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Spatial distribution and controlling factors of heavy metals in soils from Puding Karst Critical Zone Observatory, southwest China

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Abstract

Soil profile samples under different land-use types were collected at the Puding Karst Critical Zone Observatory to investigate the composition, distribution and controlling factors of heavy metals. The heavy metal contents of Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb were determined, and their relationships to soil properties were examined. The Mn, Zn, Cd and Pb contents were larger in the topsoil than the deeper layer in all land use. In secondary forest land, the Cr, Fe, Ni and Cu contents in the topsoil were lower than in the deeper layer; however, all eight heavy metal contents were enriched in the topsoil under cropland. The results showed soil organic carbon played a fundamental role in controlling of Cd, while it showed negative relationship with Cr, Fe, Ni and Cu. Soil pH was positively associated with Ni and Cu. The Cr, Fe, Ni and Cu contents were significantly correlated to proportion of micro-aggregates, while the Cd and Pb contents showed a positive correlation with proportion of macro-aggregates. According to principal component analysis, the Cr, Fe, Ni and Cu contents might be affected by soil organic matter; however, the Mn, Zn and Pb contents might be influenced by atmospheric heavy metal deposition, and the Cd content might be controlled by both organic matter and atmospheric deposition. The geoaccumulation index and enrichment factor were calculated to assess the pollution level of soils, and the results showed that most of the selected heavy metals in soils may not be present at sufficient levels for contamination, and Mn and Fe were not from a pollution source and might come from natural weathering processes. This research will help researchers make strategic decisions about food security in the choice of agricultural land.

Keywords Soil heavy metals · Land use · Limestone soils · Geoaccumulation index · Enrichment factor

Introduction

Heavy metal contamination of soil environments from anthropogenic sources has become a globally important issue (Acosta et al. 2011; Huang et al. 2013; Sterckeman et al. 2000). Heavy metal contents in soils not only depend on the nature of parent rocks but also the sink from the deposition of particles emitted by anthropogenic sources such as agricultural practices, industrial activities and vehicle exhaust (Franco-Uría et al. 2009; Hu et al. 2018; Tang and Han 2017a; Wen et al. 2017). Anthropogenic sources of soil heavy metals tend to be more mobile than lithogenic or pedogenic sources (Basta et al. 2005; Kuo et al. 1983). Heavy metal contaminated soils can be a source of ecological environment destruction, landscape change and land resource degradation (He et al. 2005), and the metals (e.g., Cd, Cu, Pb and Zn) are toxic to plants, animals and humans (Bertocchi et al. 2006; Taylor 2010). Identifying the pollution sources (lithogenous or anthropogenic) of heavy metals (e.g., Cr, Mn, Fe and Ni) in soils is important due to their characteristics (Salehi et al. 2014). The assessment of selected heavy metal (e.g. Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb) contaminations, distribution and controlling factors under different land management types is important, and it will help researchers make strategic decisions about food security in the choice of agricultural land, and reduce the hazard to humans and the environment.

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Karst ecosystems constitute highly fragile environments that are easily damaged by anthropogenic activities in these regions (Parise et al. 2009). Compared with non-karst areas, since the soil in karst areas is characterized by thin regolith, uneven distribution and high porosity, soil heavy metal pollution shows small carrying capacity, flexible migration (mainly refers to the migration with the surface and underground water flow), wide coverage, difficulty in treatment and great hazard (Ruan et al. 2015). The soil Mn, Ni, Zn, Pb and Cd content which developed by limestone is higher than that developed by sandstone and sand shale (CEMS 1990); thus the calcareous soils developed by limestone in study area may have higher risk. Soil progressive degradation has become a serious ecological problem in karst regions of southwest China, and intensive agricultural activities have caused karst rocky desertification (Ding et al. 2011; Legrand 1973; Zhang et al. 2016). Depending on the different land uses and land-cover types, gradient distribution changes in soil organic carbon (SOC) content, soil aggregates and other soil properties have been observed in soil profiles (Han et al. 2015; Liu et al. 2017), and they influence the vertical transport processes of heavy metals. However, studies on the distribution changes of heavy metals and controlling factors in modern soils at different depths with contrasting land uses are not always consistent. Therefore, the objectives of this study were as follows: (1) to determine the distributions of heavy metals (Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb) in soil profiles under different land uses from Puding country; (2) to assess heavy metal ecological risks using the geoaccumulation index (I_{geo}) and enrichment factor (EF); (3) to define the natural and/or anthropogenic sources of the selected metals; and (4) to investigate the relationships between soil heavy metals and soil properties under different land-use types.

Materials and methods

Study area

The study site is located at the Puding Karst Critical Zone Observatory within Puding county ($26°15'$–$26°16'$N, $105°46'$–$105°47'$E), which is the typical karst critical zone in Guizhou Province, southwest China (Fig. 1). This area is controlled by a subtropical monsoon climate, with an altitude of 1042–1846 m above mean sea level. The average annual temperature is 15.1 °C, the mean annual precipitation is 1400 mm and over 80% of rainfall occurs during the rainy season from May to October (Zhao et al. 2010). The research area is dominated by Permian and Triassic carbonate rocks, and the karst rocky desertification areas represent 21.5% of the total area (Han et al. 2017). The study area is located in small catchment with strong drainage that is far from cities and mining operations. Therefore, sewage, industrial waste water and heavy metal mining as sources of heavy metals are excluded as sources due to the location of the study area. This allows us to focus on the effect of agricultural activities, wet and dry deposition on accumulation features of heavy metals under different land uses.

The small watershed in the study area is a typical karst peak cluster, which is surrounded by three hills with an average gradient of more than 40°. In this catchment, the areal proportion of dryland was 55.65%, shrub land was 23.35%, paddy land was 14.39% and fruit trees and secondary forest covered 6.61% (Zhao et al. 2010). The study area was selected according to the previous studies and field surveys, and the sampling sites were designed to collect representative samples from different land-use types (Liu et al. 2017; Zhao et al. 2010). The land-use types at the sampling site included cropland (A), shrub land (B), secondary forest (C), grassland (D) and abandoned cropland (E) (Fig. 1). Dominant vegetation and features of land-use change of the sampling sites are shown in Table 1. The soils in the study area were mainly developed from limestones with thicknesses in the range of 10–160 cm.

Sampling and analysis

A total of 27 soil samples were collected in 2016 (summer) from five soil profiles with the five types of land cover shown in Table 2. For each profile, soils from different depths were sectioned into 0–10, 10–20, 20–30, 30–50, 50–70 and 70–90 cm.

All soil samples were air-dried at room temperature (25 °C) for 15 days and sieved through a 2-mm nylon sieve to remove stones and coarse materials. Afterwards, the samples were mixed and ground until all particles could pass through a 200-mesh sieve for subsequent geochemical analysis. Soil pH was determined at a soil–water ratio of 1:2.5 soil/water with a pH meter. The SOC was measured with an elemental analyzer (Vario TOC cube, Elementar, Germany) after removing soil carbonates with 0.5 mol L^{-1} HCl (Liu et al. 2017; Midwood and Boutton 1998). Total nitrogen (TN) was measured by elemental analyzer (Vario micro cube, Elementar, Germany). Soil aggregates were separated into macroaggregate (250–2000 μm), micro-aggregate (53–250 μm) and silt and clay fraction (< 53 μm) by wet sieving and measured according to the method of Six J (Six et al. 1998). For the analysis of total phosphorus (TP) and heavy metal contents, soil samples were digested with HNO_3-HF-$HClO_4$ and analyzed by ICP-OES (Optima 5300DV, Perkin Elmer, US) and ICP-MS (Elan DRC-e, Perkin Elmer, US). Quality assurance and quality control were assured using duplicates, method blanks and limestone standard reference substances (GBW07120 and GBW07404) from the Chinese Academy of Measurement Sciences.
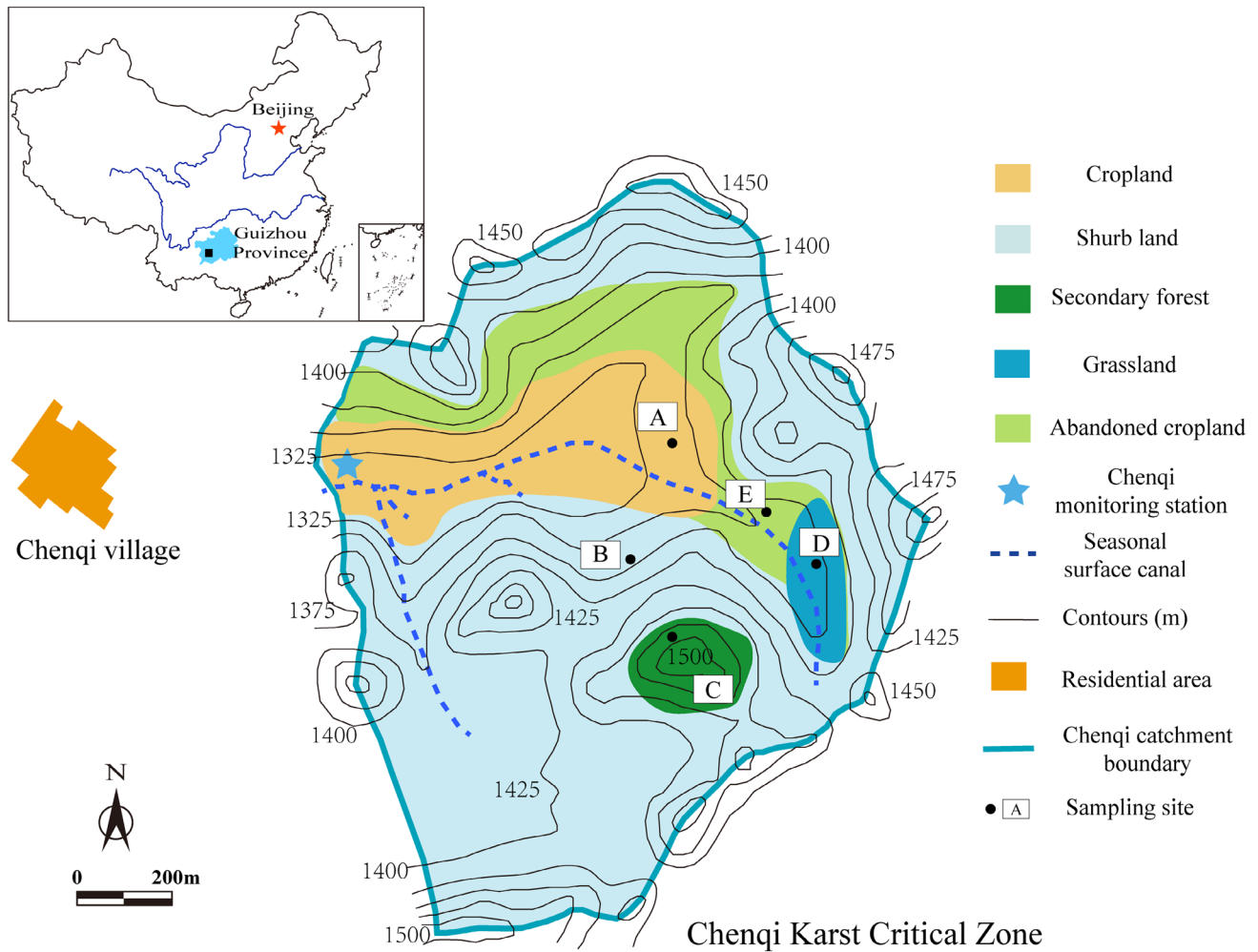
Fig. 1 Distributions of different land-use types and sampling sites

Table 1 Dominant plant and land use change of sampling sites

Sampling site	Dominant plant	Land use change
Cropland (A)	*Arachis hypogaea, Zea mays*	Cultivation over 50 years, crop rotation, plowed fallow, mixed application of manure and fertilizer
Shrub land (B)	*Eleusine indica*	Pear orchard had been abandoned for 8 years, and evolved to bush land
Secondary forest (C)	*Ailanthus altissima*	Virgin forest had been deforested for more than 50 years
Grassland (D)	*Eleusine indica*	Cropland had been abandoned for 5 years, and evolved to grass land
Abandoned cropland (E)	*Oxalis corniculata*	Cropland had been abandoned for 2 years, covered by weed

Statistical analysis

Various indicators are used to identify the metal concentrations of environmental concern, such as Geo-accumulation indexes (I_{geo}) and Enrichment factor (EF; Barbieri 2016). These indexes can identify the pollution level of soils, which are generally calculated on the soil exchangeable fractions. In the present paper, the EF and I_{geo} were selected as the indexes to assess the status and degree of anthropogenic contaminant deposition on soils.

The EF for Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb was calculated by the following formula, using Al as a conservative element which has been used successfully by several scientists (Balls et al. 1997; Ryan and Windom 1988):

$$EF = (M/Al)_{sample}/(M/Al)_{background}, \qquad (1)$$

Table 2 Soil physical and chemical properties of different sampling sites

Types of land use	Soil depth (cm)	pH	SOC (g kg^{-1})	TN (g kg^{-1})	TP (mg kg^{-1})	Proportion of soil aggregate (%)		
						Macro-aggregate	Micro-aggregate	Silt and clay size fraction
Cropland (A)	0	7.49	22.60	3.20	654.1	52.45	17.27	30.28
	15	7.39	5.33	1.80	233.5	35.06	23.25	41.69
	25	7.51	4.94	1.80	231.3	23.72	16.72	59.56
	40	7.34	4.58	1.70	232.5	35.18	20.91	43.91
	60	7.25	5.96	1.80	326.9	62.95	18.02	19.03
Shrub land (B)	0	7.01	35.22	4.10	671.3	78.54	8.36	13.10
	15	7.17	27.00	3.50	597.6	81.97	7.00	11.03
	25	7.30	20.47	2.70	583.9	75.39	10.95	13.66
	40	7.33	14.99	2.50	558.5	73.23	10.41	16.36
	60	7.40	11.06	2.40	417.6	70.80	14.91	14.29
Secondary forest (C)	0	6.90	138.84	9.60	495.4	86.86	7.33	5.81
	15	7.16	64.82	5.10	379.1	81.16	7.50	11.34
	25	7.26	24.23	2.40	256.2	71.12	8.02	20.86
	40	7.57	9.22	1.60	200.4	57.08	9.47	33.45
	60	7.63	4.73	1.30	176.4	63.36	11.32	25.32
	80	7.57	5.05	1.50	177.5	66.30	14.65	19.05
Grassland (D)	0	6.79	31.13	3.80	412.0	77.69	10.01	12.30
	15	6.66	17.59	2.70	401.8	76.50	10.02	13.48
	25	6.66	17.91	2.60	388.6	73.10	11.69	15.21
	40	6.38	16.11	2.60	350.8	75.87	9.23	14.90
	60	6.36	10.46	2.20	322.8	68.77	16.10	15.13
	80	6.47	8.38	2.10	302.5	63.92	17.65	18.43
Abandoned cropland (E)	0	7.16	27.28	3.50	596.8	65.30	12.85	21.85
	15	7.35	21.13	2.90	471.6	65.07	13.18	21.75
	25	7.52	13.87	2.40	363.0	65.59	14.73	19.68
	40	7.40	10.22	2.20	354.9	62.91	18.38	18.71
	60	7.39	10.65	1.90	334.0	51.55	24.29	24.16

where $(M/Al)_{sample}$ and $(M/Al)_{background}$ are the ratios of the determined concentrations of target elements in soils and their background levels, respectively. In this study, the reference background concentrations were obtained from the Guizhou soil (CEMS 1990). The numerical results are indicative of different pollution level. EF values less than 0.5 indicate the mobilization and loss of the determined metals relative to Al, and the values in the range of 0.5–1.5 reflect the elements are entirely from natural weathering processes or crustal materials and values higher than 1.5 imply probable anthropogenic impact (Barbieri 2016; Zhang et al. 2017).

The index of Geo-accumulation (I_{geo}) (Müller 1969) was also used to measure the contamination levels of heavy metals. I_{geo} for soil samples was calculated as follows:

$$I_{geo} = \log_2(C_n/1.5B_n), \tag{2}$$

where C_n is the measured concentration of the element, B_n is the geochemical background value of this element and 1.5 is the factor used for lithological variations of trace metals.

In this study, B_n denoted the concentration of the reference background values of Guizhou (CEMS 1990). Müller (1969) has defined seven classes of I_{geo} ranging from class 0 ($I_{geo} = 0$, uncontaminated) to class 6 ($I_{geo} > 5$, extremely contaminated).

Principal component analysis (PCA) and Pearson correlation analysis were performed to identify the relationship among different heavy metals and their possible sources using the commercial statistics software package SPSS 22.0 (IBM SPSS Statistics, Chicago, Illinois, US). Correlation was assumed to be statistically significant at $p < 0.05$.

Results and discussion

Chemical properties of soil

Soil properties such as pH, soil aggregate, SOC, TP and TN are the main factors influencing metal distributions in

soils (Du et al. 2005; Wang et al. 2006; Weng et al. 2002). The results of the soil chemical properties under different land uses in the study area are shown in Table 2. The soil pH values revealed weak acid to weak alkaline status with the values in the range of 6.47–7.52, and the calcareous soil was silt loamy texture. The pH values in cropland soils were higher in other soils with the values ranging from 7.25 to 7.49. Soil aggregates were separated into macro-aggregate, micro-aggregate and silt and clay fraction, and the aggregate compositions were determined. The results showed the proportion of macro-aggregates played a dominant role among all types of land use soils and accounted for 51.55–86.89%, while the silt and clay size fraction accounting for 5.70–31.84% was second and the proportion of micro-aggregates was the lowest.

The SOC contents in the soil profiles were in the range of 4.58–138.8 g kg^{-1}. The SOC varied with different land-use types, the contents decreased with increasing soil depth and the variation trends were more obvious in the upper 30 cm than in the lower 30 cm. Soil TN concentrations ranged from 1.70 to 9.10 g kg^{-1} and decreased with the increase of soil depth, and the variation under different land-use types was similar to that of SOC. Among all land-use types, SOC and TN contents were highest in the secondary forest soil because it contains substantial humus, plant roots and debris. Soil TP contents ranged from 176.4 to 654.1 mg kg^{-1} and decreased with increasing soil depth. The vertical gradient changes of TP contents were most obvious in cropland soils, and the contents were from 654.1 mg kg^{-1} (in the surface layer) to 233.5 mg kg^{-1} (at 15 cm-depth), which may be related to the influence of farming activities.

Profile distribution of heavy metals

The vertical distributions of eight heavy metals (Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb) down the soil profiles under five types of land use are shown in Fig. 2. The content change of each heavy metal was different, and the metal contents decreased in the following order: Fe > Mn > Cr > Zn > Ni > Cu > Pb > Cd.

The distributions of heavy metal along the soil profile varied with heavy metal type. The Mn, Zn, Cd and Pb contents in five types of land use decreased with increasing soil depth, which might be related to the accumulation of these heavy metals derived from atmospheric deposition in surface soils (Zhang et al. 2017). The selected eight metal contents in cropland showed enrichment in the soil layer 0–20 cm-depth, possibly due to applications of fertilizer and pesticide. In secondary forest land, the Cr, Fe, Ni and Cu contents in the soil layer of 0–20 cm-depth were lower than that at depth, indicating that these heavy metals were diluted associated with effects of organic matter metal availability (Zeng et al. 2011). However, the four metal contents

in shrub land, grassland and abandoned cropland did not show marked variation through soil profiles, except for that the Fe, Ni and Cu contents in the soil layer at 50–70 cm-depth increased significantly compared to that in the soil layer at 0–50 cm depth. The markedly higher Cr, Fe, Ni and Cu contents in the soil layer at 0–60 cm-depth compared to that in deeper soil layer were also observed in the soil profile of the woodland Fujian Province where the red soil was developed from granite (Sun et al. 2017). Ruan et al. (2006) reported the Cu, Zn, Cd and Pb contents in forest land without anthropogenic disturbances, where was located near steel works in Jiangsu Province, were the largest in the top layer, then decreased quickly with increasing of soil depth; however, in the 0–20 cm-depth soil layer of farmland, their contents remained at an intermediate values resulted from immixture by plow. Similar variation of these heavy metals in soil profiles were not observed in karst region, possibly due to effects of serious soil and water loss on the redistribution of these heavy metals.

The background values of Guizhou soil (CEMS 1990) were developed to evaluate ecotoxicology of heavy metals in this study, and the background values are shown in Table S1. The Pb contents were close to the background values in the surface layers and lower than the background values with the increasing depths, and the Cd and Zn contents of all the soils were lower than the background values, indicating the soils of Puding might not be contaminated by these metals. The Fe concentrations of soil profiles in all types of land use were much higher than the background values, and the Mn contents were higher than the background values in most soils except for the secondary forest soils. The Cr, Ni and Cu contents were similar to the background values in surface soils, and the metal contents varied with land-use types. These metal contents were lower than the background values in secondary forest and grassland soils and were higher than the background values in cropland and shrubland soils, but were close to the background values in abandoned cropland soils. The different distribution patterns of heavy metals in soil indicating the sources and migration characteristics were different. In the soil layer 30–90 cm-depth, the Cr contents of all land use types were similar to background values of Guizhou Province (113.3 mg kg^{-1}), and the Cd contents of all land use types were similar to background values of China (0.097 mg kg^{-1}); both of them showed heavy metal contents associated with parent rock without disturbance at depth, for example, effects of organic matter and inputs of atmospheric deposition.

Contamination assessment of heavy metals

Figure 3 demonstrates the EF values of the selected metals in soil samples under different land uses. The mean EF values of the heavy metals (except for Mn and Fe) were less than
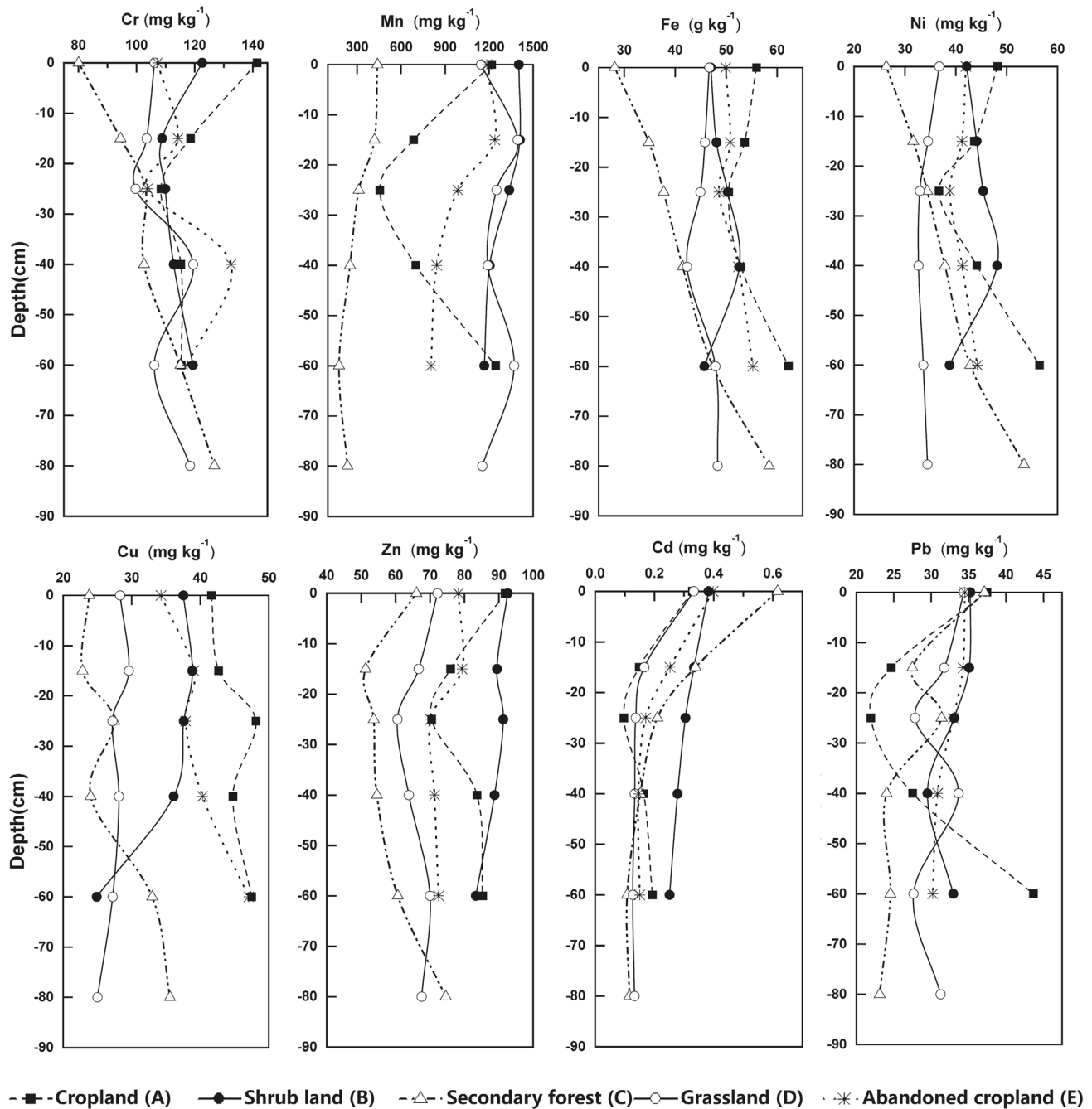
Fig. 2 Distributions of heavy metals in soils under different land uses

0.5 in most soil samples, indicating that a non-negligible portion of metals was delivered from non-crustal materials, or non-natural weathering processes and anthropogenic sources were not a contributor for these metals. The EF values of Mn were in the range of 0.5–1.0 in shrub land, grassland and abandoned cropland soils, and the EF values of Fe were in the range of 1.0–1.5 in all the soil samples, indicating the minimal enrichment of these metals. Fe and Mn are the most abundant metals in the lithosphere, and combine to

form oxides and hydroxides, which play an important role in their precipitation in soils (Bacsó et al. 1978).Therefore, Mn and Fe may come entirely from natural weathering processes in these land-use types (Zhang and Liu 2002).

Figure 4 shows the I_{geo} values of the eight metals in different layers (0–10, 10–20, 20–30 and 30–50 cm) of the soil profiles under different land uses. The I_{geo} values of most metals (except for Mn and Fe) were less than 0 in all layers, suggesting the soils of the research area may not be
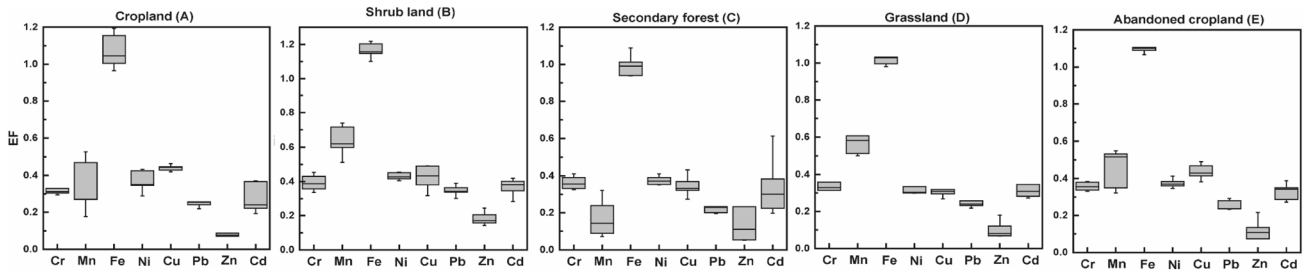
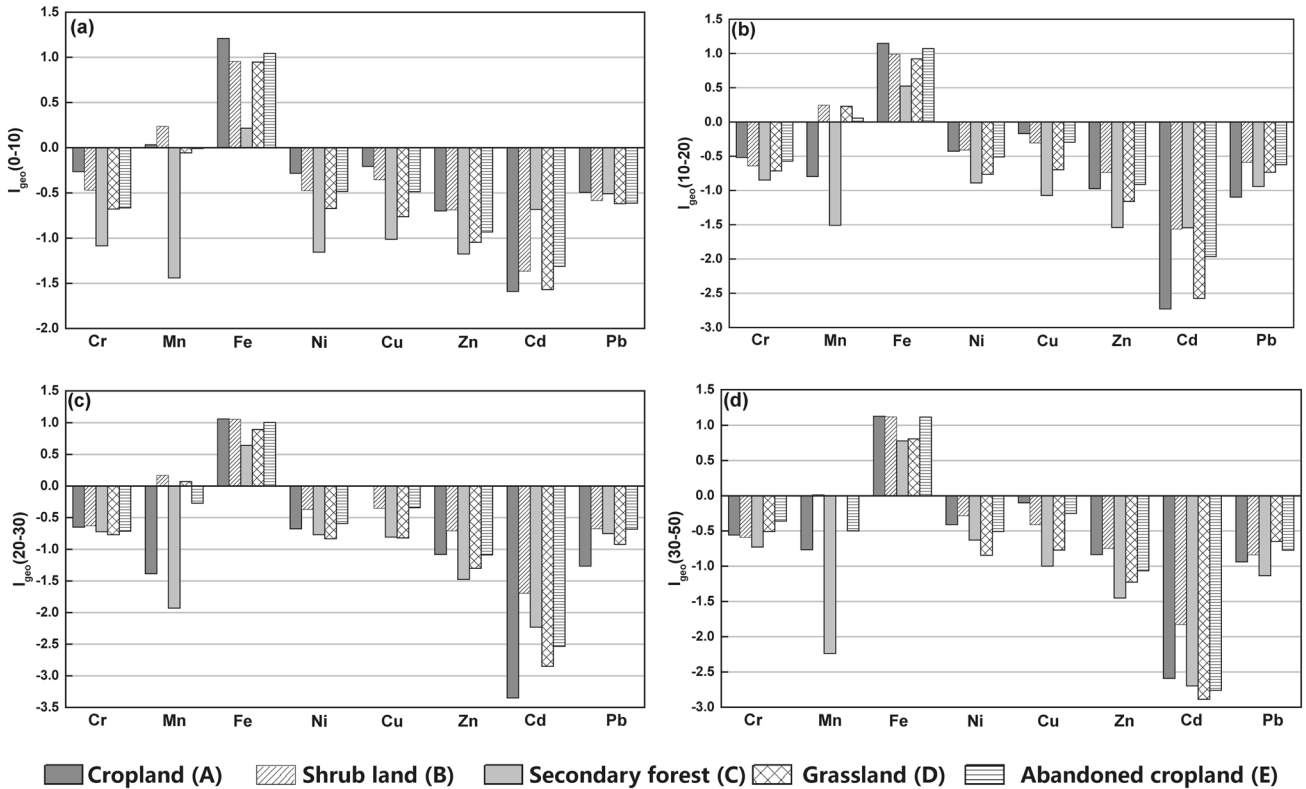**Fig. 3** Enrichment factor (EF) of heavy metals in different land use areas

Fig. 4 Geo-accumulation indexes (I_{geo}) of various heavy metals in different layers (0–10 cm, 10–20 cm, 20–30 cm, 30–50 cm) of the soil profiles

artificially polluted by these heavy metals. The I_{geo} values of Mn varied with land-use; the values in shrub land and grassland soils were in the range of 0–0.5 and were higher than those in other soils, indicating the soils in these land-use types were uncontaminated (Müller 1969). The I_{geo} values of Fe were higher than 1.0 in cropland and abandoned cropland soils, and less than 1.0 in shrub land, secondary forest and grassland soils, suggesting the soils of cropland and abandoned cropland were moderately contaminated by Fe. Soil pH was higher in cropland and abandoned cropland soils than in soils of other land-use types, resulting an increase of Fe dissolution (availability), further hindering uptake by

plants (Boxma 1972). This may explain the accumulation of Fe in cropland and abandoned cropland soils.

Multivariate statistical analyses

PCA and Pearson correlation analysis have been applied widely to identify the relationships among different metals and their possible sources in many studies (Yalcin et al. 2008, 2010). The PCA and Pearson correlation analysis of heavy metals were calculated, and the results of PCA and Pearson correlation analysis are presented in Tables 3 and 4, respectively.

Table 3 Principal component analysis of heavy metals

Element	Component matrixes	
	PC1	PC2
Cr	0.774	0.222
Mn	0.146	0.701
Fe	0.931	0.244
Ni	0.782	0.356
Cu	0.701	0.304
Zn	0.449	0.820
Cd	−0.678	0.656
Pb	−0.171	0.801
SOC	−0.893	0.268
TN	−0.896	0.388
TP	−0.231	0.893
Initial Eigenvalues	4.879	3.582
Variance %	44.353	32.566
Cumulative %	44.353	76.919

The PCA showed the factor loadings with a varimax rotation, eigenvalues and communalities in the karst soil samples. Two principal components (PC1 and PC2) were extracted with eigenvalues higher than 2 and the two factors explained 76.9% of the total variance. PC1 explained 44.4% of the total variance and showed a negative relation to Cr, Fe, Ni and Cu, and a positive correlation with SOC and significant correlations between them are also observed from Table 3. The first factor was obviously related to the process of soil organic matter. PC2, explaining 32.6% of the total variance, showed highly positive factor loadings on Mn, Zn, Pb, Cd and TP. The Mn, Zn, Pb and Cd in topsoil of the most sites were observed enrichment than at depth. Thus, these elements may be affected by atmospheric heavy metal deposition (including wet and dry deposition), such as motor vehicle exhaust (Soylak and Turkoglu 1999; Turkoglu et al. 2003), by-product of combustion of coal (Gupta et al. 2007) and pesticides and chemical fertilizer usage (Yargholi and Azarneshan 2014). Especially, the Cd showed a negative correlation with PC1, and a positive correlation with PC2, which indicated both organic matter and atmospheric deposition affected the Cd distribution.

The relationships between heavy metals and selected soil properties (e.g., pH, soil aggregates, SOC, TP and TN) were also examined by Pearson correlation analysis (Table 4). There was a positive relationship between Cd and SOC content; in contrast, Cr, Fe, Ni and Cu showed a negative relationship with SOC, indicating the soil organic matter affected immobilization or migration of these metals in the Puding area. There are two contrasting effects of organic matter on bioavailability of heavy metals. The first is the reduction of bioavailability by adsorption or forming stable complexes with organic substances (Liu et al. 2009). In contrast, organic matter releases organic chemicals into the soil solution, which may act as chelates and increase metal availability to plants (Zeng et al. 2011). In the present study, the dominant mode of different heavy metals influenced by SOC is various, leading to opposite relationship between heavy metals and SOC content.

The Cr, Fe, Ni and Cu contents were significantly correlated to proportion of micro-aggregates, indicating that adsorption and retention of these metals in the soils were influenced by soil particle size. The Cd and Pb contents showed a positive correlation with proportion of macro-aggregates, due to macro-aggregates making a greater contribution to the SOC content (Liu et al. 2017), and a positive correlation was observed between the proportion of macro-aggregates and the SOC. Other soil properties also presented some high correlations with heavy metal concentrations. Soil pH was positively associated with Ni and Cu contents, presumably because a high soil pH can reduce availability of these heavy metals in the soil solution and maintain a large heavy metal content through reducing the heavy metal uptake by vegetation (Zeng et al. 2011). Plants enhanced the absorption of Mn in higher pH soils resulting in a decrease in soil Mn content, therefore a negative relationship between soil pH and Mn content was observed in the study area (Huang et al. 1993). The correlation coefficient (r) value between SOC and TN was over 0.98, indicating that the main source of TN is plant litter. Thus, TN content was positively related to Cd and Pb contents, presumably resulting from the effect of organic matter on the bioavailability of heavy metals (Liu et al. 2009; Zeng et al. 2011). Soil TP did not show significant positive correlation with SOC and TN, which indicated that soil TP was not only affected by organic matter and might have other important sources, such as atmospheric deposition. Thus, we speculated that soil TP had a strong positive correlation with the Mn, Zn, Cd and Pb contents, presumably due to the effects of atmospheric heavy metal deposition (Yargholi and Azarneshan 2014).

Inter-element relationships provide information on metal sources and pathways. Table 4 shows the Cr, Fe, Ni and Cu contents were strongly correlated with each other ($p < 0.01$), suggesting that these elements had similar geochemical behavior, such as effect of organic matter on the migration of heavy metals. The Mn, Zn, Cd and Pb contents displayed a positive correlation with each other, indicating the possibility that they are affected by atmospheric heavy metal deposition for these elements in the Puding soils.

Correlation analysis between heavy metal concentrations and SOC

Soil organic matter plays an important role in the migration and transformation of heavy metals in ecosystems. Soil organic matter often acts as a carrier of heavy metals

Table 4 Pearson correlation between heavy metals and selected soil properties in the study area

	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb	SOC	pH	TN	TP	Macro-aggregate	Micro-aggregate	Silt and clay size
Cr	1														
Mn	0.193	1													
Fe	0.532**	0.248	1												
Ni	0.629**	0.102	0.674**	1											
Cu	0.489**	0.094	0.618***	0.697**	1										
Zn	0.474*	0.520**	0.170	0.596***	0.513***	1									
Cd	−0.285	0.096	−0.650**	−0.158	−0.208	0.431*	1								
Pb	0.046	0.578**	−0.076	0.131	0.063	0.469*	0.546**	1							
SOC	−0.605**	−0.139	−0.718***	−0.501**	−0.402*	−0.161	0.837***	0.331	1						
pH	0.274	−0.499**	0.342	0.569***	0.506***	0.200	−0.064	−0.229	−0.209	1					
TN	−0.549**	0.004	−0.670***	−0.483*	−0.372	−0.050	0.884***	0.412*	0.985***	−0.265	1				
TP	0.056	0.677**	−0.044	0.075	0.036	0.620***	0.727***	0.643***	0.373	−0.142	0.490**	1			
Macro-aggregate	−0.360	0.318	−0.500***	−0.291	−0.632***	−0.080	0.520***	0.460*	0.514***	−0.446*	0.537***	0.475*	1		
Micro-aggregate	0.511**	−0.021	0.678***	0.402*	0.617***	0.232	−0.488**	−0.165	−0.498**	0.244	−0.497**	−0.353	−0.761**	1	
Silt and clay size	0.247	−0.398**	0.357	0.205	0.552**	0.006	−0.462*	−0.519***	−0.450*	0.469*	−0.480*	−0.461*	−0.963**	0.557**	1

*Represents significant correlation at the level of $p < 0.05$

**Represents significant correlation at the level of $p < 0.01$

because of its strong capacity, which can greatly affect the activity of heavy metals (Cao et al. 2007). The SOC contents reflect the condition of soil organic matter in a certain range (Pribyl 2010). The relationships between SOC and heavy metal contents were discussed by Pearson correlation analysis in this study. The results showed that Cr, Fe, Ni and Cd contents exhibited a significant relationship ($p < 0.01$) with SOC content, and the linear relationship between these metals and SOC contents of soils under different land uses is depicted in Fig. 5.

The relationships between SOC and Cd presented the best linear relation (Fig. 5d), and $r > 0.9$ in all land-use types, indicating that the Cd was apt to adsorb to soils with high organic matter contents. Similar results have been reported that the Cd contents have an extremely significant positive correlation with the SOC or soil organic matter contents on

black soil in Northeast China (Cao et al. 2007). This may be because soil organic matter has a greatly absorptive capacity for Cd, which can greatly reduce the Cd activity, so the Cd contents in soils increase with the increase of organic matter content (Dumat et al. 2006).

The Cr, Fe and Ni contents showed a negative relationship with SOC (Table 4) and the linear relationship is depicted in Fig. 5a–c. Of the different land uses, secondary forest soils exhibited the strongest negative linear relationship between SOC content and Cr, Fe and Ni contents. This could be because the soil immobilization of metals is determined by the ability of complexation or chelation with soil organic matter, which was related to the components and content of organic matter (Zeng et al. 2011). The main substance in soil organic matter is humus, and the humic acid and humin in humus can reduce the concentrations of some metals in
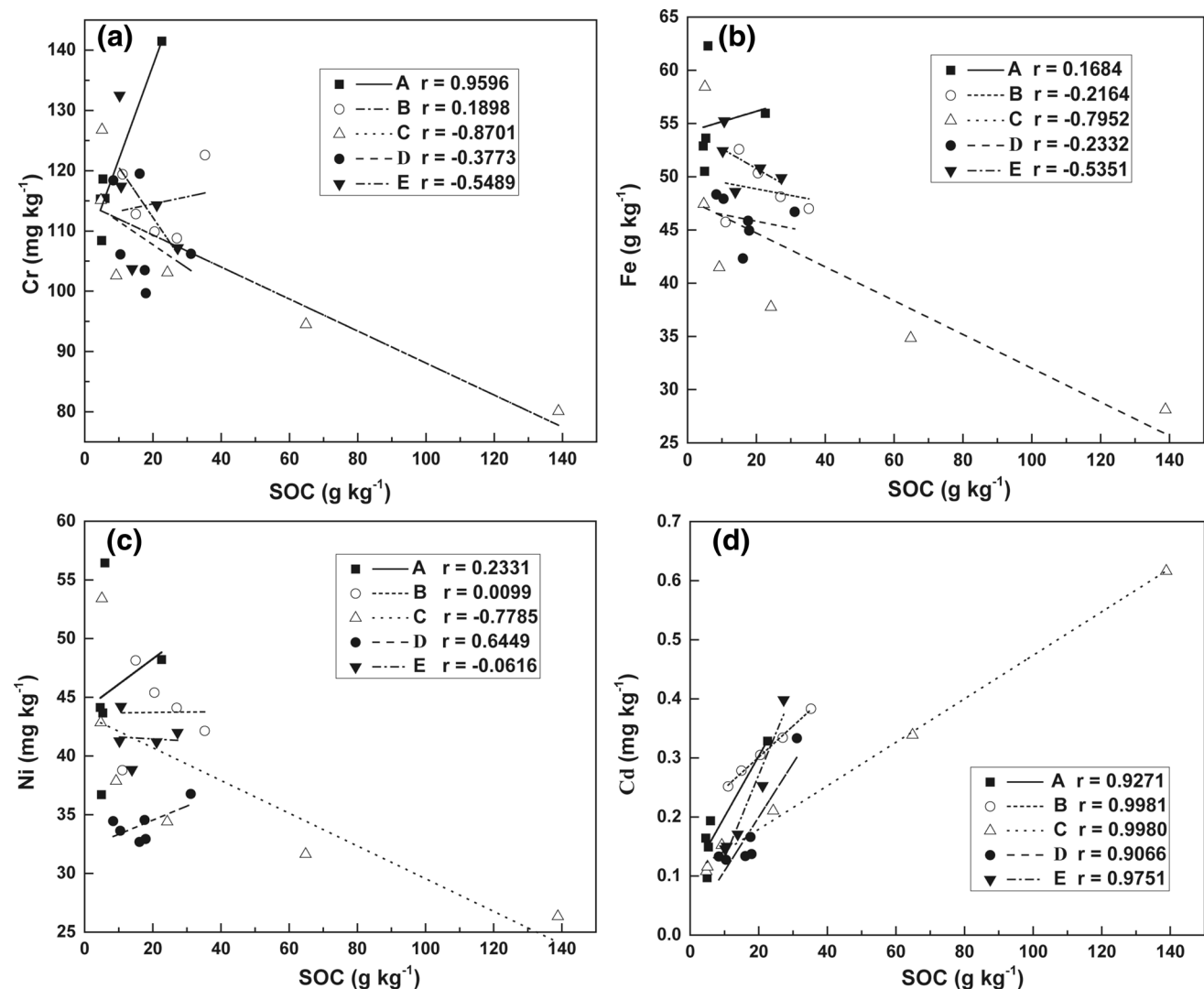

Fig. 5 Relationships between SOC and heavy metal contents of soils under different land uses. Part **a**, **b**, **c** and **d** are the relationships between SOC content and Cr, Fe, Ni and Cd content, respectively. *A* cropland; *B* shrub land; *C* secondary forest; *D* grassland and *E* abandoned cropland
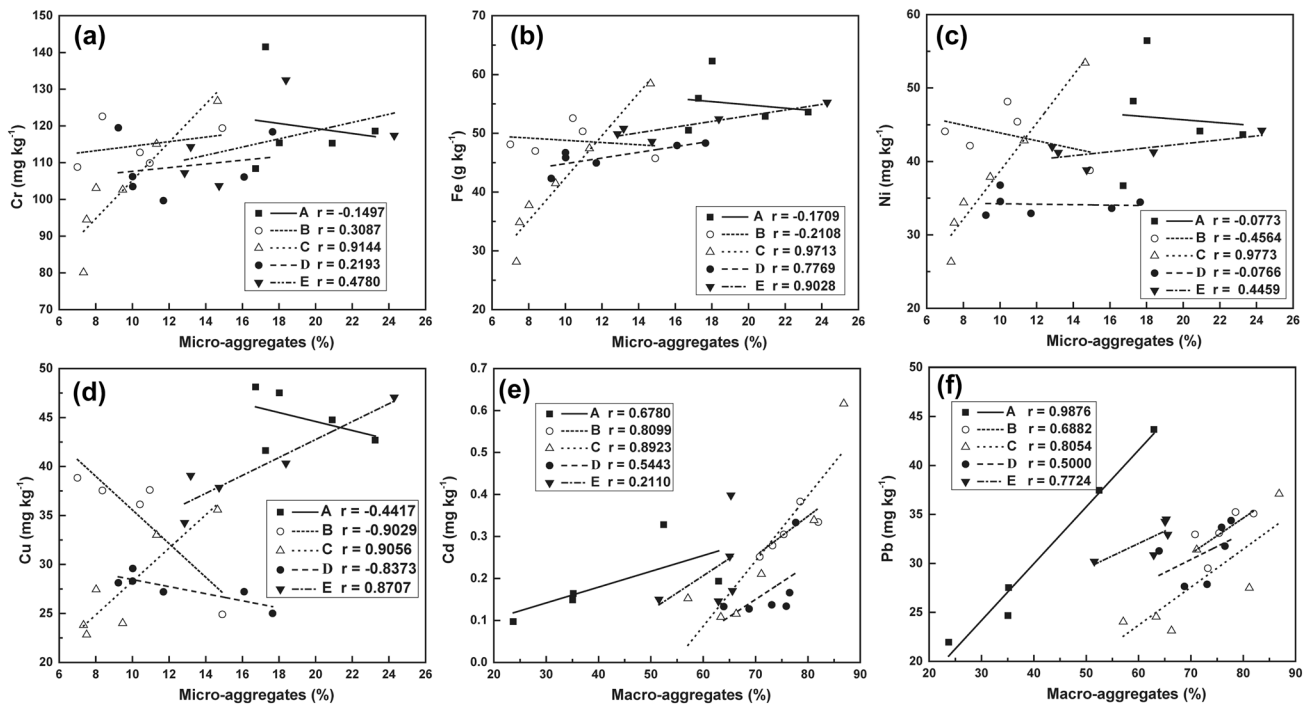
Fig. 6 Relationships between soil aggregates and heavy metal contents of soils under different land uses. Part **a**, **b**, **c** and **d** are the relationships between micro-aggregate proportion and Cr, Fe, Ni and Cu content; part **e** and **f** are the relationships between macro-aggregate proportion and Cd and Pb content, respectively. *A* cropland; *B* shrub land; *C* secondary forest; *D* grassland and *E* abandoned cropland

soils (Wang 1991); therefore, a higher organic matter content may not immobilize the metals in some soils. In the current research, the SOC contents in the secondary forest soils were higher than other soils, whereas the Cr, Fe and Ni contents reduced as the SOC content increased in secondary forest soils, indicating the input of SOC might "dilute" the Cr, Fe and Ni contents in these soils (Tang and Han 2017b).

Correlation analysis between heavy metal concentrations and soil aggregate

Soil aggregates represent the basic unit of soil structure formed by the interaction of soil organic complexes and mineral particles (Lynch and Bragg 1985), which is the main location for the decomposition and accumulation of organic matter and the migration and transformation of nutrients (Tisdall and Oades 1982). According to previous studies (Six et al. 1998; Tisdall and Oades 1982), soil aggregates were separated into macro-aggregate (250–2000 μm), micro-aggregate (53–250 μm) and silt and clay fraction (< 53 μm) in the present study.

There are numerous correlations between soil aggregates and soil properties, and SOC is the main dynamic property (Tisdall and Oades 1982). The Pearson correlation analysis in Table 4 suggests that the Cr, Fe, Ni and Cu contents exhibited a positive correlation with proportion of micro-aggregates, and the Cd and Pb contents showed a positive correlation with the proportion of macro-aggregates. The linear relationship between these metals and soil aggregates under different land uses was described in Fig. 6.

The linear relationships between Cr, Fe, Ni and Cu contents and proportion of micro-aggregates presented differently under different land uses, and no consistent relation was observed. It may be that the proportion of micro-aggregate accounting for 5.81–24.29% was the lowest among all the soil aggregates, and the influence on heavy metal contents was minimal. There was a clear linear relationship between the Cd and Pb contents and the proportion of macro-aggregates in soils of most land-use types, indicating that the coarse soil fraction exhibited a higher tendency for the adsorption of Cd and Pb than the fine fraction. This may depend on the correlation between macro-aggregates and SOC content, and a significant positive relationship has been reported between the SOC content and the Cd and Pb contents (Li et al. 2009). Secondary forest is less disturbed than other land uses, which in addition to larger SOC content may account for the greater macro-aggregate formation. Otherwise, many heavy metals could be absorbed by soil organic matter. This may explain the maximum positive correlation for macro-aggregates and metals under secondary forest than other land uses. The increase in SOC content can enhance the carbon source of microbes and promote

microbial activity and increase the formation of organic secretions, which are the key cement for the formation of soil aggregates (Jastrow et al. 1996).

Conclusions

The Zn, Cd, Pb, Cr, Ni and Cu contents in karst soils were close to or below the background values, whereas Mn and Fe were enriched likely derived from weathering products of limestone. The vertical distribution of these heavy metals in karst soils was influenced by land-use types and soil properties. Mn, Zn, Cd and Pb were enriched in the topsoil of all land use; Cr, Fe, Ni and Cu were enriched in the bottom soil of secondary forest land, were enriched in the topsoil of cropland, but were almost constant with depth in the soils of shrub land, grassland and abandoned cropland. Cr, Fe, Ni and Cu contents were significantly negatively correlated with SOC content, and positively correlated with soil micro-aggregate proportion; Cd and Pb contents were significantly positively correlated with SOC content and soil macro-aggregate proportion. Soil pH was positively associated with Ni and Cu contents, but negatively correlated with Mn contents. We suggest that although the karst soils were not contaminated by those heavy metals, migration and enrichment behavior of heavy metals in soils could be controlled by changing of soil properties under reasonable land management to reduce the risk of soil pollution.

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