Characterizing spatial distribution and sources of heavy metals in the soils from mining-smelting activities in Shuikoushan, Hunan Province, China

WEI Chaoyang¹,*, WANG Cheng¹², YANG Linsheng¹

¹. Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China. E-mail: weicy@igsnrr.ac.cn
². Graduate University of the Chinese Academy of Sciences, Beijing 100049, China

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Abstract

The spatial variation of heavy metals in the soils in Shuikoushan mining-smelting area, Hunan Province, China, was investigated using multivariate and geo-statistic analysis. A total of 106 composite soil samples were collected in an area of about 100 km². Concentrations of total As, Cd, Pb, Zn, Cu and Cr were measured using inductively coupled plasma mass spectrometry (ICP-MS). Arsenic and Pb were found to have a common source, indicating the same sources and spreading processes, such as aerosols and airborne particulates from smelting chimneys. Airborne sources from smelting chimneys contributed greatly to Cd in the area, which demonstrated the same dispersion pattern as As and Pb. However, two hot spots of Cd around smelters were possibly enlarged by wastewaters, demonstrating another important source of Cd in Shuikoushan. Geo-statistic interpolated mapping demonstrated that hot-spots of Zn were only found proximal to the large smelters, suggesting that Zn primarily came from the chimneys of larger smelters. The major Cu hot-spots appeared closely to the tailing dam, indicating that weathering and leaching of tailings were the major sources of Cu contamination in Shuikoushan. Our findings indicated that airborne volatile particles and aerosols contributed the most to As, Cd, Pb, Zn and Cu contamination, while Cd and Cu may also derive from the discharge of wastewater from smelters and the leaching of tailings, respectively.

Key words: geo-statistic interpolation; GIS; heavy metals; multivariate analysis; soils

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Introduction

Heavy metal contamination has caused serious environmental and health-related problems around the world (Alloway and Ayres, 1997). Metal mining and smelting activities are the major sources of heavy metals entering the environment. Heavy metals can enter the soils in three primary ways: by irrigation with wastewater, deposition of aerosol particulates and leaching of tailings (Salomons, 1995). Non-ferrous mining and smelting plants are widely distributed in southern China, and they are usually surrounded by paddy fields, with intensive rice cropping every year. The input of heavy metals to paddy fields has reduced rice productivity and quality, increased the presence of heavy metals in rice grains, and even rendered deserts from former paddy fields located closely to the smelters.

Currently, there is no international agreement on the metal concentrations in soils that constitute significant contamination. In several countries, soil remediation guidelines have been suggested; however, the reference values change from country to country, and even from state to state in the USA (USEPA, 1996, 2003; Wang et al., 2005). Although the standardized national guidelines for soil quality in China (GB15618-1995) were issued in 1995, which applies mainly to cropping activities in farmlands (Xia, 1996), the remediation guidelines for contaminated soils are still unavailable. Given the fact that growing metalliferous industry dominates the economy in southern China, and many such industrial plants are located in the countryside, spatial variation analyses of heavy metals around the contaminated areas are highly valuable for establishing reliable remediation guidelines.

The heavy metal contents in water, soils, crops and vegetables in mining and smelting areas have been extensively documented in China, with elevated concentrations of heavy metals measured (Zhang and Zhao, 1996; Shu et al., 2005). The incidence of occupational diseases in smelting plants has been monitored occasionally with the goal of disease prevention. However, few endeavors have been made to investigate the spatial variation of heavy metals as well as the potential risks in mining and smelting areas. With limited samples and non-accurate spatial properties, previous studies have not been able to provide a clear illustration of heavy metal variation in areas where intensive mining and smelting activities occurred, nor have they been able to interpret the possible contamination-
source relationship.

Studies combining multivariate analysis, geo-statistics and GIS-based mapping have been conducted extensively (Facchinelli et al., 2001; Kooistra et al., 2005; Zhang, 2006). Numerous reports showed that geo-statistics and GIS are useful tools for the identification of pollution sources, the assessment of pollution trends, and the potential risks of heavy metals (Markus and McBratney, 2001; Rawlins et al., 2006). Large-scale investigations of heavy metal concentrations have been conducted in China, mainly in the areas with natural background levels and minor anthropogenic pollution sources (Tao, 1995a, 1995b; Liu et al., 2006). On the contrary, the spatial variation of heavy metals around mines and smelters was rarely documented. The objectives of this study were: (1) to analyze the spatial variation of heavy metals in the areas with intensive mining and smelting activities; (2) to identify the pollution sources at the sites with both mining and smelting activities; (3) to give a primary risk assessment of heavy metals.

1 Materials and methods

1.1 Study area

The study was conducted in Shuikoushan in Changning County, Hunan Province in central south China (Fig. 1). Three large Pb/Zn mines and three big Pb/Zn smelters are located along the southern shore of the Xiangjiang River, the largest river in Hunan Province. The mines, smelters and tailing dam are distributed about 3 km away from each other in Shuikoushan. Mining and smelting activities were initiated early in 1889 and have been developed rapidly since the 1950s. Tailings from a mine in Shuikoushan have been measured to have high concentrations of heavy metals, such as Pb, Zn, Cu, and Cd, and low concentrations of N, P, and organic matter (Shu et al., 2005). Water and sediments in Kangjiaxi River, a branch of the Xiangjiang River, are highly contaminated with Pb, Zn, Cu and Cd (Zhang and Zhao, 1996). The area is within the sub-tropic zone, with average annual temperature of 18.7°C, annual rainfall of 1442 mm, and north-western prevailing winds. The land is relatively flat, with slightly hilly topology. Most of the lands are cultivated with rice from June to October every year; some lands near the smelting plants were left uncultivated because of the low productivity caused by pollution.

1.2 Sampling and chemical analysis

Sampling was conducted in an area of about 10 km × 10 km, with most of the samples collected in the southern part from the Xiangjiang River, where all the smelters, mines, and the tailing dam are located. The prevailing wind direction during the year is from the northwest. A total of 106 composite soil samples were taken from rice paddy lands, vegetable lands or hill sites. The whole area was divided into 106 cells of 0.5–1 km² in size, within which the composite topsoil samples (0–20 cm) were collected. Five sub-samples were collected in every cell from a grid of about 5 m². Soil samples collected were stored in polyethylene bags for transport and storage, and were air-dried, then sieved through a 2.0-mm mesh sieve to remove stones, coarse materials and other debris. Portions of soil samples (20 g) were ground in a mechanical agate grinder until fine particles (< 150 µm) were obtained. Digestion of milled samples was adopted from USEPA method 3050B. Levels of arsenic (As), Cd, Cr, Cu, Pb and Zn were determined using ICP-MS (Agilent-7500C, USA). Reagent blanks, 10% duplicated samples and soil standard reference materials (Center for Reference Materials, China) were employed to check the accuracy of analysis.

1.3 Data analysis

Basic data statistics were performed using SPSS 14.0. Normality was tested with the Kolmogorov-Smirnov (K-S) method; all data were logarithmically transformed to obtain a normal distribution prior to multivariate and geo-statistic analyses. Cluster Analysis (CA) and Principal Component Analysis (PCA) were carried out to explore the correlations existing among the various elements. Semi-variograms were simulated using Variowin 2.2 software; ArcGIS9.0 was used for geo-statistic interpolation and mapping.

2 Results

2.1 Heavy metal concentration in Shuikoushan

The present study was conducted to explore the spatial variation of heavy metals (As, Cd, Cu, Cr, Pb and Zn) in Shuikoushan. Chemical analysis showed that soils in Shuikoushan have been greatly contaminated by As, Cd, Pb and Zn, with the average concentrations of these four elements all exceeding Class III of the Environmental Quality Standard for Soils in China (GB 15618-1995). Soils were also found to be contaminated by Cu and the average concentration of Cu exceeded Class II (50 mg/kg) of the national soil reference value in China. On the contrary, no elevation of Cr only was found, indicating Cr...
only came from geogenic sources in Shuikoushan (Table 1).

2.2 Multivariate analysis for heavy metals

Generally, the logarithmic transformations worked well in reducing the skewness and kurtosis of the data; all the transformed data for the six heavy metals passed the test of normality (Table 1). The multivariate and geo-statistic analyses were thus performed based on logarithmic transformed data.

Significant positive correlations existed between the six elements, except for Cr-Cd and Cr-Pb pairs (Table 2). An R-type Cluster Analysis yielded two groups of elements: As, Cd, Pb, Zn as group one, while Cr and Cu appeared in the third and fourth components respectively (Table 3).

2.3 Geo-statistics and mapping of heavy metals

To make interpolation and mapping of the heavy metals in Shuikoushan, semi-variograms were created. Arsenic, Cd, Pb and Zn could be simulated by a spherical model (Table 4, Fig. 3). The ranges of As, Cd, Pb and Zn simulated in semi-variograms were about 2.5 km, indicating that our sampling density of 0.5–1.0 km² was suitable in Shuikoushan (Markus and McBratney, 2001). The nugget value of less than 0.032 and the low ratio of nugget to sill (less than 27%) for As, Cd, Pb and Zn indicated the existence of a strong spatial auto-correlation for these elements (Burgess and Webster, 1980). High nugget values that indicated a nugget effect were obtained in semi-variograms for Cr and Cu. Therefore, ordinary kriging interpolations were performed for As, Cd, Pb and Zn while Inverse Distance Weighted (IDW) interpolations were chosen for Cr and Cu.

The interpolation mapping of heavy metals is shown in Fig. 4. As seen from the maps, the variations in As and Pb demonstrated a very similar pattern, with the most heavily contaminated areas appearing in the vicinity of the smelters, and leveled off in the distance from the center of the smelters. High levels of As (> 83 mg/kg) and Pb (> 860 mg/kg) in soils caused by dispersal from chimneys of the smelters could be found at a distance about 6–8 km. Two spatial variation patterns were found for Cd in Shuikoushan; the pattern of less than 9.43 mg/kg Cd was quite similar to that of As and Pb. There were two hotspots of high Cd concentrations greater than 9.43 mg/kg in Shuikoushan, one near the smelters and another close to the western side of the former spot. The patterns of these two Cd hotspots were totally different from those observed in the vicinity of the smelters.

Table 1  Heavy metal concentrations in the soils of Shuikoushan (mg/kg) (n = 106)

<table>
<thead>
<tr>
<th></th>
<th>Raw data</th>
<th>Reference value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Min.</td>
</tr>
<tr>
<td>As</td>
<td>62.52</td>
<td>2.466</td>
</tr>
<tr>
<td>Cd</td>
<td>10.34</td>
<td>1.092</td>
</tr>
<tr>
<td>Cr</td>
<td>46.61</td>
<td>11.43</td>
</tr>
<tr>
<td>Cu</td>
<td>92.72</td>
<td>11.46</td>
</tr>
<tr>
<td>Pb</td>
<td>629</td>
<td>71.60</td>
</tr>
<tr>
<td>Zn</td>
<td>597</td>
<td>87.35</td>
</tr>
</tbody>
</table>


Table 2  Pearson correlations between difference elements in the soils of Shuikoushan (n = 106)

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.512**</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.302**</td>
<td>0.103</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.557**</td>
<td>0.509**</td>
<td>0.264**</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.874**</td>
<td>0.608**</td>
<td>0.147</td>
<td>0.673**</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.670**</td>
<td>0.821**</td>
<td>0.198*</td>
<td>0.685**</td>
<td>0.753**</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Correlation is significant at the ** 0.01 or * 0.05 level (two-tailed).

Table 3  Rotated component matrix for principle component analysis loadings for heavy metals in the soils of Shuikoushan

<table>
<thead>
<tr>
<th></th>
<th>PC1</th>
<th>PC2</th>
<th>PC3</th>
<th>PC4</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.911</td>
<td>0.263</td>
<td>0.175</td>
<td>0.188</td>
</tr>
<tr>
<td>Cd</td>
<td>0.249</td>
<td>0.935</td>
<td>0.160</td>
<td>0.022</td>
</tr>
<tr>
<td>Cr</td>
<td>0.105</td>
<td>0.041</td>
<td>0.098</td>
<td>0.988</td>
</tr>
<tr>
<td>Cu</td>
<td>0.317</td>
<td>0.290</td>
<td>0.889</td>
<td>0.135</td>
</tr>
<tr>
<td>Pb</td>
<td>0.832</td>
<td>0.363</td>
<td>0.352</td>
<td>0.000</td>
</tr>
<tr>
<td>Zn</td>
<td>0.431</td>
<td>0.758</td>
<td>0.379</td>
<td>0.088</td>
</tr>
</tbody>
</table>

Rotation method: Varimax with Kaiser normalization.

Table 4  Key parameters of the fitted spherical models of heavy metals in the soils of Shuikoushan

<table>
<thead>
<tr>
<th></th>
<th>C₀</th>
<th>C₀ + C₁</th>
<th>Range (km)</th>
<th>C₀/(C₀ + C₁) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.024</td>
<td>0.15</td>
<td>2.56</td>
<td>16</td>
</tr>
<tr>
<td>Cd</td>
<td>0.018</td>
<td>0.168</td>
<td>2.64</td>
<td>10.7</td>
</tr>
<tr>
<td>Cu</td>
<td>0.032</td>
<td>0.12</td>
<td>2.48</td>
<td>26.7</td>
</tr>
<tr>
<td>Pb</td>
<td>0.026</td>
<td>0.15</td>
<td>2.56</td>
<td>17.3</td>
</tr>
</tbody>
</table>

C₀: nugget variance; C₀ + C₁: sill variance.
for As, Pb and the Cd levels that were lower than 9.43 mg/kg in Shuikoushan. High Zn levels primarily appeared close to smelters. Two Cu hotspots could be identified; the larger one was close to the tailing dam, while the smaller one was observed in the downwind direction of the smelters. Cr was relatively low in Shuikoushan, with a relatively higher concentration appearing near the tailing dam and smelters.

3 Discussion

The results clearly showed that high concentrations of heavy metals in Shuikoushan came from intensive smelting and mining processes, and the values are much higher than the corresponding concentrations found worldwide in natural soils (Kabata-Pendias and Pendias, 2001) and urban soils (Manta et al., 2002; Li et al., 2004; Duzgoren-Aydin et al., 2006; Hu et al., 2006). All As, Cd, Pb and Zn concentrations were comparable to those measured in soils collected in an area with abandoned indigenous Pb/Zn smelters in Hezhang, Guizhou Province, China (Bi et al., 2006) and the soils around a Pb/Zn smelter in Bukowno, Poland (Verner et al., 1996). The results suggest a great elevation of heavy metals in Shuikoushan.

The results of multivariate analysis showed that As and Pb had a close association (Fig. 2, Table 3). This was consistent with the results of geo-statistic interpolated mapping, which revealed that the distribution of the two elements had a very similar dispersion pattern in Shuikoushan (Fig. 4). The primary metal-bearing minerals in Shuikoushan are galena (PbS), sphalerite (ZnS), chalcopyrite (CuFeS₂), and arsenopyrite (FeAsS) (Zeng et al., 2000). The associations and similar spatial variation for As and Pb indicate that airborne emissions, transportation, and deposition of volatile particles and aerosols from smelters are the major sources of As and Pb, demonstrating a strong anthropogenic input.

The similar dispersion pattern (less than 9.43 mg/kg) observed for Cd in comparison to As and Pb suggested Cd had important sources from the chimneys of smelters in the form of volatile particles and aerosols in Shuikoushan (Fig. 4). Cd and Zn were also found to have a relationship through CA and PCA multivariate analysis (Fig. 2, Table 3). However, the geo-statistic interpolation maps of Cd and Zn were somewhat different from these results, with an additional area of high Cd levels on the northern side of the tailing dam (Fig. 4). Cd is a relatively mobile element which can easily be released into the environment through weathering and leaching (Alloway, 1995); the absence of high Cd concentration as the case of Cu in the vicinity of the tailing dam did not support the hypothesis that Cd came mainly from the tailings. The two Cd hot spots might largely derive from Cd in wastewaters discharged from smelters, as opposed to the airborne sources represented by smelters, like the cases of As and Pb. This is in agreement with a previous report of Wang et al. (2004), who reported that the average Cd concentration in the wastewater from the smelters exceeded the reference Cd standards by 265-folds; since the wastewater was often used to irrigate rice. The additional area with high Cd levels might come from many small Zn smelters, as we saw in Shuikoushan.

It is clear that two hot-spots with high Cu concentrations existed (Fig. 4), which differed in the source and the way of transportation. The spot in the vicinity of smelters apparently came from airborne emissions of aerosols and volatile particulates of the chimneys, whereas the spot of high Cu levels near the tailing dam was the result of leaching and chemical weathering of tailings. Cu-bearing minerals are usually present with Pb and Zn minerals, and large quantities of Cu accumulated in tailings because
most of the Cu-bearing minerals were left behind when Pb- and Zn-bearing minerals were collected for mineral-processing. Avil et al. (2005) also reported that chemical leaching and precipitation were the major contributors to the heavy metal contamination in soils and sediments in areas near the Vale das Gatas mine in northern Portugal. In this study, we found smelting was the major source of heavy metal soil contamination, especially for As, Pb and Cd. The absence of spatial auto-correlation for Cu might be due to the fact that two different sources and ways of spreading existed around the smelters and tailing dam, which rendered the distribution and variation of Cu in Shuikoushan totally different. Similar to Cd, Cu could also be dispersed from smelters like As and Pb, resulting in the small hot spot of Cu in Shuikoushan (Fig. 4). Arsenic, Pb, Cd, Zn and Cu were found to be highly
concentrated in the center of smelters and level off with distance from the smelters; this is in agreement with most of literature (Verner et al., 1996; Rawlins et al., 2006; Chopin and Alloway, 2007), demonstrating that the sources mainly came from airborne volatile particulates released by large chimneys, which may spread via the prevailing north-western winds in Shuikoushan. In this study, Cd and Cu were found to originate from wastewater and tailings, respectively. The dispersion patterns from these sources were totally different as compared to the pattern of airborne transportation. Apparently, the complex sources and spreading of Cd and Cu, especially Cd, have caused the widespread and serious contamination in Shuikoushan.

Levels of Cr in soils in Shuikoushan were not high, as compared to the standard reference values for China, reflecting its geogenic source from the parent materials in the area. This is in agreement with other studies in mining and smelting areas (Facchinelli et al., 2001; Manta et al., 2002). Cr in Shuikoushan might thus distribute randomly, with no special spatial variation pattern. This is consistent with the result of PCA analysis, which revealed that Cr did not belong to any of the first three components comprising As, Pb, Cd, Zn and Cu (Table 3).

3.1 Conclusions

Spatial variation of heavy metals in the area with intensive smelting and mining activities in Shuikoushan showed high concentration levels of As, Pb, Cd and Zn around smelters. Heavy metal contamination derived largely from the emissions of airborne particulates from smelter chimneys. Arsenic and Pb were found to have the same sources and spreading patterns around smelters; Cd was spread by both airborne particulates and wastewater from smelters that produced heavy contamination throughout a large area in Shuikoushan. The weathering and leaching of tailings produced high Cu contamination in the vicinity of the tailing dam.

Acknowledgments

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