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Heavy Metal Pollution and Ecological Risk Assessment of the Agriculture Soil in Xunyang Mining Area, Shaanxi Province, Northwestern China

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Abstract

Mining is considered to be one of the most significant sources of environmental pollution with regard to heavy metals. Mineral mining causes large quantities of mercury, cadmium, and other elements to be released into the environment and naturally poses a serious threat to environment. This paper will analyze the pollution status of agricultural soil caused by the mining of heavy metals in various mining areas in the Xunyang County in the Shaanxi Province of China, an area in famous for its resource mining. Equally, it will look at the potential ecological risk assessment process that is used to analyze the ecological risks of mining heavy metals in agricultural soil located in the surrounding areas. Based on the soil investigation, As pose a moderate ecological risk on the Au mining area. In addition, the Hg metals pose a significantly high potential ecological risk and Cd metals pose a considerable potential ecological risk on the Hg mining area. In the Pb–Zn mining area, a significantly high potential ecological risk was mainly posed by Cd. These results suggest that many heavy metals pose a high potential ecological risk on the agricultural soil in these three mining areas in the Xunyang County, and may cause elevated heavy metal contents in crops, eventually jeopardizing the health of local residents who consume food grown in polluted soil.

Keywords Heavy metal pollution · Potential ecological risk assessment · Hg mining · Au mining · Pb–Zn mining

It is well known that the contamination of agricultural soil by heavy metals such as mercury (Hg), arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), copper (Cu), zinc (Zn), and nickel (Ni) is detrimental to the environment due to the toxic, accumulative and persistent nature of heavy metal in the environment and biota (Díaz et al. 2013; Lei et al. 2015). Such contamination could lead to negative influences on soil quality and soil productivity, even endangering the health and well-being of animals and human beings due to its effect on the food chain (Zhang et al. 2013). However, much contaminated agricultural soil is still used in agricultural production, due to the scarcity of availability of arable lands (Ran et al. 2017). Agricultural soil pollution is mainly the result of human activities within the industrial, farming and mining sectors. Among these, mining is considered to be one of the most significant factors in heavy metal contamination (Yao-Guo et al. 2010).

With the rapid development of mining and the exploitation of mineral resources, and agricultural soil, the peripheral area surrounding mines is often polluted by heavy metals. One may derive that large quantities of heavy metals are released from mining activities (Duan et al. 2016; Zhang et al. 2012). These significant levels of metal pollution resulting from mining activities in the surrounding agricultural soil could pose a considerable risk on ecological safety and human wellbeing (Tang and Zhao 2015). Previous research has shown that the elevated heavy metals content in agricultural soil near mining areas far exceeds the Grade II environmental quality standard for soils in China (GB15618-1995, Qiu et al. 2012a). For example, it was found that the As and Cd contents in agricultural soil in the mine tailings in the Hunan province was up to 24 and 13 times higher, respectively, than the maximum allowable concentration levels for Chinese agricultural soil (Liu et al. 2005). Similarity, Zhuang et al. (2009) reported that in Guangdong Province, concentrations of Cd, Cu and Zn in agricultural soil surrounding mining deposits surpassed 13, 10 and 2.5-fold of

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the national standard value for soil, respectively. Accordingly, heavy metal risk assessment studies in the contaminated farmlands have recently received increased attention, in particular the agricultural soil surrounding mining areas (Zhu et al. 2012). It was documented that potential ecological risk assessment, developed by Hakanson (1980), could estimate the level of contamination in soil affected by heavy metals. This method is widely used to evaluate the extent of the potential toxicity of heavy metals and ecological risks caused by toxic metals comprehensively (Gao et al. 2013).

Xunyang County, located in the Shaanxi Province of Northwestern China, is abundant in Hg, Au and Pb–Zn ore. A large quantity of tailings generated from Hg, Au and Pb–Zn mining regions, contained a large number of heavy metals including Cd, Hg, Pb, As, Cu, Zn, Ni and Cr (Li et al. 2014). Under certain conditions, these heavy metals could have been released and migrated into the soil, causing a serious threat to the environment (Guillén et al. 2012). Hence, the objective of this study is to determine the contents of heavy metals (Cd, Hg, Pb, As, Cu, Zn, Ni and Cr) in agricultural soil from the Xunyang mining area in the Shaanxi Province in order to understand the soil pollution status in these areas. Furthermore the potential ecological risk assessment was carried out to evaluate the ecological risks of heavy metals in the Xunyang mining area.

Materials and Methods

Xunyang County, located between 32°29′–33°13′ north latitude and 108°58′–109°48′ east longitude, in the south of Shaanxi Province with a total surface area of 3550 km^2, was chosen as the study area. The climate in the study area is sub-tropical humid. Xunyang County has an average temperature of 15.4°C and an average precipitation of 851 mm (Ao et al. 2017).

Xunyang County is rich in mineral resources. Presently, it has more than 39 kinds of mineral resources, including mercury, lead, zinc, gold, copper, stibium, manganese, magnesium, limestone, and dolomite ore. Among them, Hg, Au and Pb–Zn ore are the main mining deposits (Tang and Zhao 2015). Specifically, Hg mineral deposits are located in Gongguan and Qingtonggou (Qiu et al. 2012b), whereas Au mining is mainly situated in the Donghecun area. Equally, Pb–Zn mineral deposits are located in Nanshagou (Liao et al. 2008). Accordingly, the sampling points in this paper were divided into four zones which were polluted by different mining deposits. The four zones will be referred to in this paper as D (located in Donghecun and polluted by Au ore), G (located in Gongguan and polluted by Hg ore), Q (located in Qingtonggou and polluted by Hg ore) and N (located in Nanshagou and polluted by Pb–Zn ore). The sampling point in the Xunyang County is presented in Fig. 1.

Soil samples were obtained from four mining areas, including the Donghecun Au mining area, the Gongguan and Qingtonggou Hg mining areas and the Nanshagou Zn–Pb mining area. Surface soil samples (0–20 cm) were collected from farmland in the vicinity of four mining areas in November 2017. At each zone of paddy field, composite soil was obtained from five subsamples using an "S" sampling procedure (Mirzaei et al. 2014). Specifically, seven samples were collected at Zone D and the distance of each sample from the mining area was 100, 200, 300, 400, 500, 600 and 700 m, respectively. Six samples were collected at Zone G and Zone Q and the distance of each sample from the mining area was 100, 200, 300, 400, 500 and 600 m respectively. And four samples were collected at Zone N and the distance of each sample from the mining area was 100, 200, 300 and 400 m, respectively. In total, 23 composite soil samples were collected. All the samples were ground after air-drying, passed through the 0.15-mm mesh screen for the analysis of heavy metal contents (Chen et al. 2012).

The contents of Cu, Pb, Ni, Zn, Cd, As and Cr in the soils were measured using inductively coupled plasma atomic emission spectroscopy (ICP-MAS, Agilent 7700) (Lin et al. 2008). The total concentration of Hg was measured by atomic fluorescence spectroscopy (AFS-9760 produced by HAIGUANG, China) (Lu et al. 2015). The concentrations of trace metals obtained from reagents, glassware and Teflon vessels used in the study were below the detection limit. Quality control of soil analysis was performed using the standard reference material (GSS-8, GSS-10 and GSF-3) obtained from the National Center for Standard Materials in China. The recovery rates for the heavy metal contents in the standard reference material ranged from 90% to 110%.

To evaluate contamination levels of heavy metal, this experiment adopted the pollution index (PI) method. The equation for calculating PI was the ratio of heavy metal concentrations of the soils divided by the value of national environmental Quality Standards for Soils (II) (GB 15618-1995). According to the document, the variation in PI could be defined as follows: $PI \le 1$ (non-pollution), $1 < PI \le 2$ (minor pollution), $2 < PI \le 3$ (light pollution), $3 < PI \le 5$ (medium pollution), and $PI > 5$ (heavy pollution) (Izah et al. 2017).

The assessment of soil contamination was conducted using the potential ecological risk index (RI) method, proposed by Hakanson, which is now widely used in the evaluation of heavy metal risk (Du et al. 2015; Huang 2014). The RI could be calculated by the following equation (Gong et al. 2008):

$$C_r^i = \frac{C_s^i}{C_n^i}$$

$$E_r^i = T_r^i C_r^i$$

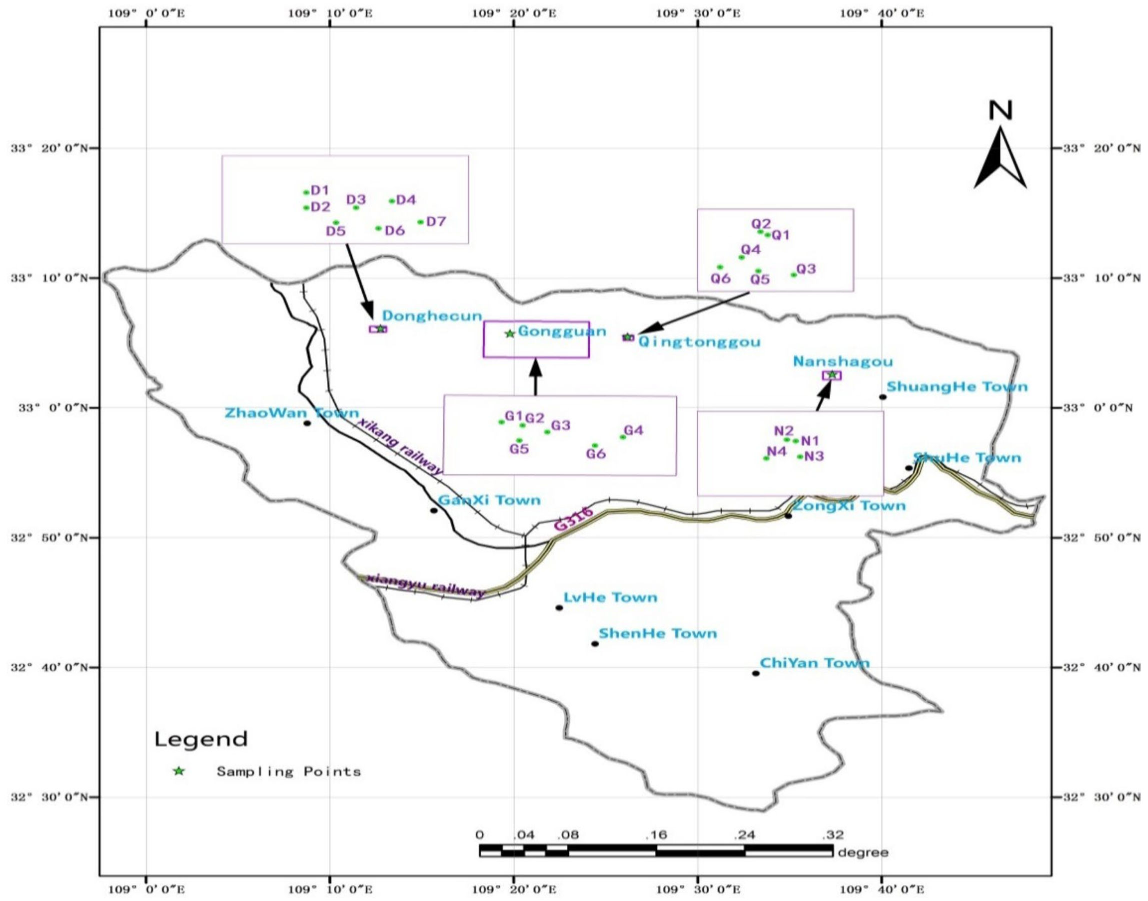

Fig. 1 Sampling points in the Xunyang County

Table 1 Environmental background values and toxicity factor of heavy metals in the sediments

Element	Cd	Cr	Hg	As	Pb	Cu	Zn	Ni
C_n^i (mg/kg)	0.76	62.5	0.063	11.1	21.4	21.4	69.4	28.8
T_r^i	30	2	40	10	5	5	1	5

where T_r^i is the toxic response factor for the given metal of "i", which demonstrate their toxic and ecological sensitivity levels; this study adopted the T_r^i proposed by Hakanson (Table 1). C_r^i is the contamination factor for the given metal. C_s^i is measured metal levels in sediments and C_n^i references background values of heavy metals (Yi et al. 2011). The background values used in this paper were based on soil element background values of the Shaanxi Province (Table 2, Xu et al. 2014).

The integrated PERI (RI) is calculated as the sum of the E_r^i for all examined heavy metals as following equation:

$$\mathrm{RI} = \sum_{i=1}^{m} E_r^i$$

Table 2 Grades of potential ecological RI of heavy metal pollution

Scope of potential ecological RI $\left(E_r^i\right)$	Scope of integrated potential ecological RI (RI)	Ecological risk level
<40	<150	Low
40–80	150–300	Moderate
80–160	300–600	Considerable
160–320	600–1200	High
≥320	≥1200	Significantly high

Statistical analyses were conducted using SPSS 10.01. The difference of heavy metal contents was tested using one-way analysis of variance (ANOVA).

Results and Discussion

As shown in Fig. 2, in Donghecun, the mean concentrations of Cd and As exceed the corresponding Grade II environmental quality standard for soils in China. The highest values in Donghecun correspond to Cr, Ni, Cu, Zn, As, Cd, Pb and Hg (149, 119, 41, 139, 196, 2.025, 47.21 and 0.169 mg/kg, respectively). In Gongguan, Hg, Cd, Cr, As and Ni surpass standard value, and were 3.9, 1.3, 1.1, 1.4 and 4.0 times greater, respectively, than the Grade II standard value. In Qingtonggou, the average concentrations of Hg, Cd, Cr and Ni surpass the standard value, and were 3.9, 1.3, 1.5 and 3.9 times greater, respectively, than the Grade II standard value. In Nanshagou, the average concentrations for Zn (327 mg/kg), Cd (1.471 mg/kg), Cr (381 mg/kg) and Ni (221 mg/kg) surpass the standard value. Based on this analysis, the agricultural soils in the vicinity of the Au mining areas were indeed contaminated by As and Cd. Equally, soils surrounding Hg ore were polluted by Hg, Cd, Cr and Ni. Soil nearby the Pb–Zn ore was contaminated by Zn, Cd, Cr and Ni.

According to results (Table 3), in Donghecun, 57% of Ni, 86% of As and 57% of Cd respectively, have a PI > 1, suggesting contamination from this heavy metal. In the Gongguan Hg mining area, there were about 34% sites with its PI for Cr from 1.0 to 5.0, indicating that 34% of soil was contaminated by Cr. In addition, about 67% sites were somewhat contaminated by Ni, and about 33% of sites were heavily contaminated by Ni. The high PI of Hg in Gongguan was about 33% above 5.0 and about 67% from 1 to 5, which was similar with the Hg result in Qingtonggou. This shows that all the Hg mining areas were under Hg contamination, and 33% of sites could be categorized as heavily contaminated by Hg. Meanwhile, in Qingtonggou, about 33% of sites were heavily contaminated by Ni and Hg, and about 17% of sites were moderately contaminated by Cr, Ni and Hg. This could be attributed to the resultant 33% of which had a PI for Hg and Ni above 5.0 and roughly 33% of sites which had a PI for Cr, Ni and Hg from 3.0 to 5.0. Concurrently, most elements except Zn and Cu had a PI above 1.

In Nanshagou, about 25% of sites were heavily contaminated by Cd, Ni and Pb and about 50% and 25% were moderately contaminated by Ni and Zn respectively. Equally, roughly 75% of sites for Cr and 25% of sites for Cd and Ni have moderate pollution status.

To investigate the common characteristics of metals in the Xunyang mining area, correlation analyses between metals were calculated. This analysis could effectively reveal the relationships among parameters and understand sources of chemical components (Shou et al. 2012). Heavy metals in the environment usually relate to each other in a complicated way. The high correlations among the parameter may imply that they came from similar pollution sources (Shou et al. 2012). Correlations between the metals Cu, Cr, Ni and Pb were significant at the $p < 0.05$ level as shown in Table 4. This suggests a common origin or similar chemical behavior for Cu, Cr, Ni and Pb (Guillén et al. 2012). Obviously, the sources of soil pollution are complex in several kinds of heavy metals, because other heavy metals are not related with each other. Therefore, it is difficult to protect the soil from the heavy metals pollution.

Table 3 Class distribution of PI for heavy metals in agriculture soil surrounding different types of examined mining areas in the Xunyang County

Sampling sites	PI	Ratio (%)							
		Cr	Ni	Cu	Zn	As	Cd	Pb	Hg
Donghe-cun	< 1	100	43	100	100	14	43	100	100
	1–3	0	57	0	0	57	43	0	0
	3–5	0	0	0	0	0	14	0	0
	> 5	0	0	0	0	29	0	0	0
Gongguan	< 1	67	0	100	83	67	50	100	0
	1–3	17	67	0	17	33	50	0	50
	3–5	17	0	0	0	0	0	0	17
	> 5	0	33	0	0	0	0	0	33
Qingtong-gou	< 1	33	0	100	100	67	33	83	0
	1–3	50	50	0	0	33	67	17	50
	3–5	17	17	0	0	0	0	0	17
	> 5	0	33	0	0	0	0	0	33
Nansha-gou	< 1	25	0	100	75	100	50	75	100
	1–3	75	25	0	0	0	25	0	0
	3–5	0	50	0	25	0	0	0	0
	> 5	0	25	0	0	0	25	25	0

Table 4 Correlation coefficients matrix among heavy metals in agriculture soil in the Xunyang County

Element	Correlation coefficients							
	Cr	Ni	Cu	Zn	As	Cd	Pb	Hg
Cr	1.00							
Ni	0.81^{**}	1.00						
Cu	0.41^{*}	0.69^{**}	1.00					
Zn	0.04	0.26	0.41	1.00				
As	− 0.41	-0.55^{**}	− 0.33	− 0.31	1.00			
Cd	− 0.33	− 0.07	0.29	0.38	0.10	1.00		
Pb	0.51^{*}	0.43^{*}	0.44^{*}	0.35	-0.42^{*}	0.02	1.00	
Hg	0.31	0.21	0.03	0.19	− 0.34	0.15	0.43^{*}	1.00

$^{*}p < 0.05$, $^{**}p < 0.01$

In Donghecun, the range and means of the potential ecological RI of As were the largest among these metals. The range of As for Donghecun gold mining sites was 15.3–126.2. The range of the potential ecological risk of soil calculated by the RI was 67–582 with a mean value of 259 and revealed a moderate ecological risk in the study area (Table 5).

Hg posed a significantly higher ecological risk in the Gongguan and Qingtonggou Hg mining areas, which could be attributed to the fact that the individual potential ecological risk value in these two areas was significantly above 320. Specifically, in Gongguan, the potential ecological RI of Hg was between 331.2 and 2387.8 with the average value of 1216.6. Considerable potential ecological risk was posed by Cd, which was in the range of 73.2–257.3. The other metal (Cr, Ni, Cu, Zn, As, Pb and Hg) hardly posed some threat on Gongguan, which is similar to the result in Qingtonggou. The significantly high potential ecological RI of Hg was 320.4–2257.8 with the mean value of 1238.3 in Qingtonggou. Simultaneously, the considerable potential ecological RI of Cd was between 51.5 and 199.6 with mean value of 141.7. The range of RI was 446–2762 with a mean value of 1339 and revealed a significantly high potential ecological risk in the Gongguan and Qingtonggou Hg mining areas.

Nanshagou was in the category of high potential ecological risk, which could be attributed to the high average RI result of 1008 in this region. In addition, this high level of potential ecological risk was mainly posed by Cd, due to its high potential ecological RI of 344.4.

The Hg contents in Gongguan and Qingtonggou area was significantly greater than that in other place (Fig. 2), which means that the Hg ore obviously affect the Hg contents in soil and pose a threat on nearby residents. Similarly the As contents in Donghecun surpass significantly than that in other place, suggesting that Au ore mainly result in As pollution. On the contrary, the Pb and Zn contents were not significantly greater than other place.

Table 5 Assessment of potential ecological risk of heavy metals in agriculture soil surrounding different types of examined mining areas in the Xunyang County

Sampling sites		Cr	Ni	Cu	Zn	As	Cd	Pb	Hg	RI
Donghe-cun	Max	4.8	20.7	9.9	2.2	126.2	357.4	7.3	53.3	582
	Min	2.2	6.4	5.4	1.2	15.3	17.1	5.0	14.3	67
	Mean	3.3	12.3	7.4	1.6	47.2	151.3	5.3	30.5	259
	Standard deviation	1.1	5.2	1.7	0.4	39.6	107.0	1.2	18.4	170
Gongguan	Max	35.6	15.5	12.1	4.9	34.8	257.3	14.2	2387.8	2762
	Min	3.1	22.9	6.0	1.6	4.5	73.2	10.2	331.2	453
	Mean	13.6	46.2	9.5	2.5	13.3	129.0	11.8	1216.6	1261
	Standard deviation	13.4	41.3	2.3	1.3	11.0	68.8	1.9	790.1	935
Qingtong-gou	Max	45.9	58.5	13.3	2.0	18.7	199.6	116.6	2257.8	2712
	Min	3.4	57.1	4.6	0.5	3.9	51.5	4.9	320.4	446
	Mean	18.1	51.5	9.3	1.5	10.1	141.7	26.9	1238.3	1417
	Standard deviation	16.0	23.6	2.9	0.5	5.8	62.0	44.0	711.3	783
Nansha-gou	Max	16.9	58.5	19.8	23.4	11.6	1052.1	277.5	57.7	1518
	Min	5.6	17.7	9.2	1.7	6.4	77.7	6.8	11.7	137
	Mean	12.6	40.8	13.2	7.7	9.2	344.4	78.2	30.8	1008
	Standard deviation	5.0	17.4	4.6	10.5	2.3	473.0	132.9	19.6	940

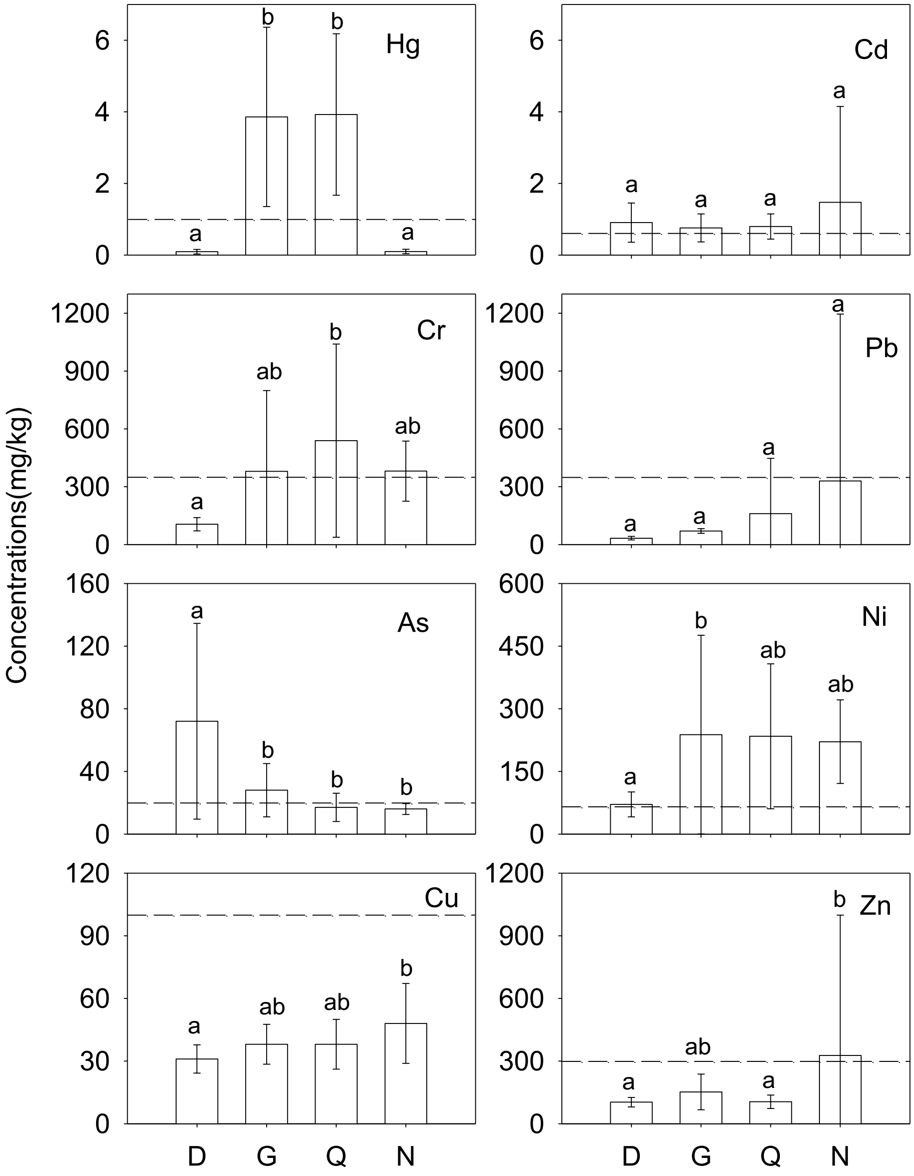

Fig. 2 The heavy metal concentrations (± standard deviation) for different types of examined mining areas: D (Donghecun), G (Gongguan), Q (Qingtonggou) and N (Nanshagou). The dotted line: Grade II environmental quality standard for soils in China. Letters (a, b) indicate significant difference of heavy metal contents in soil from different zone ($p < 0.05$, one-way ANOVA)

This could be explained by that other ore mining area also has Pb and Zn pollution.

Noticeably, it was reported that the heavy metals in the polluted soil had the potential to affect crops, and the effect could be observed (Cao et al. 2009). Previous studies have reported that the Pb content is over 20 mg/kg in the soil could result in 1 mg/kg Pb contents in most wheat seed. In our study area, the average content of Pb in the pollution zones researched is ranging from 32.9 to 329.7 mg/kg. Therefore, some plants sensitive to Pb such as soybean and rice in these areas are hard to satisfy the standard of food (Liao et al. 2008). Therefore, the quality of the crops was in a great risk and was affected by the heavy metals from those mining area.

Generally speaking, Hg represented a significantly high ecological risk for Gongguan and Qingtonggou Hg mining areas, and Cd posed a significantly high potential ecological risk on the Nanshagou Pb–Zn mining area. Contrary to this, As posed a moderate risk on the Donghecun gold mining area. The other metals represented a low environmental risk on these four areas. Further studies are necessary to assess the risk of heavy metals in crops associated with the daily diet of local residents.

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