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Pollution Assessment and Potential Sources of Heavy Metals in Agricultural Soils around Four Pb/Zn Mines of Shaoguan City, China

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A total of 455 agricultural soil samples from four nonferrous mines/smelting sites in Shaoguan City, China, were investigated for concentrations of 10 heavy metals (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn). The mean concentrations of the metals were 72.4, 5.16, 13.3, 54.8, 84.5, 1.52, 425, 28.2, 529, and 722 mg kg^{-1}*, respectively. The values for As, Cd, Hg, Pb, and Zn were more than 8 and 1.5 times higher than their background values in this region and the limit values of Grade II soil quality standard in China, respectively. Estimated ecological risks based on contamination factors and potential ecological risk factors were also high or very high for As, Cd, Hg, and Pb. Multivariate analysis (Pearson's correlation analysis, hierarchical cluster analysis, and principal component analysis) strongly implied three distinct groups; i.e., As/Cu/Hg/Zn, Co/Cr/Mn/Ni, and Cd/Pb. Local anomalies for As, Cu, Hg, and Zn by a probably anthropogenic source (identified as mining activity), Co, Cr, Mn, and Ni by natural contribution, and a mixed source for Cd and Pb, were identified. This is one of the few studies with a focus on potential sources of heavy metals in agricultural topsoil around mining/smelting sites, providing evidence for establishing priorities in the reduction of ecological risks posed by heavy metals in Southern China and elsewhere.*

Keywords Agricultural soil, ecological risk, heavy metals, multivariate analysis, source

Introduction

The past few decades have seen the rapid emergence of various contaminants, such as heavy metals (Adriano, 2001; Lu *et al.*, 2012). Heavy metals pose great risks to the environment and human health, especially once they concentrate in agricultural soils (Türkdoğan *et al.*, 2003). The inputs are largely linked to natural processing and/or anthropogenic activities (Rodríguez-Martin *et al.*, 2006). Anthropogenic activities, such as mining, smelting, and the abuse of pesticides, are major contributors to the heavy metal pollution found in agricultural

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soils of China (e.g., Wong *et al.*, 2002; Cai *et al.*, 2012). Metals can be transferred from soil to ecosystem components (Huang *et al.*, 2007; Xu, 2001). In particular, bioaccumulation in the edible parts of crops is one of the most relevant for human health (Hani and Pazira, 2011; Khan *et al.*, 2008). Consequently, investigations into the levels of heavy metals in agricultural soils deserve more attention in order to provide a benchmark for monitoring and assessing soil pollution by heavy metals (Fu and Wei, 2013; Zhang *et al.*, 2008).

Surveys of heavy metals in agricultural soils have been extensively performed in China in the past few decades, including in Beijing (Huo *et al.*, 2009), Dongguan (Cai *et al.*, 2010), Shanghai (Meng *et al.*, 2008), Huizhou (Cai *et al.*, 2012). These surveys have found considerable pollution by heavy metals in agricultural soils, especially in some areas near urbanized and industrialized zones and wastewater irrigation regions. However, most of these studies are specifically focused on local areas.

Shaoguan City is a representative area of mining activities in northern Guangdong Province, China (Yang *et al.*, 2003). This area is mainly engaged in mining and smelting, including at the Fankou Pb/Zn Mine, Lechang Pb/Zn Mine, Shaoguan Metallurgical Refinery, and Dabaoshan Mining Group (Figure 1). Previous studies report high levels of heavy metals, such as cadmium, lead, and zinc, in soils of this area (Shu *et al.*, 2004; Yang *et al.*, 2003). In particular, mean reported concentrations of Pb, Zn, Cu, and Cd are 1490, 1420, 680, and 13.6 mg kg^{-1}, respectively, in agricultural soils which received Pb/Zn mining wastewater for more than 50 years (Yang *et al.*, 2003). Moreover, a similar type of metal pollution has been found around the Fankou and Lechang Pb/Zn Mines (Figure 1), two sub-regions of Shaoguan City (Yang *et al.*, 2010). These observations actually reveal high

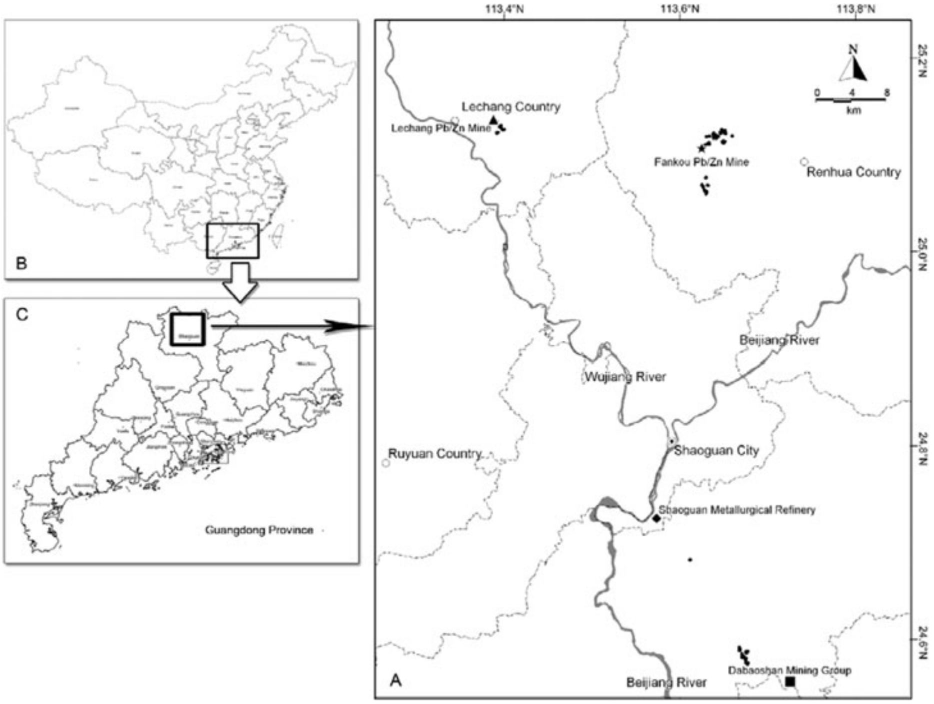

Figure 1. Soil sampling locations in the Shaoguan City (A), China (B), and Guangdong Province (C).

levels of heavy metals in Shaoguan City; however, systematic studies on concentrations and possible sources of heavy metals are limited.

In this work, concentrations of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn in agricultural topsoil collected around four nonferrous mines/smelting sites were quantified. The main aims of this study were: (1) to determine the concentrations of the 10 heavy metals; (2) to assess the potential ecological risk of heavy metals; and (3) to identify the possible sources of heavy metals using multivariate analysis.

Materials and Methods

Sampling and Preparation

The sampling scheme was carried out from March to July 2010. The sampling period was chosen in order to reduce an influence of precipitation and to meet the need of collecting plant samples. A total of 455 agricultural plots were chosen around four nonferrous mines/smelting sites in Shaoguan City. At least five random subsamples were collected at each plot and mixed into one composite sample at a depth of 0-20 cm using a stainless-steel auger. Among these samples, 117 were collected around Lechang Pb/Zn Mine, 171 around Fankou Pb/Zn Mine, 121 around Dabaoshan Mining Group, and 46 around Shaoguan Metallurgical Refinery (Figure 1). Typic paleudults, aquic kanhaplohumults, and andic Hapludox, all with Kaolin-based mineral composition, according to the taxonomy suggested by Food and Agriculture Organization of the United Nations (FAO), dominate in the area. Rice, water spinach, and pawpaw tree are the three main crops in the sampling region. Under field condition, pH, EC, Eh, and moisture content were determined using a Redox potential analyzer (FJA-15, Nanjing Chuan-Di Instrument & Equipment Co., Ltd., China). All of the soil samples were transported to Guangdong Key Laboratory of Plant Resources, Sun Yat-sen University, where they were air-dried at ambient temperature for about one week. The samples were sieved to remove stones and plant debris, mechanically ground to pass through a 2 mm nylon sieve, and then mixed thoroughly to obtain representative samples. The pretreated soil samples were stored in polyethylene bags at 4°C until chemical analysis.

Soil Digestion and Heavy Metal Analysis

Soil samples were digested according to Method 3051A adopted by the United States Environmental Protection Agency (USEPA, 1998). In brief, approximately 0.5 g soil sample was added into a 100 mL Teflon tube and was kept over 12 h after 5 mL of aqua regia was added. Soil digestion was preceded using a microwave accelerated reaction system (WX-8000, Shanghai PreeKem Scientific Instruments Co., Ltd., China) according to a standard procedure. The oven temperature was programmed as follows: 100°C for 3 min, ramped at 10°C per min to 150°C and held for 5 min, ramped at 6°C per min to 180°C and held for 25 min. After complete digestion, digested solutions were diluted to 50 mL with double deionized water and then filtered into a clean volumetric bottle. The digestion was kept at 4°C prior to analysis. Ultra-pure grade acids were used and other reagents were of analytical grade. All glass- and plasticware used was soaked overnight in a HNO_3 solution (10%, v/v) and then rinsed thoroughly with deionized water prior to use.

Concentrations of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn in the digestion were determined using inductively coupled plasma atomic emission spectroscopy

(ICP-AES) (Yang *et al*., 2010). For every 20 samples, a reagent blank and a standard reference material of soil (GBW-08303, China Standard Materials Research Center, Beijing, P. R. China) were processed for quality control to verify the accuracy of the digestion procedure. Detection limits for As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn were 30, 2, 4, 3, 6, 40, 0.5, 8, 30, and 2 ng/mL, respectively, following the manufacturer's instructions on their optimal wavelengths. Recovery rates were: As (88–99%), Cd (92–101%), Co (89–97%), Cr (96–100%), Cu (95–106%), Hg (90–115%), Mn (90–95%), Ni (90–95%), Pb (95–105%), and Zn (99–110%), which are within acceptable ranges according to the USEPA Method 3051A (1998).

Statistical Analysis

Pearson correlation analysis, hierarchical cluster analysis (HCA), and principal component analysis (PCA) were performed using SPSS statistical package (v. 18.0). These analyses allow us to infer heavy metal sources by measuring the degree of correlation among heavy metal concentrations (Franco-Uría *et al*., 2009).

Pearson's correlation analysis was run to determine the relationships among the measured heavy metals. Prior to correlation analysis, the raw data were standardized according to the Z-Score that indicates by how many standard deviations a variable is above or below the mean (Lee *et al*., 2006). In order to find a rational solution, PCA was successively run with and without Varimax rotation (Tahri *et al*., 2005). The principal components were extracted with eigenvalues > 1 (Loska and Wiechula, 2003). Source categories were subsequently identified only considering variables with factor loadings > 0.5 (absolute value) (Micó *et al*., 2006). HCA was run to cluster heavy metals profiles among the sampling sites using squared Euclidean distance with Ward's clustering method (Franco-Uría *et al*., 2009). Prior to PCA and HCA, the concentration data sets were Log10-transformed. Concentrations below the detection limit were assigned values of half of the limit when processing normalization. The level of significance was set at $p < 0.05$, $p < 0.01$, or $p < 0.001$.

Results and Discussion

Descriptive Statistics

Table 1 summarizes the statistics of 14 geochemical variables in soils from the study area. The raw data followed a positively skewed distribution, except for pH and Eh. Median values for all variables were lower than their mean values, except for pH. Over 80% of soil samples were in the range of $6 < \text{pH} < 8$, indicating an approximately neutral soil.

A wide range of heavy metal concentrations was observed (Table 1). Concentrations of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn in mg kg^{-1} ranged from 1.9-1333, <0.02-95.4, 2.65-49.0, 3.09-189, 4.7-6048, <0.02-10.7, 9.25-3508, 5.5-78.3, 16.2-10157, and 31-8348, with mean concentrations of 72.4, 5.16, 13.3, 54.8, 84.5, 1.52, 425, 28.2, 529, and 772 mg kg^{-1}, respectively. The concentrations of heavy metals showed a high coefficient of variations, ranging from 2.01% for Cr to 17.0% for Cu. Moreover, the Kolmogorov-Smirnov (K-S) test indicated that almost all of the analyzed geochemical variables are not normally distributed (Table 1, $p < 0.05$ or $p < 0.001$). The lack of normal data distribution could be related to the inherent spatial heterogeneity of the large sampling area (more than 100 thousand km^2) (Zhang *et al*., 2008).

The mean concentrations of all of the measured metals in the soils were considerably higher than the background values in Guangdong Province, especially for As, Cd, Cu, Hg,

Table 1

Summary statistics for 14 geochemical variables in agricultural soils of Shaoguan City, China ($n = 455$)

Parameters	n < DL	Min	Max	Median	Mean	S.E.	CV%	Skewness	Kurtosis	K-S p	Background value[a]	Guide value[b]
pH	0	4.23	7.94	6.83	6.65	0.04	0.59	−0.61	−0.59	< 0.001	—	—
EC	0	0.53	11.7	2.75	3.25	0.09	2.65	1.33	1.98	< 0.001	—	—
Eh	0	10	1280	508	482	5.83	1.21	−0.60	5.20	< 0.001	—	—
MC	0	0.01	0.75	0.22	0.22	0.01	2.30	0.48	0.37	0.030	—	—
As	0	1.9	1333	60.8	72.4	4.64	6.41	8.17	93.5	< 0.001	8.9	30
Cd	8	< 0.02	95.4	2.27	5.16	0.49	9.45	4.73	26.0	< 0.001	0.056	0.3
Co	0	2.65	49.0	11.9	13.3	0.29	2.17	0.98	1.96	< 0.001	7.0	—
Cr	0	3.09	189.6	50.1	54.8	1.10	2.01	0.87	1.74	0.020	50.5	200
Cu	0	4.71	6048	41.6	84.5	14.4	17.0	16.9	318	< 0.001	17.0	100
Hg	9	< 0.02	10.66	1.39	1.52	0.07	4.50	1.55	4.95	< 0.001	0.078	0.5
Mn	0	9.25	3508	327	425	19.1	4.50	4.21	24.8	< 0.001	279	—
Ni	0	5.5	78.3	24.8	28.2	0.65	2.31	1.03	0.94	< 0.001	14.1	50
Pb	0	16.18	10157	217	529	42.4	8.03	5.23	38.8	< 0.001	36.0	300
Zn	0	31	8348	512	722	37.5	5.19	4.27	29.3	< 0.001	47.3	250

Units are reported in mg kg^{-1} except for moisture in%; pH in pH unit; EC in mS cm^{-1}, Eh in mV.

DL: detection limit.

MC: moisture content.

S.E.: standard errors; CV: coefficient of variation.

[a]the soils background values in Guangdong Province (Wong *et al.*, 2002); [b]Chinese Environmental quality standard for soil (Grade II: 6.5 < pH < 7.5; GB15618-1995).

Min. - minimum value; Max. - maximum value; K-S p – Kolmogorov-Smirnov test.

Pb, and Zn. This indicated that 84.0% for As, 98.2% for Cd, 86.2% for Co, 48.8% for Cr, 88.6% for Cu, 77.8% for Hg, 60.0% for Mn, 87.7% for Ni, 95.8% for Pb, and 99.3% for Zn of the observed concentrations were above the corresponding background values, respectively. Also, the mean concentrations of As, Cd, Hg, Pb, and Zn in the soils were about 2.4-, 17.2-, 3.4-, 1.8- and 2.9-fold, respectively, when compared with the corresponding limit values of the Grade II ($6.5 < \text{pH} < 7.5$) quality standard in China (GB15618–1995, Table 1). These findings highlighted the fact that the relatively high concentrations of As, Cd, Hg, Pb, and Zn in the investigated soils should receive special attention.

Compared to other studies shown in Table 2, it was shown that the mean concentrations of Co, Cr, Hg, Mn, and Ni in this study fall in the normal values, while the mean concentrations of As, Cd, Cu, Pb, and Zn were higher than those from Huizhou (10.2 mg As kg^{-1}, 0.10 mg Cd kg^{-1}, 16.7 mg Cu kg^{-1}, 44.7 mg Pb kg^{-1}, 57.2 mg Zn kg^{-1}; Cai *et al.*, 2012), Leipzig-Halle-Bitterfeld (6.9 mg As kg^{-1}, 27.9 mg Cu kg^{-1}, 40.0 mg Pb kg^{-1}, and 75.0 mg Zn kg^{-1}; Manz *et al.*, 1999), Tehran (0.77 mg Cd kg^{-1}, 36.1 mg Cu kg^{-1}, 16.5 mg Pb kg^{-1}, 218 mg Zn kg^{-1}; Hani and Pazira, 2011), and Poirino (2.7 mg Cd kg^{-1}, 19.0 mg Cu kg^{-1}, 141 mg Pb kg^{-1}, 82 mg Zn kg^{-1}; Abollino *et al.*, 2002) and other sites (Micó *et al.*, 2006; Mitsios *et al.*, 2003; Saint-Laurent *et al.*, 2010). These results clearly indicate an influence of anthropogenic activities on metal (As, Cd, Hg, Pb, and Zn) contamination in the region. This influence is likely associated with mining activities near the sampling sites.

Sources Identification by Multivariate Analysis

Correlation between heavy metals. Relative abundance of metals in soils is controlled by many factors, such as original contents of heavy metals in parent materials, soil formation processes, and anthropogenic activities (Grant and Sheppard, 2008; Kabata-Pendias and Mukherjee, 2007). Note that a complicated relationship exists among heavy metals in soils (Rodríguez-Martin *et al.*, 2006; Hani and Pazira, 2011). In this study, Pearson's correlation analysis showed that many of the correlation coefficients (r) are significant ($p < 0.05$) and some (e.g. Ni/Cd, Ni/Cr, Cu/Zn, Pb/Zn or As/Zn) are very strong ($p < 0.001$, Table 3). The highest r was 0.84, observed between Co and Ni. It was also found that negative (e.g., Cu/Cd, $\text{r} = -0.01$) and less significant (e.g., Hg/Mn, $\text{r} = 0.08$) correlations were detected between Cu/Hg/Pb with other metals. Lack of significant correlation among heavy metals might be attributed to the presence of various pollution sources (Chen *et al.*, 1999; Lu *et al.*, 2012). Another possible explanation may be linked to variations in soil type (Typic paleudults, aquic kanhaplohumults, and andic Hapludox), cultivation system (rice, vegetable, and fruiter), and fertilizer use within the sampling area (chemical fertilizer, poultry manure, and human waste) (Lu *et al.*, 2012).

The correlations with positive significance among heavy metals in the soils indicate, to some extent, a common source or geochemical activity (Rodríguez-Martin *et al.*, 2006). Rodríguez-Martin *et al.* (2006) observed relatively high relationships with significance between Zn and Cu ($\text{r} = 0.66$) and between Zn and Pb ($\text{r} = 0.80$) of agricultural topsoil in the Ebro basin (Spain), comparable to our results (Zn/Cu, $\text{r} = 0.46$; Zn/Pb, $\text{r} = 0.68$, $p < 0.001$). Significant correlation with relative low r ($p < 0.001$) was also found between Zn and Hg ($\text{r} = 0.21$; Rodríguez-Martin *et al.*, 2006) and between Zn and As ($\text{r} = 0.52$; Cai *et al.*, 2012), similar to our results (0.33 and 0.60, respectively). These results suggest that As, Cu, Hg, and Zn might have a common source as anthropogenic activities, partially evidenced by the high concentrations of the four metals found in the investigated soils (Table 1).

Table 2

A summary of heavy metal concentrations in agricultural soil of various areas (mg kg-1)

Country	Area	Soil layer (cm)	Number of samples (*n*)	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn	References
China	Huizhou	0–20	104	10.2	0.10	N/A	27.6	16.7	0.22	N/A	14.0	44.7	57.2	Cai *et al.*, 2012
	Dongguan	0–20	118	12.8	0.12	N/A	43.0	21.8	0.24	N/A	20.5	65.4	66.2	Cai *et al.*, 2010
	Beijing	0–20	385	9.1	0.13	19.0	53.6	22.0	0.08	N/A	24.8	N/A	65.4	Huo *et al.*, 2009
	Shanghai	0–20	2265	7.8	0.20	N/A	85.6	31.4	0.13	N/A	N/A	26.4	106.2	Meng *et al.*, 2008
	Yangzhong	0–20	76	10.2	0.3	N/A	77.2	33.9	0.2	N/A	38.5	35.7	98.1	Huang *et al.*, 2007
	Pearl River Delta	0–15	38	N/A	0.58	9.11	71.4	33.0	N/A	N/A	21.1	40.0	84.7	Wong *et al.*, 2002
German	Leipzig- Halle-Bitterfeld	0–70	30	6.9	n.d.	N/A	52.4	27.9	0.35	N/A	20.9	40.0	75.0	Manz *et al.*, 1999
Iran	Tehran	0–25	106	N/A	0.77	13.3	68.0	36.1	N/A	N/A	36.9	16.5	218	Hani and Pazira, 2011
Canada	Québec	0–20	18	n.d.	n.d.	N/A	3	7	N/A	N/A	3	12	15	Saint-Laurent *et al.*, 2010
Spain	Ebro basin	0–25	624	N/A	0.42	N/A	20.3	17.3	35.6	N/A	20.5	17.5	17.5	Rodriguez *et al.*, 2006
	Alicante	0–25	54	N/A	0.34	7.1	26.5	22.5	N/A	295	20.9	22.8	52.8	Micó *et al.*, 2006
Italy	Poirino	5–15	N/A	N/A	2.7	N/A	124	19	N/A	525	32	141	82	Abollino *et al.*, 2002
				N/A	0.10	N/A	N/A	22.2	N/A	3300	N/A	8.9	27	Mitsios *et al.*, 2003
This study	0–20	455	72.4	5.16	13.3	54.8	84.5	1.52	425	28.2	529	722		

[a]n.d.: not detected; [b]N/A: not available.

Table 3

Pearson's correlations matrix for the heavy metal concentrations ($n = 455$)

	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
As	1									
Cd	−0.06	1								
Co	−0.20***	**0.32*****	1							
Cr	−0.16***	**0.26*****	**0.74*****	1						
Cu	**0.60*****	−0.01	−0.02	−0.05	1					
Hg	**0.44*****	0.13**	−0.16***	−0.20***	0.11*	1				
Mn	−0.02	**0.23*****	**0.42*****	**0.45*****	0.01	0.08	1			
Ni	−0.21***	**0.40*****	**0.84*****	**0.81*****	0.01	−0.13**	**0.44*****	1		
Pb	**0.66*****	−0.01	−0.16***	−0.11*	**0.26*****	**0.52*****	0.04	−0.16***	1	
Zn	**0.60*****	−0.03	−0.15**	−0.14**	**0.46*****	**0.33*****	0.02	−0.18***	**0.68*****	1

Levels of significance (2-tailed): $^{*}p < 0.05$; $^{**}p < 0.01$, $^{***}p < 0.001$.

It was also found that Cr was significantly correlated with Ni ($r = 0.81$, $p < 0.001$), as was also found by Rodriguez-Martin *et al.* (2006, $r = 0.68$) and Cai *et al.* (2012, $r = 0.60$). This significant relationship is also found in sandy loam soil and sandy soil (De Temmerman *et al.*, 2003). The mean concentration of Cr (54.8 mg kg^{-1}) in this study was approximately equal to the background value (50.5 mg kg^{-1}, Table 1), suggesting a lithogenic control over its level and distribution. However, the mean concentration of Ni (28.2 mg kg^{-1}) was higher than the background value (14.1 mg kg^{-1}) by two times, possibly indicating an anthropogenic source for Ni. Overall, the divergent results indicated that the significant correlation did not always expect to be a common source. In other words, correlation analysis alone is not enough for source identification of heavy metals; it should be conducted together with other analysis tools.

Principal component analysis. PCA together with Varimax rotation was applied to discriminate the degree of heavy metals pollution from natural processing and anthropogenic origins. Three principal components (PC1, PC2, and PC3) were extracted with eigenvalues > 1, which explain 71.1% of the data variation (Table 4). Three main sources can be thus identified according to PCA rotated component matrix, which was partially confirmed by HCA (Figure 2).

PC1 accounted for 34.8% of the total variation and was strongly and positively related to Co, Cr, Mn, and Ni with high factor loadings of 0.89, 0.88, 0.63 and 0.93, respectively (Table 4). Cr and Ni are known to be geogenically influenced (Hanesch *et al.*, 2001). In fact, in this study the concentrations of Co, Cr and Mn were slightly higher (1.9 and 1.5 times for Co and Mn, respectively) than or approximately equal to their corresponding background values, suggesting a lack of influence by human activities. As for Ni, its mean (28.2 mg kg^{-1}) was twice as high as its background value (14.1 mg kg^{-1}). However, strongly positive correlations were found among Co, Cr, Mn, and Ni ($r = 0.42{\sim}0.84$, Table 3), suggesting, to some extent, a common source. As a consequence, a lithogenic control on the concentrations and distribution of Co, Cr, Mn, and Ni can be strongly suggested.

PC2, explaining 25.4% of the total variation, was characterized by high positive loadings of As, Cu, and Zn (>0.79, Table 3). PC2 can be interpreted as due to an anthropogenic input of As, Cu, and Zn, since the concentrations of these three elements were more than

Table 4
Total variance explained and matrix of principal components analysis (significant loading factors are remarked in bold)

	Initial Eigenvalues			Rotation Sums of Squared Loadings		
Component	Total	% of Variance	Cumulative%	Total	% of Variance	Cumulative%
1	3.48	34.8	34.8	3.09	30.9	30.9
2	2.55	25.5	60.3	2.59	25.8	56.8
3	1.07	10.7	71.1	1.43	14.3	71.1
4	0.82	8.15	79.2			
5	0.64	6.38	85.6			
6	0.54	5.35	90.9			
7	0.35	3.46	94.4			
8	0.24	2.36	96.8			
9	0.20	1.99	98.7			
10	0.13	1.27	100			

Elements	Rotated component matrix		
	PC1	PC2	PC3
As	−0.12	**0.86**	0.23
Cd	**0.48**	−0.14	**0.46**
Co	**0.89**	−0.07	−0.12
Cr	**0.88**	−0.04	−0.14
Cu	0.06	**0.82**	−0.25
Hg	−0.10	0.28	**0.82**
Mn	**0.63**	0.02	0.23
Ni	**0.93**	−0.08	−0.08
Pb	−0.09	**0.67**	**0.54**
Zn	−0.09	**0.79**	0.24

Extraction method: principal component analysis. Rotation method: Varimax with Kaiser Normalization. Rotation converged in 25 iterations.

five times as high as the background values (Table 1). The anthropogenic input of these metals might be attributed to irrigation with sewage water (Zhang, 2006). In the study area, agricultural soils have received wastewater containing considerable amounts of heavy metals, including As, Cu, and Zn (Yang *et al.*, 2003). In addition, the anthropogenic input of these metals could mainly result from atmospheric deposition, as a consequence of an increase in mining activities (Chen *et al.*, 1999; Manno *et al.*, 2006; Bermudez *et al.*, 2012). Thus, PC2 can be regarded as the contribution of atmospheric deposition and long-term sewage irrigation (which should be related to mining activities) to As, Cu, and Zn in the region.

PC3 explained 10.7% of the total variation with a high loading of Hg (0.82). The deposition of atmospheric Hg may result in an accumulation of Hg in soils (Lin *et al.*, 2012), as its mean concentration (1.52 mg/kg) in the soil samples is 3.4 times higher than the limit value of Grade II quality standard in China (GB15618–1995, Table 1). This contribution may be largely linked to emissions from non-ferrous metal smelting (Bermudez *et al.*, 2012; Suresh *et al.*, 2012), since the investigated soil samples were collected near

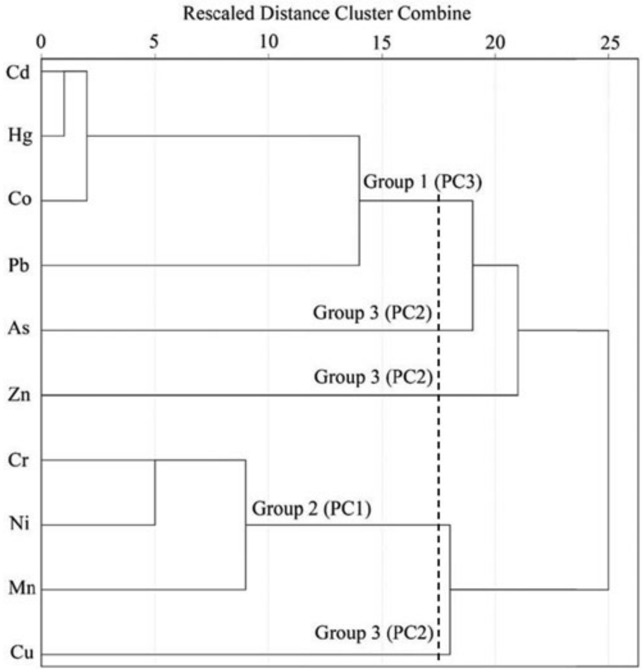

Figure 2. Dendrogram of hierarchical cluster analysis for concentrations of heavy metals in soil samples (measure: Squared Euclidean distance; linkage method: Ward's method).

Pb/Zn mines or smelting sites. An additional contribution of irrigation water for such high levels of Hg cannot be excluded (Lin *et al.*, 2012).

As for Cd and Pb, they are typically anthropogenically influenced (Dang *et al.*, 2002), which was partially evidenced by the high coefficient of variations found for Cd (9.5%) and Pb (8.0%) (Table 1). However, Cd had the moderate loadings of both in PC1 and PC3 (0.48 and 0.46, respectively), similar to Pb in PC2 and PC3 (0.67 and 0.54, respectively). The loadings of Cd and Pb were lower than those of other elements in the same PC, indicating a uniqueness of the two elements. The hybrid behavior of the two elements (Cd and Pb) reflected a mixed source, possibly both natural and anthropogenic.

Heavy Metal Pollution Assessment

The potential ecological risk index (*RI*) is used to assess effects of soil heavy metals' contamination on the environment (Liu *et al.*, 2005; Zhou *et al.*, 2014). The *RI* was calculated using the following equations (Hakanson, 1980; Franco-Uría *et al.*, 2009):

$$C_f^i = C^i / C_n^i$$

$$C_{\deg} = \sum C_f^i$$

$$E_r^i = T_r^i \times C_f^i$$

$$RI = \sum E_r^i$$

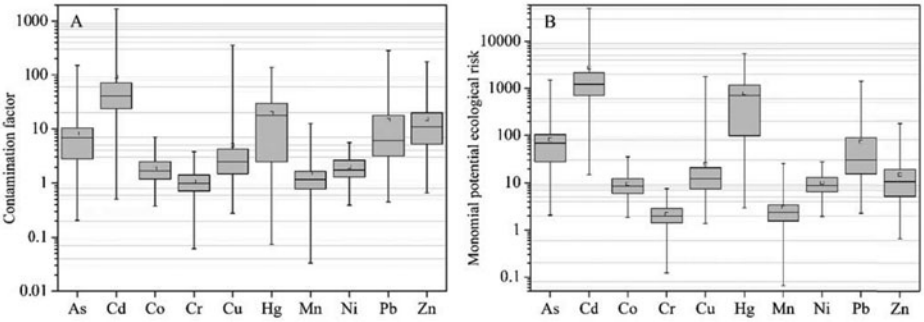

Figure 3. Contamination factors (a) and monomial potential ecological risk factor (b) for heavy metals in agricultural soils around Pb/Zn Mines of Shaoguan City, China. Contamination factors: Clean ($C^i_f \leq 1$), Low ($1 < C^i_f \leq 3$), Moderate ($3 < C^i_f \leq 6$), Considerable ($6 < C^i_f \leq 9$), and High ($C^i_f > 9$). Ecological risks: Low ($E^i_r \leq 15$), Moderate ($15 < E^i_r \leq 30$), Considerable ($30 < E^i_r \leq 60$), High ($60 < E^i_r \leq 120$), and Very high ($E^i_r > 120$).

where C^i_f is the contamination factor for the individual *ith* metal species; C^i_n is the concentration of the *ith* metal species; C^i_n is the pre-industrial concentration of the individual *ith* metal species, as the background values of heavy metals in Guangdong Province (Table 1). C_{deg} represents the integrated pollution level, as expressed by the sum of C^i_f for all examined metals. One may distinguish between four pollution levels: $C_{deg} < 5$, low pollution; $5 \leq C_{deg} < 10$, medium pollution; $10 \leq C_{deg} < 20$, high pollution; $C_{deg} \geq 20$, very high pollution (Loska *et al.*, 2004). E^i_r is the monomial potential ecological risk factor of the *ith* metal species, and T^i_r is the toxic factor for the *ith* metal species. Referring to Hakanson (1980), we use the following T^i_r values: Hg: 40, Cd: 30, As: 10, Pb: 5, Ni = Cr: 2, Zn: 1. *RI* is defined as the sum of E^i_r for all heavy metals. *RI* can be grouped into four categories: low risk ($RI \leq 50$), moderate risk ($50 < RI \leq 100$), considerable risk ($100 < RI \leq 200$), and high risk ($RI > 200$), in accordance with the recommended values by Zhu *et al.* (2008).

The C^i_f values varied considerably for the measured heavy metal and showed a marked difference in the soil samples (Figure 3A). The average value of C^i_f in agricultural soils were their highest at 92.1 for Cd (range: 0 to 1700) and lowest at 1.09 for Cr (range: 0.06–3.75). Consequently, 98.0% of all of the soil samples were classified as heavily contaminated ($C^i_f > 3.0$) by Cd and only 0.22% as heavily contaminated for Cr (Loska *et al.*, 2004; Modis and Vatalis, 2014). The proportion that was considered as high contamination for As, Hg, Pb, and Zn had relatively high values of 72.8%, 75.8%, 76.7%, and 87.7%, respectively. Considering all metals, the C_{deg} values varied from 2.42 to 183 with an average of 16.12, suggesting moderate and high contamination for 98.7% of the investigated soils (Loska and Wiechula, 2003). The E^i_r values of the studied metals varied from 2.17 (Cr) to 2760 (Cd), with a mean of 376 (Figure 3B). This result suggested a very high ecological risk for Cd and Hg and a high ecological risk for As and Pb, but a low or medium potential ecological risk for other metals, which is generally consistent with conclusions by Suresh *et al.* (2012). The E^i_r difference between Cd/Hg and the other metals results from their high toxic factors (Suresh *et al.*, 2012) and abnormal high concentration at some sites.

The mean of *RI* was 3760 (range: 340-52200), indicating a very high ecological risk, according to the recommended values ($RI > 200$) by Zhu *et al.* (2008). This was partially evidenced by no significant difference ($P > 0.05$) among the *RI* of the four groups of soil samples, Lechang, Shaoguan, Fankou and Dabaoshan (data not shown). This very high ecological risk is linked to the soil samples collected around Pb/Zn mines. Based on the estimates of the C_f^i, $C_{\deg}$, E_r^i, and RI, it seems reasonable to conclude that the investigated soils fall within high or very high contamination of heavy metals, which may represent a very high potential ecological risk to the ecosystem at almost all locations.

Conclusion

Agricultural soils in Shaoguan City have been suspected of high contamination due to mining activities of free hazardous waste and effluents discharge for many years. This speculation is to a great extent verified by the high level of heavy metal pollution in the agricultural soils around four Pb/Zn mines in Shaoguan City, based on a comparison with natural background values and assessment of ecological risks. Moreover, multivariate analysis revealed that the main sources of the investigated heavy metals which likely derive from mining activities might be identified as atmospheric deposition and use of contaminated wastewater. This study is one of the few studies focused on heavy metal contamination on a local scale of agricultural topsoil around mining and smelting sites, providing evidence for establishing priorities in the reduction of ecological risks posed by heavy metals in Southern China and elsewhere.

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