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Pollution characteristics and ecological risk assessment of heavy metals in three land-use types on the southern Loess Plateau, China

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Abstract The accumulation of heavy metals in agricultural soils has been the subject of great concern because these metals have the potential to be transferred to soil solutions and subsequently accumulate in the food chain. To study the persistence of trace metals in crop and orchard soils, representative surface soil samples were collected from terrace farmland that had been cultivated for various numbers of years (3, 8, 12, 15, and >20 years), terrace orchard land that had been cultivated for various numbers of years (4, 7, 10, 12, 15, 18, 25, and >30 years), and slope farmland with various gradients (3°, 5°, 8°, 12°, 15°, and 25°) and analyzed for heavy metals (As, Cr, Cu, Hg, Ni, and Zn). These samples were collected from Nihegou catchment of Chunhua county in the southern Loess Plateau of China. The six heavy metals demonstrated different trends with time or gradient in the three land-use types. The Cu and Zn contents of the soil were higher than the referee background values of the loessal soil, and the contents of Cr and Ni, and especially those of As and Hg, were lower. Cu was the only heavy metal that just met the Grade III Environmental Quality Standard for Soils of China, while the others reached grade I. Cu and Hg were considered contaminant factors and Hg was a moderate potential ecological risk factor in the catchment. Of the sites investigated, 89.5% fell into the category with a low degree of contamination (C_d) and rest were moderate, while all three land-use types had low potential ecological risk (*RI*). Changes of C_d and RI were consistent with the cultivated time in the terrace farmland and terrace orchard land. Values of RI increased while C_d decreased with the increasing of slope gradient in the slope farmland. Evaluating the ecological risk posed by heavy metals using more soil samples in a larger study area is necessary on the Loess Plateau of China.

Keywords Heavy metals · Land-use types · Pollution characteristics · Potential ecological risk assessment · Southern loess plateau

Introduction

Heavy metal contamination has become a worldwide environmental concern due to its potential ecological effects. As heavy metals, whether essential or not, are frequently related to soil contamination and are potentially toxic to living organisms (Chen et al. 1996), heavy metals in agricultural soils may accumulate to toxic concentrations that can lead to ecological damage and pose long-term environmental and health implications (McLaughlin et al. 1999; Margin et al. 2002; Gu et al. 2005; Cao et al. 2009). Heavy metal contamination of agricultural soils has also become increasingly serious in China due to the country's rapid economic development (Wong et al. 2002). The general condition of the

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nation's soil environment is not pristine in China, approximately one sixth (or 16.1%) of the cultivated land in China's territorial land areas, excluding Hong Kong SAR, Macao SAR, and Taiwan Province, may suffer from heavy metal pollution, according to the Grade II Environmental Quality Standard for Soils of China (Song et al. 2013; Ministry of Environmental Protection and Ministry of Land and Resources 2014).

The Loess Plateau is recognized as one of the optimal regions for the cultivation of high-quality apples in China and the world. In recent years, because of the increased application, and especially the improper use, of fertilizers and pesticides, more heavy metals are entering the loess-based orchard soils and are accumulating with the rapid development of apple production (Liang et al. 2008; Zhu et al. 2009; Liu et al. 2010; Hu et al. 2012), posing a risk of potential toxic effects. Ecological risk assessment on heavy metal was put forward by Håkanson (1980) and widely used to evaluate the potential ecological risk in sediment of industrial area, mining, river, wetland, coast, or marine environment (Tannenbaum 2005; Jensen and Pedersen 2006: Krishna and Govil 2007; Fock 2011; Perrodin et al. 2011; Anderson et al. 2013; Baran et al. 2014; Lago-Vila et al. 2016; Makokha et al. 2016; Dahms et al. 2017; Wang et al. 2017). However, there are only a few studies that assess the ecological risks posed by heavy metal contamination and focus on their spatial and temporal differentiations of agricultural soil (Chen et al. 2011a; Liu et al. 2015), especially the exposure concentrations and potential ecological risks posed by heavy metals in different land-use types, such as terrace farmland and terrace orchard land that have been in cultivation for different years, or slope farmland with different gradients in the region. Thus, the exposure concentrations and potential ecological risk posed by heavy metals to crops or apples grown on the slope farmland, terrace farmland and terrace orchard land on the southern Loess Plateau were investigated in this study.

In this study, attempts were made (1) to investigate the characters of As, Cr, Cu, Hg, Ni, and Zn; (2) to assess the potential ecological risk posed by heavy metals using the potential ecological risk index method; and (3) then to illustrate the changes of the potential ecological risk under three land-use types, such as the terrace farmland, terrace orchard land with different cultivated years, and slope farmland with different slope gradients, in Nihegou catchment of Chunhua county, Shaanxi Province, China.

Materials and methods

Study area

This study is conducted in Nihegou catchment of Chunhua county (34° 37′–35° 39′ N, 108° 38′–108° 39′ E; Fig. 1), which lies in the southern Loess Plateau in Shaanxi Province, China. It covers an area of 9.48 km^2. The altitude range is from 712 to 1193 m. The region has a semi-humid continental climate and lies in a warm temperate zone with an average annual temperature of 9.8 °C. The average temperature is −4.3 °C in January and 23.1 °C in July. The frost-free season is 183 days and extends from the middle of October to the middle of April. The cumulative temperatures ≥ 0 and ≥ 10 °C are 3899.2 °C in 269 days and 3281.0 °C in 173 days, respectively. The average annual precipitation is 600.6 mm, and it is concentrated such that 50% falls between July and September. The K value of dryness is 1.10–1.38. This small watershed is characterized by residual loess platforms separated by gullies, and the gully density is 4.71 km/km^2. The areas of tableland and gullies are 5.61 and 3.87 km^2, which occupy 59.2 and 39.8% of the watershed area, respectively. The soil in the study area is mainly derived from loess (Institute of Soil Science, Chinese Academy of Science 2001), which has a grain size ranging from fine silt to silt, has low fertility (the soil's organic matter content is less 0.6–0.8%), and is weakly resistant to erosion. In the study area, small amounts of natural vegetation made up of herbs and shrubs are distributed in gullies and valleys because of the destruction caused by cultivation. The runoff modulus is approximately 2.01×10^4 $m^3/km^2/a$ from slope runoff that exceeds infiltration. The cumulative control area of soil loss is 8.13 km^2, which occupies 86.3% of the watershed, including 3.25 km^2 of the level terrace. The soil erosion modulus decreased from 4000 in 1986 to 437.5 $t/km^2/a$ in 1999 (Zhang 2005). Crop plants and the fruit industry make up the main land-use types in the local rural area.

Methods

Field survey techniques were used to recognize eight main land-use types in the study area. These are farmland, orchard land, natural grassland, artificial grassland, forestland, residential land, unused land, and other lands; the areal percentages of these land-use types in the

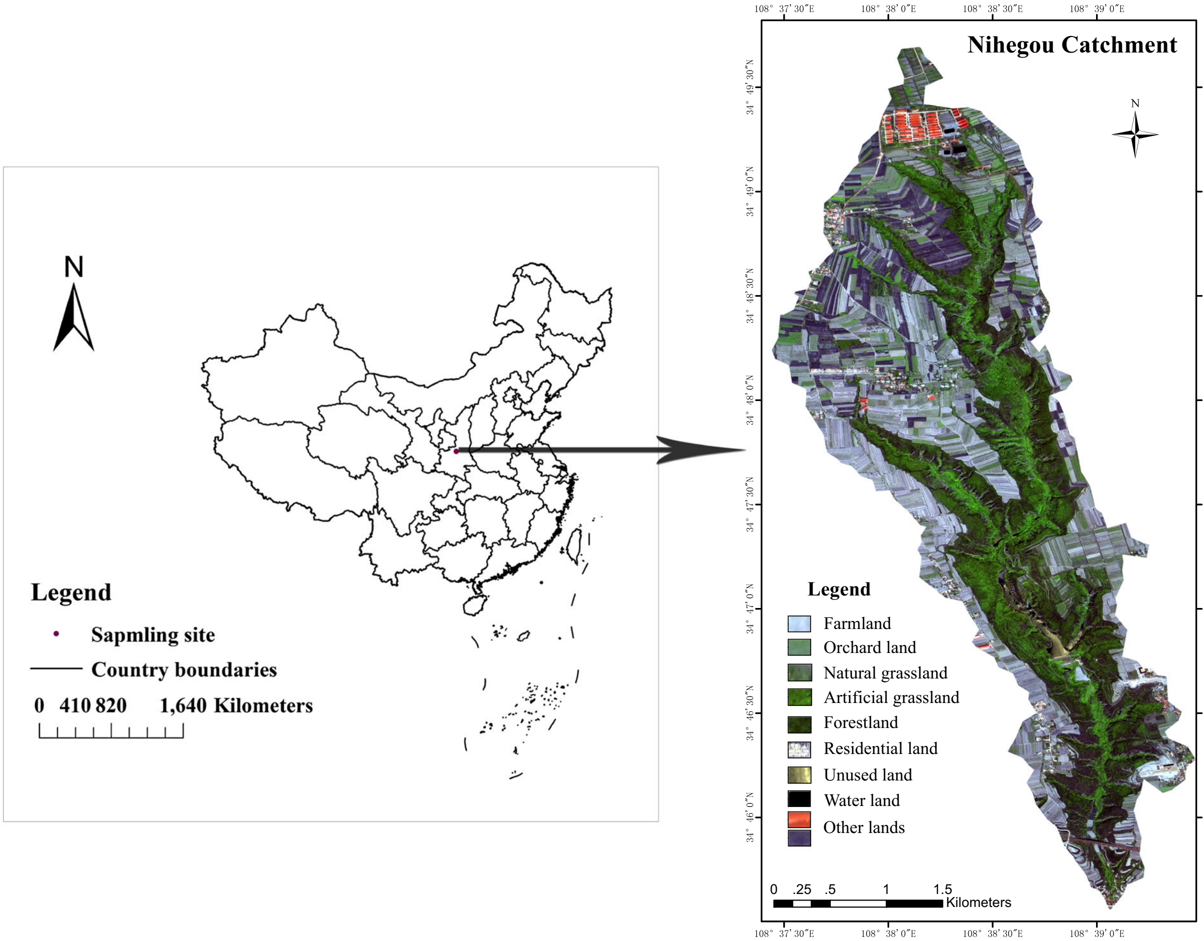

Fig. 1 Location of Nihegou catchment in Chunhua county, Shaanxi Province, China

catchment are 28.12, 22.11, 13.60, 0.25, 13.16, 6.46, 13.42, and 2.88%, respectively (Zhang 2005).

Three transects that crossed typical land-use structures in existence for approximately 30 years were selected as the slope farmland, terrace farmland, and terrace orchard land in the Nihegou catchment. Winter wheat was grown on slope farmland and terrace farmland while the terrace orchard land was planted with Fuji and Qinguan apple trees. Gradients ranged from 3°, 5°, 8°, 12°, 15° to 25° in the slope farmland. The ages of the apple trees were 4, 7, 10, 12, 15, 18, 25, and >30 years in the terrace orchard lands and the terrace farmlands had been in cultivation for 3, 8, 12, 15, and >20 years. Soil samples were collected at depths of 0–20 cm from at least five points in an S pattern from each parcel of terrace farmland, orchard land, and slope farmland, using a wooden knife, in October 2002. Soil samples were homogenized by hand mixing, and major live plant materials and pebbles were separated and discarded. To determine the sources of heavy metals in this study, soil samples were collected at six depths within the soil profile, 0–20 cm, 20–40 cm, 40–60 cm, 60–100 cm, 100–150 cm, and 150–200 cm, in the slope farmland with a gradient of 15°, terrace farmland that had been cultivated for 3, 12, and 15 years, and terrace orchard land that had been cultivated for 12 years.

As concentrations were determined by potassium borohydride-silver nitrate spectrophotometry after digestion with HNO_3-HCl-$HClO_4$. Cr concentrations were determined by ammonium chloride solution-flame atomic absorption spectrophotometry (AAS) after digestion with H_2SO_4-HNO_3-HF. The concentrations of Cu, Ni, and Zn were measured by flame atomic absorption spectrophotometry after digestion with HNO_3-HCl-$HClO_4$. The concentrations of Hg were determined by the cold vapor atomic absorption method after digestion with HNO_3-H_2SO_4-V_2O_5. The atomic absorption spectrophotometer was 5100PC Spectrometer, PerkinElmer Inc., USA.

Quality assurance and quality control

AAS has been widely used to analyze the heavy metals in the soil samples (Bao 2000; Pansu and Gautheyrou 2006). All data were subjected to strict quality assurance and control procedures. The QA/QC procedures were conducted by using a blank assay and a standard reference soil (GSS-5, National Standard Detection Research Center, Beijing, China) for each 20 samples were processed to verify the accuracy of the digestion procedure. The recovery rates for metals ranged from 92.1 to 116.5%.

Assessment of potential ecological risk

The potential ecological risk was assessed using the potential ecological risk index reported by Håkanson (1980).

The index was calculated using the following equations:

$$C_f^i = C_s^i \Big/ C_n^i \qquad (1)$$

$$C_d = \sum_{i=1}^{n} C_f^i \qquad (2)$$

$$E_r^i = T_r^i \cdot C_f^i \qquad (3)$$

$$RI = \sum_{i=1}^{n} E_r^i \qquad (4)$$

where C_j^i is the contamination factor of a single metal; C_s^i is the measured concentration in the sample; C_n^i is the background concentration of the soil; C_d is the degree of contamination, or the pollution coefficient based on many metals; E_r^i is the potential ecological risk factor for a single metal; T_r^i represents the toxicity coefficients of different metals; and RI is the potential ecological risk index based on many metals.

The toxicity coefficients of heavy metals and consult values are shown in Table 1. The toxicity coefficients of heavy metals were selected from the results of Håkanson (1980) and Xu et al. (2008). The consult values as background concentrations were selected of the concentrations in the layer of 150–200 cm on the soil profiles of the three land-use types; meanwhile, the background arithmetic mean values of loessal soil in Shaanxi province (Chinese National Environmental Monitoring Center 1990; Chen 2002) were selected as referee background values.

Statistical analysis

Summary statistics, such as the maximum, minimum, arithmetic mean values, standard deviation (STD), and coefficient of variation (CV), were calculated based on the contents of the heavy metals. Meanwhile, the mean values were compared with the referee background values of the loessal soil by applying single-sample *t* tests at 95%, and analysis of Pearson correlation coefficients between heavy metals was carried out using SPSS 18.0 (SPSS Company, USA). The figures were laid out using SigmaPlot 10.0 (Systat Software, Inc., USA).

Results

Characteristics of heavy metals

Table 2 shows the maximum, minimum, arithmetic mean, STD, and CV values of the contents of heavy metals in terrace farmland, terrace orchard land, and slope farmland. Compared with the background values of the loessal soil (Table 1), the concentrations of Cr and Ni, and especially As and Hg, were lower than that of the background in the slope farmland, terrace farmland, and terrace orchard land, which illustrated an internal source of input. On the other hand, the Cu contents in the slope farmland, terrace farmland, and terrace orchard land were 11.12, 12.93, and 12.94 times greater than the referee background values, respectively, which suggested that the sources of copper might be similar in the three land-use types. The Zn content in the slope farmland was less than the background value, while those of the terrace farmland and terrace orchard land were 1.04 and 1.09 times greater than the background, respectively. Compared with the Environmental Quality Standard for Soils in China (Table 1; State Environmental Protection Administration and State Bureau of Technical Supervision of China 1995), the Cu content only satisfied grade III and was more than the critical concentration of 100 mg/kg that result in a

Table 1 Toxicity coefficient, background concentration of soil and the Environmental Quality Standard for Soils of China

Parameter		Elements (mg/kg)					
		As	Cr	Cu	Hg	Ni	Zn
Background values, C_n^i		13.09[e]	2.29	253.63	0.11[e]	2.12	72.23
Referee background value of loessal soil[a]		10.5	57.5	23.0	0.016	29.3	67.9
Toxicity coefficient[b], T_r^i		10	2	5	40	5	1
Environmental quality standard for soils[c]	Grade I	≤15	≤90	≤35/–[d]	≤0.15	≤40	≤100
	Grade II (pH 6.5–7.5)	≤30	≤200	≤100/200[d]	≤0.50	≤50	≤250
	Grade III	≤40	≤300	≤400/400[d]	≤1.5	≤200	≤500

Background values, C_n^i, data sourced from collected soil in the depth of 150–200 cm on four soil profiles of the three land-use types

– the standard of Cu in grade I for orchard land is absent; here it is considerate as same with that of farmland

[a] Data sourced from Chinese National Environmental Monitoring Center (1990) and Chen (2002)

[b] Data sourced from Håkanson (1980) and Xu et al. (2008)

[c] Data sourced from the Environmental Quality Standard for Soils in China (No. GB 15618-1995) by State Environmental Protection Administration and State Bureau of Technical Supervision of China (1995).

[d] The number before the symbol of "/" is the standard for farmland; later is the standard for orchard land

[e] The units of As and Hg were micrograms per kilogram

reduction of 10% in production (Xia et al. 1992; Xia 1996). While the contents of the other elements (As, Cr, Hg, Ni, and Zn) were all lower than Grade I of the standard, the Cr, Ni, and Hg contents in the terrace farmland were greater than in terrace orchard land. In contrast, the Cr, Cu, and Zn contents in the terrace farmland and terrace orchard land were greater than of the slope farmland. However, the contents of Ni and Hg

Table 2 Statistic description of heavy metal contents in soils

Land type		As µg/kg	Hg µg/kg	Cr mg/kg	Cu mg/kg	Ni mg/kg	Zn mg/kg
Terrace farmland	Max.	13.44	0.138	3.13	311.98	3.15	85.29
	Min.	6.98	0.091	1.44	282.98	0.57	64.28
	Mean	10.18	0.116	2.09	297.51	1.35	70.70
	STD	2.47	0.018	0.69	11.92	1.05	8.35
	CV (%)	24.26	15.73	32.90	4.01	78.08	11.80
	Sig.	0.001	0.000	0.002	0.000	0.046	0.000
Terrace orchard land	Max.	14.00	0.112	2.78	319.31	1.60	82.86
	Min.	11.57	0.094	0.61	281.92	0.39	67.27
	Mean	12.93	0.102	1.53	297.69	1.05	73.85
	STD	0.87	0.006	0.72	14.57	0.45	5.24
	CV (%)	6.80	6.20	46.71	4.89	43.00	7.09
	Sig.	0.000	0.000	0.001	0.000	0.000	0.000
Slope farmland	Max.	12.89	0.125	1.61	272.07	1.81	73.68
	Min.	10.97	0.098	1.29	243.55	0.68	60.06
	Mean	12.22	0.113	1.37	255.81	1.38	65.79
	STD	0.70	0.01	0.12	13.31	0.43	5.12
	CV (%)	5.73	10.80	8.82	5.20	31.10	7.78
	Sig.	0.000	0.000	0.000	0.000	0.001	0.000

were less, and the order of As concentrations from high to low was the terrace orchard land, slope farmland, and terrace farmland. We suspected that Cu might be the pollutant metal in this watershed.

In the terrace farmland, terrace orchard land, and slope farmland, the CV of Ni was the highest; it was 78.08, 43.00, and 31.10%, respectively. The CV of Cu was the least, and it was 4.01, 4.89, and 5.20%, respectively (Table 2). In the terrace farmland and terrace orchard land, the CV of Cr and Ni was higher (32.90–78.08%) than that of the other heavy metals, and the CV of Zn, As, and Hg in the terrace farmland was higher (10% < CV < 25%) than that in the terrace orchard land (<8%). In the slope farmland, the CV of As, Cr, Cu, Hg, and Zn was less than 11%. The results indicated that the differences in the distribution of As, Cr, Hg, Ni, and Zn were greater, while Cu was equally distributed and its pollution degree was similar within the catchment.

Variations of heavy metals with cultivation time or slope gradient

Contents of heavy metals changed irregularly with cultivation time or gradient and displayed different variations in the terrace farmland, terrace orchard land, and slope farmland (Fig. 2). In the terrace farmland, Hg content was the least when it had been tilled for approximately 12 years and then increased; the As content was the least for cultivation times of 8 years and then increased. In contrast, the contents of Cu, Cr, Ni, and Zn in soil that had been cultivated for 8 years were the highest and then decreased with time. For the heavy metals in the terrace orchard land, Hg concentrations were highest at 7 years and increased from 10 to >30 years. As concentrations were smallest at 10 years and showed a decreasing trend with time. Cr and Cu varied within narrow ranges over time; and Ni and Zn had the smallest concentrations at 15 years and their concentrations changed irregularly. Ni varied in a "W" size while Zn had an "M" shape with time. In the slop farmland, Cr concentrations increased with increasing gradient, Hg showed a similar trend but was stable from 15° to 25°, and Cu decreased with increasing gradient and remained stable from 12° to 25°; meanwhile, the contents of As, Ni and Zn varied irregularly.

Variation of heavy metal concentration with depth

Table 3 illustrates that the contents of heavy metals in top soil layer (0–20 cm) were different with those in deeper layer (150–200 cm). The contents of As, Cr, Cu, Hg, and Ni in top soil were greater than those of deeper soil layer, while Zn was opposite in the terrace orchard land and slope farmland. For the terrace farmland, the contents of heavy metals in top and deeper soil of tilled 8 years were different with tilled 3 and 15 years; the contents of As, Cr, Ni, and Zn in top were greater than deeper soil of tilled 8 years, which was opposite of tilled 3 and 15 years; and the contents of Cu and Hg of 3, 8, and 15 years in the top soil layer were different in the 150–200 cm layer. For the three land-use types, the contents of heavy metals except Zn in the top soil layer were lower than in the deeper layer when they were cultivated over 12 years, which indicated that the contents of heavy metals might have same transferring trend with the increasing cultivated years, on the other hand, which also illustrated that the sources of the six heavy metals were more likely to be internal than external sources.

Correlations among heavy metals

Pearson correlation coefficients between the elements of Hg, Cu, As, Cr, Ni, and Zn in the terrace farmland, terrace orchard land, and slope farmland are shown in Table 4. The correlation between Ni and Zn in terrace farmland was positive and significant at the 0.01 level, indicating that they might have identical or similar pollutant sources. The correlation between Cu and Hg was negative and significant at the 0.01 in slope farmland, which showed that their sources were different. In terrace farmland, the source of As was similar to that of Hg but different from those of the other five heavy metals, and the other five elements might have similar pollutant sources due to their positive correlations. In terrace orchard land, there were no significant correlations among the six heavy metals. The correlations between Cr and Zn, Cu and Ni, Cu and Zn, and Hg and Ni were negative, showing that their sources varied. In the slope farmland, the sources of As and Hg, Cr and Cu, Cu and Zn, Hg and Ni, and Ni and Zn As were probably different because of their inverse correlations.

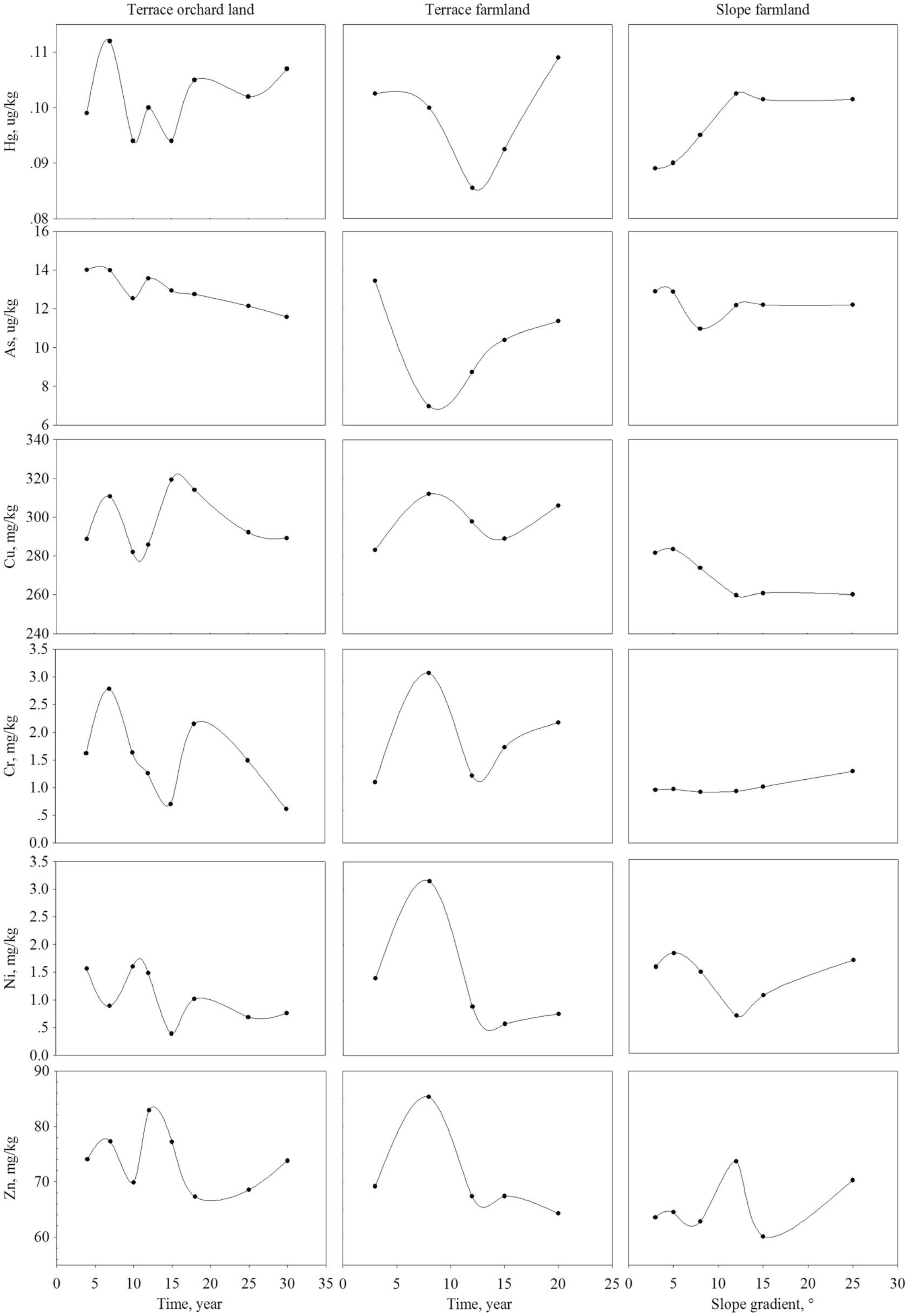

Fig. 2 Contents of Hg, As, Cu, Cr, Ni, and Zn in soil derived from terrace orchard land that has been in cultivation for different numbers of years, terrace farmland that has been in cultivation for different numbers of years, and slope farmland with different gradients

Table 3 Concentrations of heavy metals in the top and bottom soil under the three land-use types

Land-use type	Year/slope gradient	As (μg/kg)		Cr (mg/kg)		Cu (mg/kg)		Hg (μg/kg)		Ni (mg/kg)		Zn (mg/kg)	
		0–20 cm	150–200 cm	0–20 cm	150–200 cm	0–20 cm	150–200 cm	0–20 cm	150–200 cm	0–20 cm	150–200 cm	0–20 cm	150–200 cm
Terrace farmland	3	13.44	12.51	1.44	2.58	282.98	278.80	0.125	0.143	1.39	2.43	69.18	74.57
	8	6.98	13.63	3.13	1.30	311.98	284.35	0.120	0.120	3.15	1.89	85.29	55.43
	15	10.40	12.06	1.98	3.22	288.86	326.42	0.105	0.095	0.57	2.97	67.40	90.10
Terrace orchard	12	13.56	14.68	1.26	2.44	285.69	293.51	0.100	0.097	1.48	1.72	82.86	58.44
Slope farmland	15	12.21	12.57	1.37	1.91	245.00	285.07	0.123	0.099	1.05	1.60	60.06	82.61

Assessment on potential ecological risk posed by heavy metals

The potential ecological risks associated with different numbers of years in the cultivation of terrace farmland, orchard land, and slope farmland were described in quantitative terms using the potential ecological risk index (Håkanson 1980). Variations in the pollution coefficients $\left(C_f^i\right)$ and the potential ecological risk factors $\left(E_r^i\right)$ of the different heavy metals, as well as the degrees of contamination (C_d) and the potential ecological risk indexes (*RI*) of the three land-use types, are provided in Table 5. Evaluation of the *RI* values showed that the soils were slightly polluted in the Nihegou catchment. The average value of C_d in the slope farmland was lower than that of the terrace farmland and terrace orchard land. The average value of *RI* in the terrace orchard land was the lowest. The variations in C_d and *RI* with cultivated time or slope gradient were different in terrace farmland, terrace orchard land, and slope farmland; C_d and *RI* showed similar change with cultivated time under the terrace farmland and orchard land; meanwhile, *RI* increased while C_d decreased with the increasing of slope gradient in the slope farmland (Fig. 3).

Compared with the grade standards associated with the Håkanson potential ecological risk index values shown in Table 6, the current study shows that the highest potential ecological risk factor $\left(E_r^i\right)$ was Hg (greater than 33.0), then it was As, Cu, Ni, Cr, and Zn, in the terrace farmland and terrace orchard land. The C_f^i of Cu was greater than 1.0, reflecting a moderate contamination factor. The most pollution coefficients $\left(C_f^i\right)$ of As, Cr, Ni, and Zn were less than 1.0, reflecting low contamination factors. Meanwhile, the average C_f^i of Hg was greater than 1.0 in the terrace farmland, reflecting a moderate contamination factor, which was lower than 1.0 in the terrace orchard land, meaning low contamination factor. The potential ecological risk factors $\left(E_r^i\right)$ of As, Cr, Ni, and Zn were all less than 11.0, reflecting low potential ecological risk. Meanwhile, the E_r^i of Hg was greater than 30 and less than 60, indicating a moderate potential ecological risk.

In terrace farmland, the values of C_d and *RI* were highest at 8 years (6.89) and >20 years (70.03), respectively, and these quantities reached their lowest values (4.69 and 49.98, respectively) at 12 years; the orders of

Table 4 Person correlation analysis between heavy metals

Land type	Elements	As	Cr	Cu	Hg	Ni	Zn
Terrace farmland	As	1					
	Cr	−0.641	1				
	Cu	−0.728	0.844	1			
	Hg	0.424	0.383	0.237	1		
	Ni	−0.560	0.701	0.538	0.192	1	
	Zn	−0.668	0.725	0.519	0.039	0.974**	1
Terrace orchard land	As	1					
	Cr	0.540	1				
	Cu	0.179	0.240	1			
	Hg	0.047	0.507	0.219	1		
	Ni	0.403	0.264	−0.669	−0.236	1	
	Zn	0.522	−0.197	−0.014	0.003	0.069	1
Slope farmland	As	1					
	Cr	0.090	1				
	Cu	0.326	−0.457	1			
	Hg	−0.366	0.416	−0.993**	1		
	Ni	0.212	0.339	0.652	−0.660	1	
	Zn	0.055	0.299	−0.453	0.456	−0.324	1

*Correlation is significant at the 0.05 level; **correlation is significant at the 0.01 level

C_d and *RI* from 3 years to >20 years were 8>>20>3>15>12 years and >20>3>8>15>12 years, respectively. In terrace orchard land, the values of C_d and *RI* were highest at 7 years (6.01 and 63.13, respectively), and these quantities reached their lowest values at 10 years (4.64) and 15 years (52.96), respectively. The orders of C_d and *RI* from 4 years to >30 years, which were 7 > 4 > 18 > 12 > 10 > 25 > 15> > 30 years and 7 > 18 > 4 > 12> > 30 > 25 > 10 > 15 years, respectively, were different from those of the terrace farmland. The values of C_d in the terrace farmland and terrace orchard land were all less than 6.0, indicating a low degree of contamination, except 8 years in the terrace farmland (6.89) and 7 years in the terrace orchard land (6.01) and which were in a moderate degree. Meanwhile, the values of *RI* were all less than the standard's low-grade value (150), indicating low ecological risk.

In the slope farmland, C_f^i and E_r^i of Cu and Hg illustrated moderate degree contamination while those of As, Cr, Ni, and Zn were in low degree. Values of C_d indicated a low degree of contamination with a decreasing trend as the increased slope gradient, and the *RI* values illustrated that the soils posed low ecological risks and while showed an increasing trend with increasing gradient.

The results of C_j^i and E_r^i suggested that Cu and Hg were the main factors in soil pollution and the soils were in low degree contamination and low ecological risk from the values of C_d and *RI* in Nihegou catchment.

Discussion

The characteristics of heavy metals in soil

In the current study, the contents of heavy metals such as Cr and Ni, and especially As and Hg, were lower than the referee background values. However, Cu only satisfied Grade III of the Environmental Quality Standard (GB15618-1995, State Environmental Protection Administration and State Bureau of Technical Supervision of China 1995) and was a pollutant metal, and the heavy metals showed different trends under apple trees of different years in cultivation and slope gradients (Table 2; Fig. 2). The characteristics such as concentration and variation in heavy metals may differ from other studies due to the effects of sampling time (before or after pesticide applied) or the application rates (increasing with times) or types of fertilizers (as phosphate fertilizer) and pesticides (as Bordeaux mixture).

Table 5 The potential ecological risk factor and index

Land-use type	Year/slope gradient	As		Cr		Cu		Hg		Ni		Zn		C_d	RI
		C_f^i	E_r^i	C_f^i	E_r^i	C_f^i	E_r^i	C_f^i	E_r^i	C_f^i	E_r^i	C_f^i	E_r^i		
Terrace farmland	3	1.0267	10.267	0.6288	1.258	1.1157	5.579	1.1364	45.455	0.6557	3.278	0.9578	0.958	5.52	66.79
	8	0.5332	5.332	1.3668	2.734	1.2301	6.150	1.0909	43.636	1.4858	7.429	1.1808	1.181	6.89	66.46
	12	0.6669	6.669	0.6725	1.345	1.1736	5.868	0.8273	33.091	0.4151	2.075	0.9323	0.932	4.69	49.98
	15	0.7945	7.945	0.8646	1.729	1.1389	5.695	0.9545	38.182	0.2689	1.344	0.9331	0.933	4.95	55.83
	>20	0.8678	8.678	1.0306	2.061	1.2067	6.033	1.2545	50.182	0.3538	1.769	0.8899	0.890	5.60	69.61
	Average	0.7778	7.778	0.9127	1.825	1.1730	5.865	1.0527	42.109	0.6358	3.179	0.9788	0.979	5.53	61.74
Terrace orchard	4	1.0695	10.695	0.6288	1.415	1.1380	5.690	0.9000	36.000	0.7358	3.679	1.0252	1.025	5.58	58.50
	7	1.0680	10.680	1.2140	2.428	1.2248	6.124	1.0182	40.727	0.4198	2.099	1.0696	1.070	6.01	63.13
	10	0.9572	9.572	0.7118	1.424	1.1115	5.558	0.8545	34.182	0.7547	3.774	0.9668	0.967	5.36	55.48
	12	1.0359	10.359	0.5502	1.100	1.1264	5.632	0.9091	36.364	0.6981	3.491	1.1472	1.147	5.47	58.09
	15	0.9885	9.885	0.3057	0.611	1.2590	6.295	0.8545	34.182	0.1840	0.920	1.0689	1.069	4.66	52.96
	18	0.9733	9.733	0.9389	1.878	1.2385	6.193	0.9545	38.182	0.4811	2.406	0.9313	0.931	5.52	59.32
	25	0.9267	9.267	0.6507	1.301	1.1518	5.759	0.9273	37.091	0.3255	1.627	0.9485	0.948	4.93	55.99
	>30	0.8839	8.839	0.2664	0.533	1.1396	5.698	0.9727	38.909	0.3585	1.792	1.0216	1.022	4.64	56.79
	Average	0.9879	9.879	0.6681	1.336	1.1737	5.868	0.9239	36.955	0.4947	2.473	1.0224	1.022	5.27	57.53
Terrace (farmland + orchard)		0.8829	8.829	0.7904	1.581	1.1733	5.867	0.9883	39.532	0.5653	2.826	1.0006	1.001	5.40	59.63
Slope farmland	3	0.9847	9.847	0.5764	1.153	1.0637	5.318	0.8909	35.636	0.7358	3.679	0.8794	0.879	5.13	56.51
	5	0.9840	9.840	0.5808	1.162	1.0727	5.364	0.9091	36.364	0.8538	4.269	0.8923	0.892	5.29	57.89
	8	0.8380	8.380	0.5633	1.127	1.0267	5.133	1.0000	40.000	0.6934	3.467	0.8694	0.869	4.99	58.98
	12	0.9305	9.305	0.5677	1.135	0.9603	4.801	1.1364	45.455	0.3208	1.604	1.0201	1.020	4.94	63.32
	15	0.9328	9.328	0.5983	1.197	0.9660	4.830	1.1182	44.727	0.4953	2.476	0.8315	0.832	4.94	63.39
	25	0.9320	9.320	0.7031	1.406	0.9624	4.812	1.1182	44.727	0.7925	3.962	0.9726	0.973	5.48	65.20
	Average	0.9337	9.337	0.5983	1.197	1.0086	5.043	1.0288	41.152	0.6486	3.243	0.9109	0.911	5.13	60.88
Catchment		0.8998	8.998	0.7263	1.453	1.1184	5.592	1.0018	40.072	0.5930	2.965	0.9707	0.971	5.31	60.05

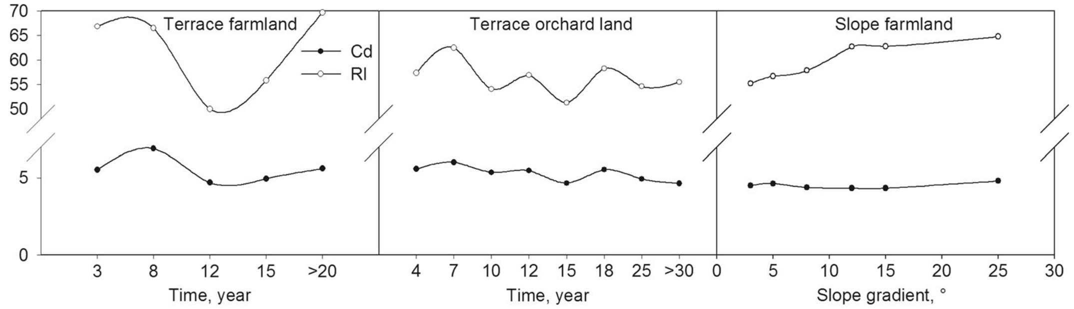

Fig. 3 Change of Cd and RI under the three land-use types, with different cultivation years of the terrace orchard land and terrace and different slope gradients of slope farmland

Previous studies on orchard soils showed that heavy metals accumulated with tilled time and increased of the application rates of fertilizers and pesticide; the heavy metals, especially As and Cr, should be closely monitored on the Loess Plateau, such as in Baishui county (Liang et al. 2004), Changwu county (Li et al. 2007; Liu et al. 2009a, b, 2010), Luochuan county (Zhu et al. 2009), Lanzhou city (Luo et al. 2011), Shaanxi province (Zhang et al. 2004), Tianshui area (Chen et al. 2011a, b) and the Weibei region (Hu et al. 2012). However, the concentrations of heavy metals, including Cu, in orchard soils were all lower than specified by the grade II environmental quality standard (GB15618-1995), although they were greater than the referee values (Chinese National Environmental Monitoring Center 1990; Chen 2002). Meanwhile, few studies have reported on the features of heavy metals in agricultural soil, such as terrace farmland planted with crops, especially in slope farmland on the Loess Plateau. As Li et al. (2007) reported, the contents of Cu, Cr, Hg, and As varied with the apple trees' ages, and different heavy metals showed different increasing variation characteristics because of their different characteristics in soil. Simultaneously, Cu contents under apple trees of different ages were all lower than that of the grade II environmental quality standard (GB15618-1995). Zhu et al. (2009) illustrated that the distribution of heavy metal pollution in agricultural soil was obviously different from that in apple orchard soil, and the As and Cr contents of the two soils exceeded the warning threshold for soil environmental quality for vegetable production.

Mackie et al. (2012) noted that Bordeaux mixture ($CuSO_4$), a pesticide, is a primary source of Cu in vineyards because of commonly applied to prevent disease worldwide. However, our results indicated the source of Cu might be the parent material, rather than other potential sources because the copper concentrations were evenly distributed and its pollution degree (C_d) was similar in terrace farmland, terrace orchard land, and slope farmland. However, Cu concentrations were significantly different from the referee value (Tables 1 and 2) (Chinese National Environmental Monitoring Center 1990; Chen 2002). In Table 3, the contents of Cu in 0–20 cm and 150–200 cm on the five soil profiles were all greater than the grade II environmental quality standard (GB15618-1995). These observations supported the hypothesis that the source of Cu was the parent material rather than fertilizers, pesticides, or atmospheric sedimentation, which agrees with the results reported by Chen et al. (2011b). The results as Table 3 shown agreed that the parent material, pollutant source, physicochemical properties, precipitation, irrigation, tillage mode and system, and the regional environment affect the contents and distribution of heavy

Table 6 Grade standard of Håkanson potential ecological risk (1980)

Ecological risk	Low	Moderate	Considerable	High	Very high
C_f^i	<1	≤1, <3	≤3, <6		≥6
C_d	<6	≤6, <12	≤12, <24		≥24
E_r^i	<40	≤40, <80	≤80, <160	≤160, <320	≥320
RI	<150	≤150, <300	≤300, <600		≥600

metals (Håkanson 1980; Andreu and Gimeno-Garc 1999; Wang 2000; Zhu and Chen 2001; Ren et al. 2008; Wang et al. 2017).

Potential ecological risk assessment

It was observed that Cu was considered as a contaminant based on the values of the contamination factor $\left(C_f^i\right)$ and the potential ecological risk factor $\left(E_r^i\right)$ in terrace farmland, terrace orchard land, and slope farmland. Contamination degrees (C_d) were considerable in the terrace farmland and terrace orchard land. In the slope farmland, the contamination degrees were considerable as the gradient increased from 3° to 8°, while they were moderate for gradients between 12° and 25°. The values (Table 5) of the potential ecological risk index (*RI*) indicated that the potential ecological risk was low (<150; Table 6) in this catchment. Our results differ from those of Huang et al. (2009) but are consistent with those reported by Chen et al. (2011a). Huang et al. (2009) reported that the quality of orchard soil cultivated for 5–15 years was the best assessed by an integrated fertility index with a fuzzy comprehensive evaluation method for different cultivation periods, while our results showed that the highest *RI* values occurred for cultivation periods of >20 and 7 years in terrace farmland and terrace orchard land, respectively. Chen et al. (2011a) stated that the potential ecological hazard in Tianshui apple orchard soil was slight, based on a potential ecological risk assessment. Soils were at the warning level of contamination in orchard soils using other methods in other places on the Loess Plateau, such as soils quality were evaluated by the single factor index method in Baishui county (Liang et al. 2004). Similar results were also assessed by the single factor index combined with the Nemerow index method in Lanzhou city (Luo et al. 2011), Luochuan county (Zheng and Yue 2008; Zhu et al. 2009), Changwu county (Liu et al. 2009a, b), and Shaanxi province (Zhang et al. 2004; Liu et al. 2009a, b), respectively. Simultaneously, the *RI* values increased with increasing gradient in slope farmland did not clearly state in the relevant literature; soil erosion might affect the contamination of heavy metals and should be further study.

Conclusions

The average concentrations of Cu and Zn were higher than the elemental referee background concentrations of the loessal soil, while Cr, and Ni and, especially, As and Hg were lower than the referee background values in terrace farmland, terrace orchard land, and slope farmland. Cu was the only heavy metal that just met the Grade III Environmental Quality Standard for Soils of China, while the others reached grade I. Cu and Hg were considered as contaminant factors $\left(C_f^i\right)$, and Hg was associated with a moderate potential ecological risk factor $\left(E_r^i\right)$. The six heavy metals showed different trends with time or gradient in the three land-use types. Of the sites investigated, 89.5% fell in the category with a low degree of contamination (C_d) and rest were moderate, while all three land-use types had low potential ecological risk (*RI*). Variations of C_d had similar change of *RI* with cultivated time in the terrace farmland and terrace orchard land. Values of *RI* increased while C_d decreased with the increasing of slope gradient in the slope farmland.

Furthermore, it might be necessary to compare the results obtained using different methods to evaluate the degree of pollution of agricultural soils or the ecological risk posed by heavy metals in a potential ecological risk assessment based on more soil samples from a larger study on the Loess Plateau of China. The relation between soil erosion and heavy metal pollution should be paid more attention to study in the slope farmland.

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