite was detected in samples with high S. Compared to the continental crust (Wedepohl, 1995), Cd (4.70 mg/kg), Cr (159 mg/kg), Cu (63.3 mg/kg), Ni (81.9 mg/kg), V (1836 mg/kg) and Zn (285 mg/kg) were significantly enriched in local black shales, particularly for Cd, V and Zn, which displayed a magnitude of enrichment. Compared with

the average concentrations of trace metals in black shale (Ketris and Yudovich, 2009), the concentrations of Cr, V and Zn were higher in the studied samples, but the concentrations of Cd, Cu and Ni were similar. It is difficult to compare the chemical compositions of the fresh rock and rock debris samples because of significant heterogeneity. Pearson correlation analysis showed significantly positive correlations for Zn vs Cd, Cu vs Cr, Zn vs Ni, and Cr vs V ($p < 0.05$), implying their coupling mineral affinity. For Cd and Zn, previous studies have shown that sulfide minerals, such as pyrite and sphalerite, are the major host minerals in black shale (Tuttle et al., 2009; Perkins and Mason, 2015), and Cd may concentrate in apatite or calcite via isomorphous substitution of Ca as well, due to the similar charge and ionic radius of Cd^{2+} and Ca^{2+} (Andersson et al., 2014; Liu et al., 2017). Black shales are formed under reducing conditions, once exposed to the surface environment, sulfide minerals in black shales would be weathered quickly and produce acid drainage that dissolve other minerals (e.g., carbonate, Ling et al., 2016), such that heavy metals are released into the surface environment and undoubtedly pose potential risks to the local eco-environmental system. Previous laboratory leaching studies of black shales have detected high concentrations of heavy metals in the leachate, and the pH value of the leachate decreases continuously during the leaching process (Falk et al., 2006; Yu et al., 2014). These results pointed to the potential risks from weathering of metal-rich black shale to the local environment.

3.2. Physical-chemical characteristics of soil

The compositions of soils are summarized in Table 2. The average contents of major elements in local soils descended in the order of $\text{Al} > \text{Fe} > \text{K} > \text{Mg} > \text{Ca} > \text{S}$, with lower Al, Ca and S concentrations and similar K, Mg and Fe concentrations compared to the Chinese soil background values (Wei et al., 1991; Yan et al., 1997). The concentrations of major elements in soils were likely controlled by the geochemical compositions of parent rocks, varying among sampling locations, particularly for Ca and S, which showed an order of magnitude differences between the minimum and maximum values (Table 1). The correlation coefficients (Fig. 2) showed a negative relationship between Al and Ca ($r = -0.432$) and a positive correlation between Fe and Mn ($r = 0.74$). The relationship between Al and Ca may be explained by the different behavior of these two elements during weathering processes, Al was most likely to accumulate in soils during weathering due to the immobile nature and soil pH (4.11–7.78), while Ca would leach out due to its mobile property (Ling et al., 2015; Weil and Brady, 2017). Iron and manganese most likely occur as (hydr)oxides due to the drainage conditions of upland soils.

The local soils were strongly influenced by the heterogeneity of parent rocks. The pH ranged from 4.11 to 7.78, consistent with the soil type of yellow soil and calcareous soil in the study area. Low soil pH may result from acid generation from oxidative weathering of sulfide minerals (e.g., pyrite) in black shales, which was a general problem in soils derived from black shale and could increase the mobility of toxic metals (Kim and Thornton, 1993; Park et al., 2010; Liu et al., 2013, 2017). However, weathering of carbonate minerals, as detected in some black shale samples, could consume protons and consequently result in circumneutral pH (6.5–7.5) in many soil samples (33.9% of the total). The effective cation exchange capacity (ECEC) ranged from 0.22 to 43.8 cmol^+/kg , depending on the soil texture, minerals, and organic matter, and was also highly correlated with soil pH (Weil and Brady, 2017). Montmorillonite was detected in some soil samples by XRD (data not shown), and this 2:1 type clay mineral could provide high cation exchange sites due to Mg^{2+} substitution for Al^{3+} in the octahedral layer (Strawn et al., 2015). Additionally, Fe and Al oxides and humus may also provide negative surface sites at high pH ($r = 0.226$ for ECEC vs pH). Soil organic matter (SOM) in local soil samples ranged from 1.00 to 26.0 g/kg (average at 22.1 g/kg), which is quite close to the average SOM (24.82 g/kg) of Chinese surface soil (Liang et al., 2019) and

Table 1
Selected major and trace elements and mineral compositions in black rock series samples.

Sample	Al	Ca	Fe	Mg	S	Mn	P	Cd	Cr	Cu	Ni	Pb	V	Zn	Mineral compositions
	%	%	%	%	%	mg/kg									/
Fresh Black rock series (n = 5)															
CKR362	3.67	0.09	1.73	0.42	0.66	38	600	1.61	186	85.8	151	17.3	2460	256	Quartz, Barite, Albite, Muscovite, Apatite
CKR347	4.80	2.14	1.84	0.63	1.17	145	710	1.52	79	36.2	118	15.1	1020	175	Quartz, Pyrite, Albite, Calcite, Muscovite
CKR320	2.63	8.29	1.74	0.69	0.06	101	1800	4.64	64	84.1	85.8	16.1	180	88	Quartz, Albite, Calcite, Muscovite
CKR382	4.05	0.09	1.01	0.43	0.03	30	660	0.44	109	28.1	64.8	18.2	1970	131	Quartz, Barite, Albite, Muscovite
CKR352	3.80	0.05	1.21	0.42	0.09	35	380	1.75	507	124	65.0	19.8	2840	237	Quartz, Barite, Albite, Muscovite
Average	3.79	2.13	1.51	0.52	0.40	69.8	830	1.99	189	71.6	96.8	17.3	1694	177	
Rock debris (n = 7)															
CKR394	3.19	3.88	3.91	2.77	2.02	568	2040	16.1	61	27.9	174	15.6	1090	1350	Quartz, Pyrite, Dolomite, Muscovite, Apatite
CKR388	2.97	0.17	0.62	0.30	0.03	26	210	5.35	277	72.7	43.8	14.7	3440	137	Quartz, Barite, Albite
CKR367-1	3.15	0.12	1.56	0.39	0.08	35	700	5.20	181	61.4	79.9	15.3	3860	206	Quartz, Barite, Albite
CKR315	3.83	0.19	1.75	0.44	0.09	143	330	0.55	112	22.3	29.7	10.5	1640	97	Quartz, Albite
CKR314	5.84	0.38	3.32	0.84	0.05	191	1230	2.65	70	44.6	77.0	16.2	413	284	Quartz, Albite, Muscovite
CKR317	1.56	0.12	1.07	0.18	0.09	160	330	1.16	75	57.7	18.6	5.5	513	61	Quartz, Rutile, Muscovite
CKR398	3.75	0.27	1.48	0.43	0.04	57	690	15.4	186	115	75.2	20.5	2610	396	Quartz, Barite, Albite, Muscovite
Average	3.47	0.73	1.96	0.76	0.34	169	790	6.63	137	57.3	71.2	14.0	1938	362	/
Continental crust ^a	7.96	3.85	4.32	2.2	0.07	716	757	0.1	126	25	56	14.8	98	65	/
Black shale ^b	/	/	/	/	/	400	/	5	96	70	70	21	205	130	/

^a Wedepohl, 1995.^b Ketris and Yudovich, 2009.

SOM (24.11 g/kg) in dry farming soils of mountainous regions in south-western China (Tu et al., 2018). The samples with lower SOM values were collected from hill slope washing materials with a faint yellow color and scarce vegetation cover.

3.3. Geogenic enrichment of heavy metals in soils

The soil samples from the study area presented high concentrations of heavy metals compared to the Chinese soil background (Wei et al., 1991) and the average of world soils (Adriano, 2001), except for Pb. The averaged concentrations descended in the order of V > Zn > Cr > Ni > Cu > Pb > Cd (Table 2). The correlation analysis showed significantly positive correlations among metals in the local soils (Fig. 2), implying the same origins. No industrial activity was developed in the study area, and only local agricultural activities including the use of phosphate fertilizer may introduce metals into the soil,

because phosphate fertilizer is an important source of trace metals in arable soils (Loganathan et al., 2003; Bigalke et al., 2017). Although a significant correlation coefficient was observed between Cd and P in soils ($r = 0.796$), we cannot attribute the Cd enrichment to P fertilizer. First, highly positive relationships also existed between P and other heavy metals (Cr, Cu, V and Zn), some of which were not supposed to be enriched in P fertilizers. In fact, phosphorus may also originate from parent rocks of black shale, as high P concentrations and apatite were detected in some black shale samples from the study area (Table 1). Therefore, the geogenic weathering of local black shales was the main reason of the enrichment of Cd and other metals in local soils.

The enrichment of heavy metals in soils derived from black shales has been reported in many areas all over the world and presents an emerging concern (Lee et al., 1998; Park et al., 2010; Yu et al., 2012; Xu et al., 2013; Zhao et al., 2018; Duan et al., 2020; Nganje et al., 2020). The distribution of heavy metals showed significant

Table 2
Soil physical-chemical parameters and concentrations of selected elements.

Samples	Statics	pH	ECEC	SOM	Al	Ca	K	Mg	Fe	S	P	Mn	Cd	Cr	Cu	Ni	Pb	V	Zn
		/	cmol+/kg	g/kg	%	%	%	%	%	%	mg/kg								
All soils (n = 112)	Min	4.11	0.33	1.00	3.65	0.13	1.07	0.48	1.79	0.01	330	137	0.44	50.0	21.7	27.8	17.3	148	93.0
	Max	7.78	43.8	26.0	7.35	5.64	2.20	1.56	5.32	0.35	7940	1270	64.5	674	465	510	42.5	5050	3060
	Average	6.10	11.2	21.0	5.47	0.69	1.48	0.89	3.03	0.08	2085	430	9.36	173	121	104	25.4	1249	609
	Median	6.10	10.0	22.1	5.45	0.55	1.49	0.87	2.92	0.07	1640	370	5.23	116	81.0	92.4	24.6	836	408
	SD	0.81	6.06	4.06	0.61	0.63	0.20	0.22	0.56	0.04	1346	207	11.3	137	99.6	66.9	4.37	986	495
Natural soil (n = 9)	Min	4.51	1.38	1.00	4.05	0.14	1.16	0.50	2.31	0.01	330	209	0.50	70.0	22.8	38.5	17.5	548	131
	Max	7.78	20.9	25.3	6.21	5.64	1.78	1.56	5.32	0.35	5580	1270	48.7	653	465	510	42.5	5050	3060
	Average	6.09	9.53	19.60	5.19	1.25	1.41	0.88	3.40	0.10	2290	590	13.4	232	190	177	27.6	1737	932
	Median	5.91	9.52	21.79	5.33	0.65	1.37	0.74	3.10	0.06	1540	526	6.51	87.0	84.5	125	25.3	787	503
	SD	1.05	6.57	6.97	0.71	1.64	0.18	0.38	1.04	0.10	1918	372	14.3	229	170	146	8.42	1518	860
Residual soil (n = 47)	Min	4.51	0.59	13.37	3.65	0.13	1.07	0.48	2.30	0.03	810	207	0.44	52.0	21.7	27.8	17.3	162	93.0
	Max	7.28	23.8	26.0	7.35	2.25	2.20	1.53	4.83	0.14	7940	1070	64.5	674	412	361	37.8	4910	2350
	Average	5.91	11.1	21.3	5.37	0.71	1.42	0.89	3.15	0.07	2466	492	13.1	209	153	115	26.6	1523	737
	Median	5.90	10.2	22.1	5.37	0.57	1.35	0.86	3.04	0.06	2120	466	6.38	139	103	107	26.4	1270	571
	SD	0.67	5.31	3.35	0.71	0.52	0.23	0.24	0.54	0.03	1674	195	14.7	162	114	65.5	4.86	1161	557
Alluvial soil (n = 56)	Min	4.11	0.33	9.86	4.59	0.27	1.24	0.58	1.79	0.03	930	137	0.73	50.0	24.5	30.1	19.9	148	110
	Max	7.70	43.8	25.8	6.65	2.07	1.87	1.22	3.85	0.14	3890	786	19.6	362	201	135	27.1	2460	1540
	Average	6.26	11.5	21.0	5.59	0.59	1.54	0.89	2.87	0.08	1733	351	5.59	133	83.67	83.3	24.0	941	450
	Median	6.50	9.92	22.1	5.61	0.54	1.52	0.87	2.85	0.08	1545	326	4.74	115	78.15	80.6	24.2	772	384
	SD	0.84	6.50	3.93	0.47	0.30	0.15	0.15	0.38	0.03	653	135	3.51	63.6	35.9	23.3	1.77	497	233
Sediments (n = 2)	Average	7.94	3.83	18.4	4.94	2.17	1.54	1.12	3.47	0.09	1775	652	5.48	133	76.5	82.1	19.0	1069	384
Chinse soil ^{a,b}	/	/	/	6.62	1.54	1.86	0.78	2.94	0.01 ^b	520	583	0.10	61.0	22.6	26.9	26.0	82	74.2	

^a Wei et al., 1991.^b Yan et al., 1997.

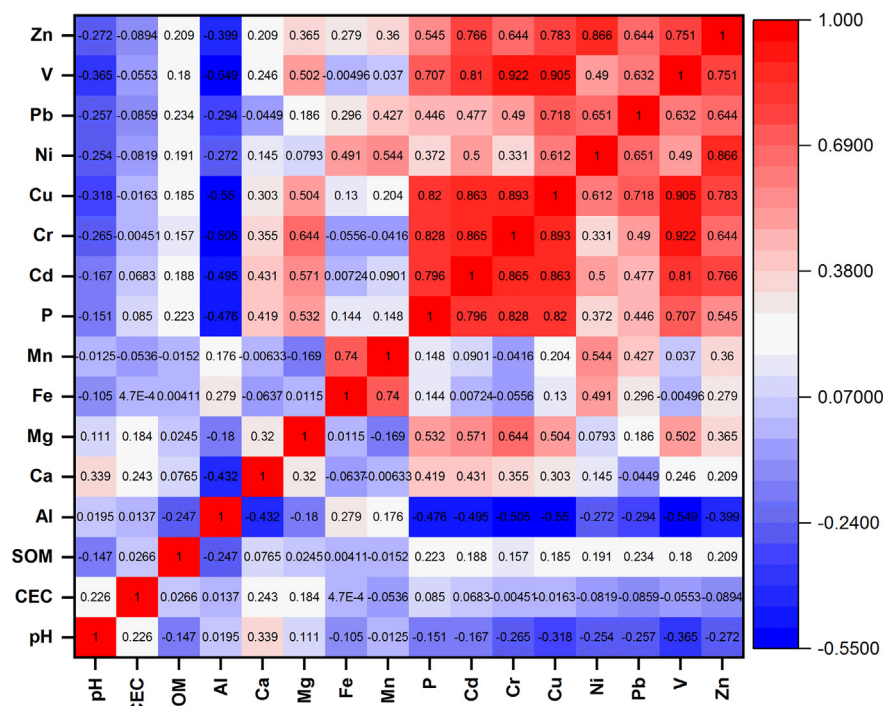


Fig. 2. Correlation coefficients of the major parameters and elements in soils.

heterogeneity, taking Cd and Zn for examples, total Cd in these soils ranged from 0.04 to 104.48 mg/kg, total Zn ranged from 50 to 1100 mg/kg. The spatial distribution of metals in soils highly depends on the geochemical composition of parent rocks. The total concentrations of heavy metals (e.g., Cd: 0.44–64.5 mg/kg, Zn: 93–3060 mg/kg) in collected soils of this study were higher than most reported cases. In fact, most of our samples presented even higher contents of heavy metals than anthropogenically polluted soils, particularly compared to those soils polluted by non-point sources, such as fertilization and wastewater irrigation (Bigalke et al., 2017; Khan et al., 2008). An investigation in southwestern China, where the elevated heavy metals in soils were attributed to the residual accumulation of carbonate rock weathering, also showed large variance, in terra rossa samples, Cd ranged from 0.12 to 17.9 mg/kg, and Zn ranged from 28.2 to 732 mg/kg, compared to low metal contents in the parent rocks (Wen et al., 2020a). In addition to the heterogeneity of parent rocks, mineral weathering and pedogenic processes may also contribute, as heavy metals released from parent rocks could be retained by soil constituents, such as clay minerals and Fe–Mn concretions. The retention by soil constituents was likely the major controlling factor for heavy metal enrichment in the karst terrain in southwestern China, where the heavy metals in parent rocks were generally low (Wen et al., 2020a) and the warm temperature and high precipitation would leach out most of dissolvable material.

The enrichment of heavy metals in soils is controlled by soil constituents and multiple physical and chemical parameters (Bradl, 2004). In the study area, sulfides were supposed to be the major host minerals for most trace metals, from which heavy metals were released into solution after oxidative weathering and then redistributed in soils. Among them, soil pH was considered a vital factor constraining metal behaviors. In general, a low pH accelerates the dissolution of minerals and suppresses the adsorption of cations, such that metal retention is favorable at higher pH due to the stability of minerals and deprotonation of some functional groups (Bradl, 2004; Zeng et al., 2011). However, heavy metals showed a very weak negative correlation with pH in the study area. The negative correlation can be attributed to the influence of oxidative weathering of sulfides in parent black shales. Organic

matter in soils could impact the fate of heavy metals, because solid organic matter can form colloids or ligands, provide negatively charged surface sites and immobilize cations in solution by adsorption (Ling et al., 2015; Boguta and Sokolowska, 2016; Kwiatkowska-Malina, 2018). The weak positive correlation between heavy metals and SOM ($r \sim 0.2$) in local soils implied the contribution of the organic fraction to metal enrichment.

Minerals inherited from parent rocks or neo-formed during pedogenic processes account for large fractions in soils. Clay minerals play such a significant role, and the negative charge resulting from the basal layer or edge could provide many sorption sites for cations (Bradl, 2004). The sorption capacity differs between different metals and clays. Montmorillonite detected in local soils, which may be transformed from mica under acidic conditions (Ling et al., 2018), could form outer-sphere and inner complexes and then stabilize cations (Bhattacharyya and Gupta, 2008). Carbonates are important minerals in the study area, and they may be inherited from black shales or precipitated during pedogenic processes. Considering the pH range in the studied soils, some metals (e.g., Cd and Zn) could precipitate as carbonates directly (Kabata-Pendias and Pendias, 2001). In addition, precipitation of calcite or dolomite could also entrain metals, for example, Cd could enter carbonate crystals by substitution with Ca because of similar ionic radius and charge (Andersson et al., 2014; Liu et al., 2017). The occurrence of carbonates could enhance the pH buffer capacity and increase the soil pH, which in reverse favored precipitation of carbonate minerals, impacted the variable charges, and finally favored the retention of heavy metals. The importance of carbonates could be supported by the positive correlation between heavy metals and Ca and Mg (Fig. 2), although Mg also exists in clay minerals. Iron and manganese form (hydr)oxides in well-drained uplands, such as in the study area, which could adsorb or coagulate heavy metals, as evidenced by the positive correlations of Ni, Pb, Zn with Fe and Mn (Fig. 2).

3.4. Geochemical fractionation of Cd and Zn in soils

The total concentrations of heavy metals are not enough to explain their bioavailability, mobility and geochemical enrichment in soils.

Sequential extraction is a useful approach to provide the necessary information. In this study, sequential extraction was performed on nineteen representative soil samples, which consisted of 6 alluvial soils (AS), 10 residual soils (RS) and 3 natural soils (NS), and one stream sediment sample (SD), and the results for Cd and Zn were plotted in Fig. 3. The geochemical speciation of soil Cd descended in the order of exchangeable (48.1%) > Fe-Mn oxides (18.7%) > carbonate (14.4%) > residual (13.9%) > organic (4.95%). In local soil samples, exchangeable Cd fraction was predominant, ranging from 28.1% to 61.9%, which was likely to be adsorbed by clay minerals, Fe—Mn (hydr)oxides, and/or humus (Tessier et al., 1979). The carbonate fraction ranged from 9.4% to 24.6%, which was retained by substitution of Ca in carbonate or CdCO_3 , demonstrating the importance of carbonate minerals on Cd enrichment. Cadmium coagulated by Fe and Mn oxides, which may form concretion, cement or coating particles, accounted for 13.1% to 32.1%, except for one residual sample with an extremely low portion at 0.1%. A low fraction of organic binding indicated a small contribution from organic debris. Soil Zn showed different geochemical speciation, and the trend was residual (67.1%) > Fe-Mn oxides (17.9%) > organic (7.50%) > exchangeable (5.06%) > carbonate (2.42%). Therefore, the majority of Zn occurred in mineral crystals of aluminosilicates, followed by Fe—Mn coagulation, and the mobile fraction was quite low. When comparing these two metals, Zn presented a much lower exchangeable and carbonate fraction but a significantly higher percentage in the residual fraction, and the organic fraction was slightly higher than that of Cd. These findings were consistent with previous studies on soils from black shale outcropped areas, which showed elevated Cd in the mobile fraction compared to other heavy metals (Lee et al., 1998; Liu et al., 2013; Duan et al., 2020). Although some studies have shown that Cd from anthropogenic sources has a higher exchangeable fraction than Cd from geogenic sources, Cd may also pose a high portion of exchangeable fractions in soils related to black shale weathering, according to the present study and previous studies in the literature.

Although Cd and Zn have similar geochemical behaviors and present significantly positive correlations, the geochemical fractionation differs. Sulfide minerals are supposed to be the major host minerals for Cd and

Zn in local black shales, which are susceptible to oxidative weathering and then release Cd and Zn into solution. Therefore, we speculate that the fractionation of Cd and Zn in local soils was likely influenced by redistribution and pedogenic processes. Coagulation by Fe and Mn oxides is likely a physical process that retain metals, such that there was no selectivity for Cd and Zn, each accounting for approximately 18%. Because of the similar ionic radius and same charge of Cd^{2+} and Ca^{2+} , Cd tends to enter the lattice or sorb onto the surface of carbonate minerals by the surface precipitation of solid solutions with a calcite-type structure (Prieto et al., 2003; Andersson et al., 2014; Liu et al., 2017), in addition to precipitation as CdCO_3 . This may explain the higher carbonate fraction of Cd than Zn. Zinc is more likely to precipitate as secondary minerals due to the higher absolute concentration in solution; for example, zinc enters layer lattice silicate structures by substitution with Mg^{2+} (Kabata-Pendias and Pendias, 2001). Zinc fixed by clay minerals was also found to be an important Zn species in soils derived from carbonate soils in which sphalerite was regarded as a host mineral of Zn in parent rock, and Zn-rich clay minerals may also be produced during the oxidation of parent rocks in addition to pedogenic processes (Jacquat et al., 2009). These processes may explain the high percentage of Zn in the residual fraction. Even if Zn could compete with Cd for surface sites, the Cd concentration in solution is much lower than the Zn concentration; thus, most Cd is adsorbed by minerals and humus. This may explain the significant differences in exchangeable and residual fractions between Cd and Zn, although we cannot rule out the influence of parent rocks of black shale, such as the partial oxidation of sulfide and formation of secondary minerals inherited by soils. Overall, the elevated Cd in soils from the study area was mainly controlled by adsorption, followed by coagulation of Fe—Mn oxides and carbonate. The enrichment of Zn was likely attributed to the preservation of primary minerals or neo-formed secondary clay minerals.

When considering different soil types, no obvious differences were observed for Cd and Zn fractionations. Two residual soil samples showed abnormal characteristics: sample RS-2 showed a relatively higher fraction of Fe—Mn oxides for Cd and Zn, and RS-3 showed an extremely high residual fraction for Zn but a higher carbonate fraction for

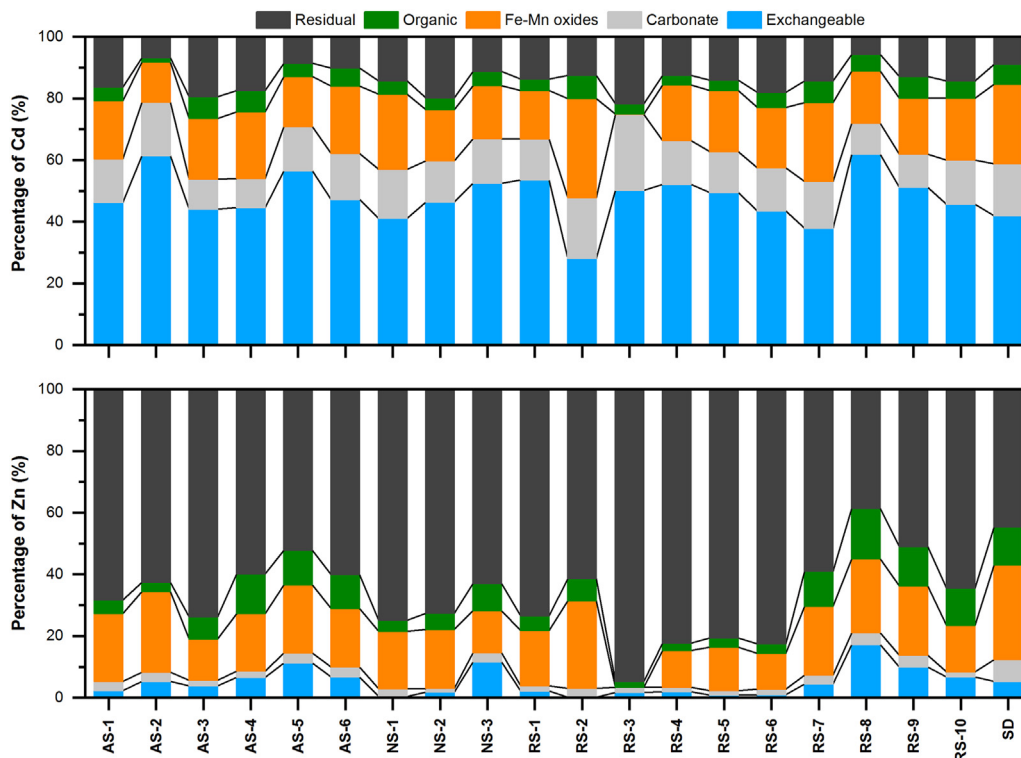


Fig. 3. The geochemical partition of Cd and Zn in soils.

Cd. The sediment sample showed higher carbonate and Fe—Mn oxides fractions than the soil samples for Zn, but there was no obvious difference for Cd in the soil and sediment. These results revealed that geochemical fractionation was quite similar for residual, alluvial and natural soils even though they varied in major composition or physical-chemical parameters. This may also suggest that the primary migration pathway of Cd and Zn in this small basin was through the migration of soil particles.

3.5. Differentiation of heavy metals in residual and alluvial soils

The topographical relief in the study area may result in soils from different locations (e.g., steep and flat area) fractionated in physical-chemical properties (e.g., particle size, organic matter, mineralogy and redox condition) due to the influence of topography on runoff, drainage, weathering and soil erosion (Norton et al., 2003; Ampontuah et al., 2006; Thanachit et al., 2006; Yoo et al., 2009; Khomo et al., 2011; Ling et al., 2015; Liu et al., 2016; Hawkins and Graham, 2017; Tu et al., 2018; Fang et al., 2019). The geogenic originated heavy metals, which exist in soils from the initial stage of weathering and pedogenic processes, were supposed to respond to these physical-chemical differentiations, and may displayed topographically distributed characteristics and consequently varied on risks. Although no profiles from soil catena were collected in this study, the statistical comparison of the available dataset (Fig. 4) indicated the differentiation of heavy metals, which showed residual soils with a wider range of total concentrations and a higher average and median of heavy metals than alluvial soils.

Interestingly, the drastic erosion of soils into the down slope may make the residual soil layer thinner and may be accompanied by weak weathering intensity and pedogenic evolution, so that the chemical compositions were highly related to the parent rocks of black shale during the early stage of pedogenesis (Bonifacio et al., 1997; Badía et al., 2013; Ling et al., 2015). In a similar region, Ling et al. (2016) reported the weathering intensity of black shale profile from valley was stronger than that from near mountaintop and mid-ridge. The scatter distribution and weaker correlation between Cd and Zn in residual soils

(Fig. 5) may be explained by the heterogeneity of outcropping black shale (Table 1). Calcium and Mg mainly exist in carbonate minerals in studied soils, and the positive correlation with Cd documented the importance of carbonates on the retention and enrichment of Cd in soils, which was consistent with the results of sequential extraction. The different coefficients of Cd and Ca, Mg may result from the different intensities of weathering and soil developing, because Ca and Mg showed higher coefficients ($r^2 = 0.4516$) in residual soils than that in alluvial soils ($r^2 = 0.1116$), suggesting the dissolution and re-precipitation of carbonates during soil developing processes. The alluvial soils from the valley floor were expected to be mixed well with abundant materials from upslope washing and upstream alluvial deposits due to intensive agricultural activities and pedogenic development. The distribution was more uniform as a result of mixing and dilution effects of all materials. In addition, weathering and intensive cultivation may favor the leaching of metals due to the abundant water available in these soils, for example, Zn, Cu and Cr were found to be depleted in regolith of a weathering profile from valley, which was demonstrated to present stronger weathering intensity than profiles from mid-ridge and near mountaintop (Ling et al., 2015). Although the data in this study were not sufficient to fully demonstrate the differentiation of heavy metals in residual and alluvial soils, the present results indicated that in mountainous regions, heavy metals may present topographically dependent distributions, and the enrichment mechanism may also be different. The findings were important for land management in similar areas with high geochemical backgrounds of heavy metals.

3.6. Potential risks of metals in soils

The enrichment of heavy metals in local soils may pose potential risks for the local eco-environmental systems. In the view of total concentrations, all collected soil samples had Cd concentrations that exceeded the risk screening value for Chinese agricultural land (0.3 mg/kg for pH < 7.5 and 0.6 mg/kg for pH > 7.5; GB 15618-2018). The percentage above the safe limit was 87.5% for Zn, 62.5% for Cu, 56.3% for Ni and 30.4% for Cr, but there were no samples exceed the

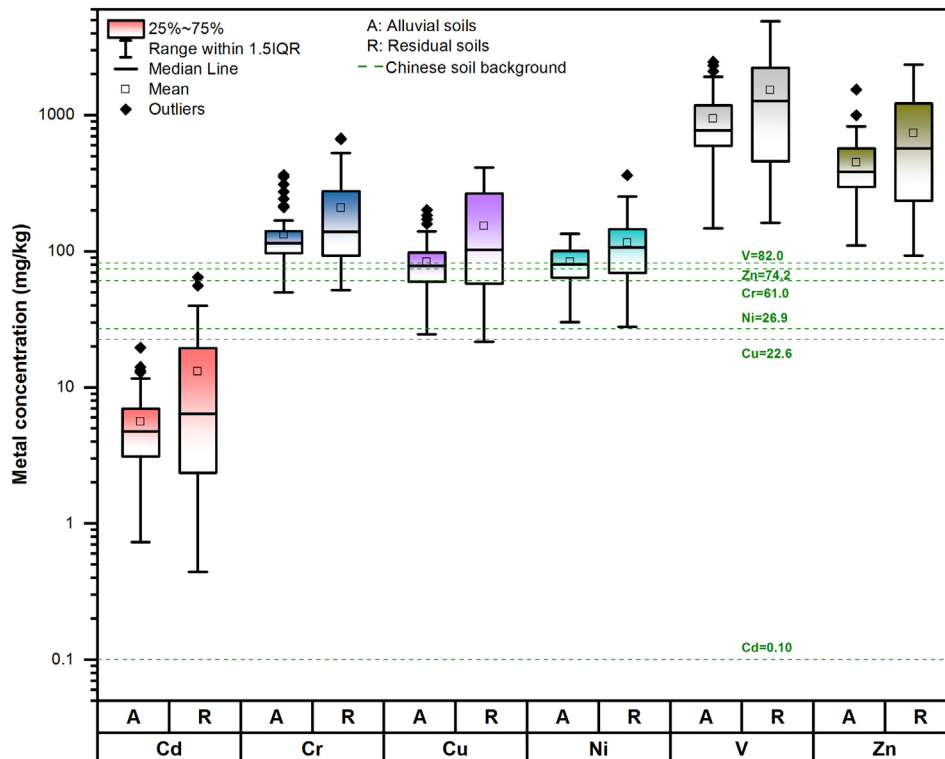


Fig. 4. Differentiation of heavy metals between the residual and alluvial soils (Chinese soil background from Wei et al., 1991).

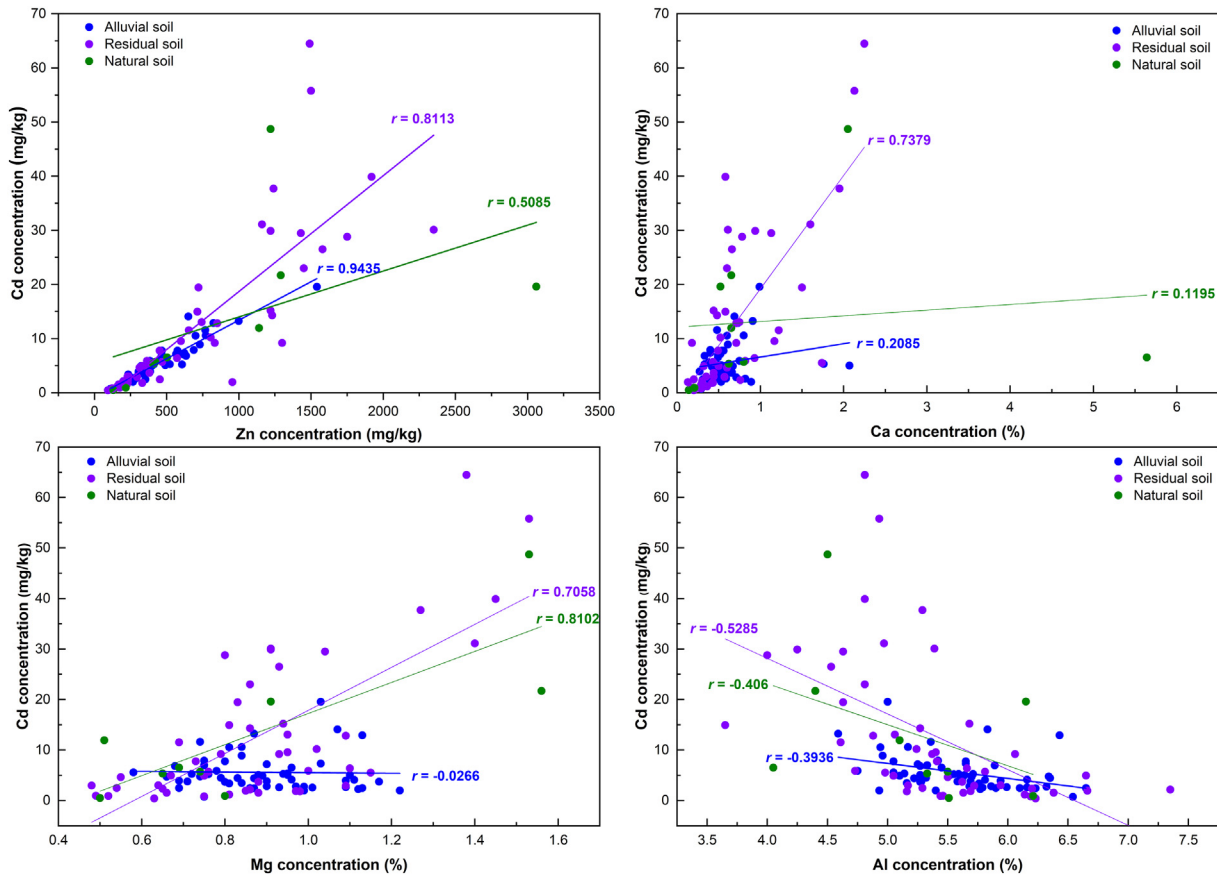


Fig. 5. The relationship of Cd and Ca, Mg, Al, and P in soils.

safety limit for Pb. With 78.6% of soil samples presents total Cd concentration exceed the risk intervention values (1.5 mg/kg for $pH \leq 5.5$, 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 $pH > 7.5$), no samples exceed that values for Cr and Pb, and no intervention values are set for Zn, Cu and Ni. In the view of the pollution accumulation index (P_{ai}), the enrichment of heavy metals decreased in the order of $Cd > V > Zn > Cu > Ni > Cr > Pb$, and the Cd content was one order of magnitude higher than the other heavy metals. The averaged single pollution index (P_i) descended in the order of $Cd (30.9) > Zn (2.88) > Cu (2.14) > Ni (1.42) > Cr (1.07) > Pb (0.28)$, and the P_i for Cd was an order of magnitude higher than that of other metals. Thus, Cd is a highly concerning metal pollutant in local soils. The geo-accumulation factor (I_{geo} , Fig. 6) was calculated to categorize the soil pollution level of heavy metals. The average I_{geo} of heavy metals in local soils decreased in the order of $Cd (3.08) > V (1.97) > Zn (1.76) > Cu (1.51) > Ni (1.13) > Cr (0.84) > Pb (-0.26)$. Among the metals, Cd was the major metal pollutant in local soils, with 77.7% of I_{geo} above 2, i.e., moderate to extreme contamination. In the present study, over 98% of soil samples were contaminated with Cd. The I_{geo} of soil samples above 2 was 46.4%, 38.4%, 26.8%, 13.4% and 8.04% for V, Zn, Cu, Cr and Ni, respectively. The local soils were not contaminated with Pb, which was consistent with the low total concentration of soil Pb. The ecological risk index (E_r) calculated for heavy metals descended in the order of $Cd (638) > Cu (28.0) > Ni (18.8) > Cr (6.64) \sim Zn (6.55) \sim Pb (6.35)$, and the E_r of Cd ranged from 30 to 4398. Approximately 58.0% of the soil samples had very high ecological risk, and 26.8% of samples had high potential ecological risk due to the extreme enrichment and high toxic factor (30) for Cd. Most of the soil samples did not have a potential ecological risk for Cu (80.4%) or Ni (93.8%), and there was no potential ecological risk for samples with Cr, Pb and Zn. Regarding the soil groups, residual soils presented slightly higher

pollution levels (I_{geo}) and ecological risks (E_r) than alluvial soils, implying that cultivation in alluvial soils from the valley was likely safer, but controlling countermeasures are still necessary due to the elevated contents of heavy metals.

The potential risk of heavy metals also depends on their chemical speciation. Exchangeable and carbonate fractions from sequential extraction can be categorized into mobile fraction (Duan et al., 2020). The mobile fraction ranged from 47.9% to 78.7% (average at 62.3%) for

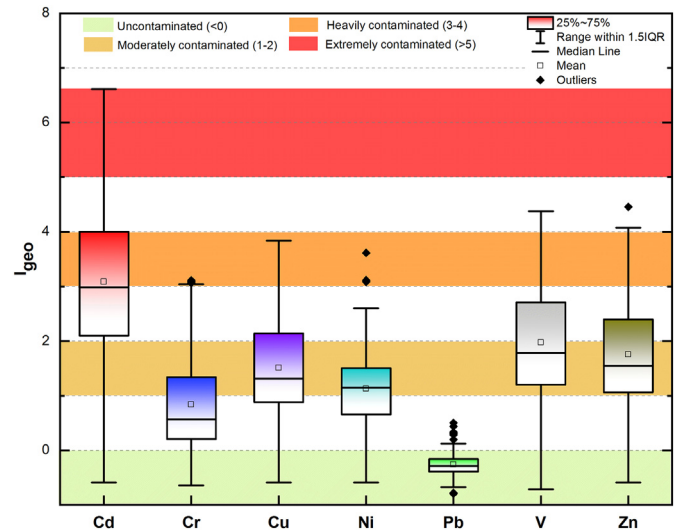


Fig. 6. Boxplot of the geo-accumulation index of heavy metals in soils.

Cd and from 2.27% to 21.1% (average at 7.48%) for Zn. The mobile fraction was sensitive to the ionic strength and pH (Tessier et al., 1979). Adding competitive cations and decreasing the pH value would enhance the release of Cd and Zn into solution. The organic fraction accounted for a low contribution and was expected to be stable in the short term. The iron and manganese oxide fractions are also regarded as immobile considering the drainage conditions of upland soils, and the reductive dissolution of these oxides may only occur in some saturated soil fractions. Finally, soluble toxic metals may be translocated into crops and vegetables or leached into water, threatening the health of the local community via the food chain (Lee et al., 1998; Liu et al., 2015). In particular, Cd was highly concerning because of its high mobility. Other metals (Cu, Cr and Ni) usually existed in the residual fraction (more than 80% for Cu and Ni, and over 90% for Cr), as reported in other studies (Liu et al., 2019). Although larger-scale sampling was not conducted in this study, the diffusion of metals in the basin was still quite possible, as the enrichment of Cd (average at 5.48 mg/kg) and other metals were detected in local stream sediment samples (Table 2). Metals in local sediments tend to be adsorbed on clay minerals and form new minerals, coagulated by Fe—Mn oxides, or formed carbonate, based on the sequential extraction. Heavy metals in these fractions can be released again when hydrological conditions change, such as in an anoxic environment, where Fe—Mn oxides may be dissolved and acidification of water may accelerate the dissolution of carbonate minerals. Overall, Cd posed high potential risks to the local eco-environmental systems and community due to its high mobility and toxicology.

4. Conclusions

This study investigated the geogenic enrichment of heavy metals in a mountainous region with high geochemical background. The study area presents high geochemical baseline of heavy metals due to the outcropping of Lower Cambrian metals-rich black shales. Heavy metals in soils with geogenic pollution are highly related to parent rocks and display large variation. Metals released from the weathering of black shale enter soils and then redistribute during pedogenic processes, resulting in the enrichment of Cd, Cr, Cu, Ni, V and Zn in local soils. Cadmium was the main pollutant in the study area because of the high concentration and pollution indices. Cadmium and Zn fractionate in local soils, and adsorption and precipitation within Fe—Mn oxides coagulation and carbonates present the dominant processes that retain Cd in soils, whereas neo-formed secondary minerals and Fe—Mn oxides dominate the Zn geochemical speciation. The majority of Cd in soils exist in the mobile fraction (47.9% to 78.7%), posing a high potential risk to local eco-system. Soils from different topographic locations present differentiation of heavy metals, residual soils on mountain slopes are highly related to parent rocks of black shale. Compared to residual soils, alluvial soils in river basins show a more uniform distribution of heavy metals due to the mixing and dilution effects and stronger weathering intensity, and likely pose less risk. The weathering of metal-rich black shale may be an important source of the anomalously elevated heavy metals in soils of Southwest China, and pose potential risks to local eco-environmental systems. The results of this study provide new insight into the naturally occurring pollution of heavy metals in soils from mountainous areas with black shale outcrops, which is significant for the appropriate land use management and ecological risk control.

CRedit authorship contribution statement

Yizhang Liu: Funding acquisition, Methodology, Writing - original draft. **Tangfu Xiao:** Funding acquisition, Conceptualization, Validation, Writing - review & editing. **Zhengjie Zhu:** Investigation, Methodology, Writing - review & editing. **Liang Ma:** Investigation, Data curation, Formal analysis. **Hang Li:** Investigation, Methodology. **Zengping Ning:** Investigation, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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