Spatial Distribution of Potentially Toxic Trace Elements in Soils Downstream of a Lead–Zinc Mine in Southern China

Pengwei Qiao[1], Sucai Yang[1*], Nan Dong[2], Mei Lei[3] and Yanjun Cheng[1]

[1]*Beijing key Laboratory of Remediation of industrial Pollution Sites, Environmental Protection Research Institute of Light Industry, Beijing 100089, China.*
[2]*Comprehensive Institute of Geotechnical Investigation and Surveying, Ltd., Beijing 100007, China.*
[3]*Institute of Geographic Sciences and Natural Resources Research, Chinese, Beijing 100101, China.*

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Abstract: Spatial distribution of potentially toxic trace elements (PTEs) concentrations in soils is essential for pollution and risk evaluation. In this study, 33 samples were collected downstream of a lead–zinc mine in Southern China. Contamination factors (CFs) of As, Pb, Zn, Cu, Cr, and Ni were all near 1 (low contamination), while 12% of the sample sites showed high contamination of Cd (CF>6). The highest concentration of Cd was about 40× natural background value of study area. Variogram analysis allowed detecting the principal direction of variation. High soil pH value and rocks could prevent PTEs vertical migrating in the mountain. The spatial distribution of Zn and Cu may be resulted from lateral transportation with soil erosion.

1 INTRODUCTION

Potentially toxic trace elements (PTEs) in soils have negative effects on environment and food quality (Song et al., 2009; Liu et al., 2015), and may threaten human health (Chen et al., 2005; Salehipour et al., 2015; Praveena et al., 2015). Spatial distribution of PTEs is important for evaluation of contamination level.

There are many occurrence elements in Pb-Zn mine, such as Cd (Hosseini-Dinani et al., 2015; Ye et al., 2016). These elements have potential hazards for environment. Therefore, assessment contamination level of PTEs in Pb-Zn mine is necessary.

In addition, the study area is located in the downstream of Pb-Zn mine in southern China, which is near residence community. Therefore, assessment contamination level in this region is important. However, the exist researches mainly been conducted in upstream regions that are heavily polluted (Zhang et al., 2013), while few studies about downstream areas have been conducted.

The objectives of this paper were to: (1) assess contamination degree of PTEs, (2) analyse spatial distribution of PETs downstream a Pb-Zn mine.

2 MATERIALS AND METHODS

2.1 Study Area

The study area lies in Huanjiang County in southern China. Study area is located downstream of a lead–zinc mine with an area about 300 km2, where was polluted by a tailing dam break in 2001. This region was contaminated by PTEs, such as As, Pb, Cd, Cu, Cr, Ni, Zn. Mountains with calcareous soil are located in the east of the study area, while the west is relatively flat with red soil. The land use types include farmland, forests, orchards and grasslands. Forests are mainly distributed in the eastern mountains (Figure 1). After the tailing dam broke, the flood level reached about 123 m above the Huanjiang River surface, while low-lying areas in the west were submerged.
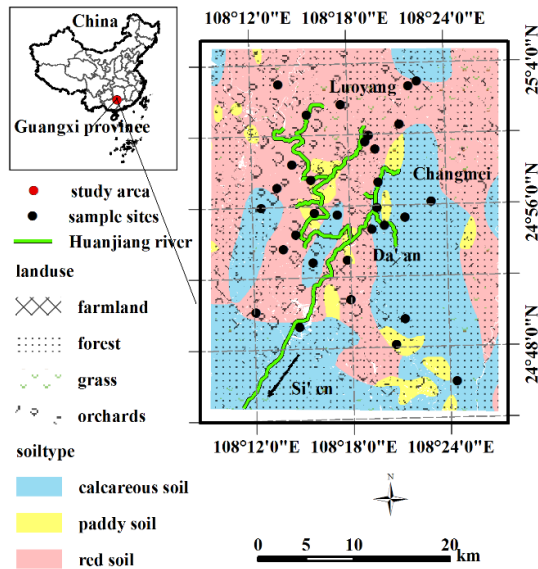
Figure 1: Soil sample locations.

2.2 Sampling and Chemical Analysis

Approximately 33 topsoil samples (0–20 cm) were collected from the study area (Figure 1). Of these, 11 samples were from forest areas with calcareous soil, while 19 samples were from orchard areas with red soil, and 3 samples were from orchard areas, where were underlain by paddy soil.

Soil samples were air-dried and ground to be able to pass through a 100-mesh sieve. And then they were digested with HNO_3 and H_2O_2, and added HCl adapting to the follow-up instrument according to USEPA (United States Environmental Protection Agency) Method 3050B (1996). The concentrations of As were determined by atomic fluorescence spectroscopy (HG-AFS, AFS-9800, Haiguang Instrumental CO., China), whereas Pb, Cd, Cu, Zn, Ni, and Cr were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 5300DV, PerkinElmer, USA). Samples of certified standard reference materials for soil (GSS-2) were obtained from the Chinese National Standard Material Centre, which was used for quality control. Soil pH values were determined in solution using a portable pH meter (Orion Model 868 pH).

2.3 Data Processing Methods

Theoretical variogram models were fitted by GS+ (version 9). Spatial distribution maps of PETs were produced by ArcMap (version 9.3) and ArcScene (version 9.3). Contamination level graphic of PTEs was produced by Origin (version 8).

In addition, the contamination level of PTEs is expressed in terms of contamination factor (CF), which is the common evaluation method in many existing literatures (Hakanson, 1980; Liu et al., 2005). The assessment results of CF are trustworthy. The greater the CF value, the more serious pollution of PTEs in soils.

$$CF=C_mSample/\ C_mStandard \qquad (1)$$

CmSample is the PTEs concentration (mg/kg) of sample, and CmStandard is the Environmental Class 2 Standard (mg/kg). CF<1 refers to low contamination; $1 \leq CF < 3$ indicates moderate contamination; $3 \leq CF \leq 6$ indicates considerable contamination; and CF>6 indicates very high contamination (Mmolawa et al., 2011).

3 RESULTS AND DISCUSSION

3.1 Degree of PTEs Contamination in Soils

The concentrations of Cd ranged from 0.28 mg/kg to 3.22 mg/kg, with a geometric mean of 0.80 mg/kg. CVs of all PTEs were all less than 13%, indicating weak variability. For all samples, the exceeding standard rate of As, Pb, Cd, Zn and Ni was 3%, 45%, 97%, 15% and 24% respectively. The standard value refer to Class 2, environmental quality standard for soils (GB15618-1995), which is a national standard of People's Republic of China.

Table 1: Standard concentration (mg/kg) of PTEs.

Metals	As	Pb	Cd	Cr	Cu	Zn	Ni
Class 2	30	300	0.3	200	100	250	50
Natural background	15.7	18.9	0.08	67.5	17.3	42.6	9.81

Based on CF, only Cd reached high contamination level, 12% of sample sites showing very high contamination, 24% with considerable contamination and 60% with moderate contamination. Low contamination levels of As, Pb, Zn, Cr, Cu and Ni were observed (Figure 2). This reflected that, Cd was the most important contaminant downstream of a Pb–Zn mining facility. These results were accordance with previous study (Wang et al., 2009). This phenomenon could be interpreted that, Cd was the occurrence trace element and was enriched surrounding Pb-Zn mine (Ye et al., 2016).
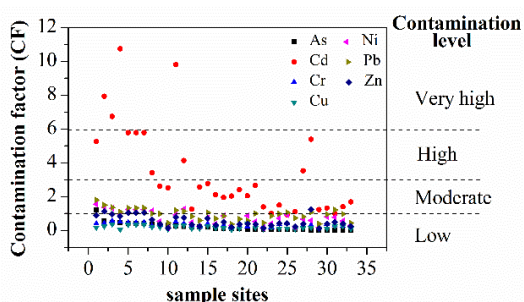
Figure 2: Contamination factors of As, Cd, Ni, Pb and Zn concentration for the 33 sites studied.

According to the natural background value of Huanjiang County (Ban and Ding, 1991) (Table 1), all the PTEs had accumulated in topsoils. These PTEs may result from the tailing dam broke, but also may result from irrigation with the water from Huanjiang River. Concentrations of PTEs in the branches of Huanjiang river were as follows: As (0.015 mg/L), Cd (0.002 mg/L), Cr (0.058 mg/L), Cu (0.024 mg/L), Ni (0.037 mg/L), Pb (0.040 mg/L), Zn (0.606 mg/L). These values were all near the standard for domestic drinking water quality (GB5749-85). But use of water containing PTEs at this levels could result in their accumulation in soils.

3.2 Spatial Distribution of PTEs

Spatial distribution characteristic was expressed by variogram models fitted by GS+ software. The best-fit theoretical models were selected based on the highest decision coefficient value (r2), while the ratio of nugget to sill (RNS) reflected the degree of spatial dependence. Principal direction was the spatial distribution trend of PTEs (Table 2).

Table 2: Theoretical variogram models and their fitting effect for PTEs.

Metals	Model	RNS	R^2	Principal Direction
As	Gaussian	0.05	0.96	E-W
Pb	Gaussian	2.95	0.82	E-W
Cd	Exponential	24.0	0.97	E-W
Cr	Spherical	21.3	0.91	E-W
Cu	Exponential	6.12	0.90	E-W
Zn	Gaussian	0.50	0.98	NW-SE
Ni	Gaussian	25.7	0.85	E-W

Semivariances of Cd and Cu were best fit with exponential model, while As, Pb, Ni, and Zn were best fit with Gaussian model and Cr with Spherical

model. RNS for Ni was between 25% and 75%, reflecting moderate spatial dependence, while for As, Pb, Cd, Cr, Cu and Zn were all less than 25%, showing strong spatial dependence. The principal direction of variation of Zn was NW–SE, while that of the other PTEs were E–W. The principal direction of pH value was E–W, with high pH value on the west (Figure 3).

The regions with higher concentrations of As, Pb, Cd, Cr, Ni were mainly in higher terrain area, where with calcareous soil, and higher pH value. These areas were not flooded (Figure 3). This might because that, higher pH value decreased the vertical migration ability of PTEs, while rocks on the mountain also could prevent the transportation of PTEs. Additionally, lower pH value in relatively flat regions in the west likely increased PTEs bioavailability, enabling plants to absorb the PTEs, reducing concentrations of PTEs in soils. Furthermore, calcareous soil on the mountain has a high background value. this phenomenon was accordance with the conclusion of (Ban and Ding, 1991) and (Wang et al., 2005), the difference between concentrations of PTEs in soil parents is significant.

Higher concentrations of Zn were observed in the north and northwest, that was parallel to the direction of the Huanjiang River flow. Overall, concentrations of PTEs were relatively high in the downstream region, which could be explained by lateral migration and accumulation downstream (Qiao et al., 2014).
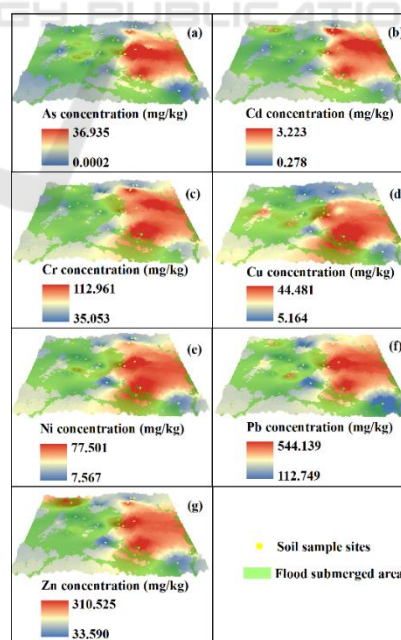

Figure 3: Spatial distribution of seven PTEs.

4 CONCLUSIONS

Overall, low contamination levels of As, Cu, Cr, Zn, Ni were observed in the study area, while Pb and Cd were present at considerable contamination levels. However, based on natural background values of study area, all PTEs had an accumulation trend in soils. Spatial anisotropy of the seven PTEs was significant, with the principal direction of variation of As, Pb, Cd, Cr, and Ni being E–W and that of Zn and Cu being NW–SE. Spatial anisotropy of As, Pb, Cd, Cr and Ni were in accordance with the spatial distribution of soil type and pH value. Higher pH values and rocks on the mountain could prevent vertical migration of PTEs. Lower pH value in the flat regions could increase transportation of PTEs. Spatial distribution of Zn and Cu may result from lateral transportation by soil erosion.

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