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Spatial-Based Assessment of Metal Contamination in Agricultural Soils Near an Abandoned Copper Mine of Eastern China

Chun Qin · Chunling Luo · Yahua Chen · Zhenguo Shen

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Abstract An investigation about metal contamination on agricultural soils was carried out near an abandoned copper mine in eastern China. Results showed the average concentrations of Cu, Pb, Zn and Cd in the 155 soil samples were 147, 53.8, 158, 0.32 mg kg^{-1} respectively, which were 4.6-, 2.2-, 2-, 1.7-fold of the corresponding background value. According to the Chinese Farmland Environmental Quality Evaluation Standards for Edible Agricultural Products, it was found 18.4 % of the soils belonged to heavily and moderately contaminated soils.

Keywords Abandoned mine · Agricultural soil · Metals · Geostatistic

Metals are becoming a major type of environmental contaminants with the rapid industrialization and urbanization worldwide. Mining and related activities, such as metal processing and smelting discharge large amounts of metals to the environment (Tordoff et al. 2000; Wang et al. 2004; Peng et al. 2006). Once the metals enter soils, they can not only lead to the phytotoxicity at high concentrations, but can be transferred to crops grown in the soil and ultimately pose potential dangerous effects on the human beings through food ingestion (Luo et al. 2005; Sipter et al. 2008). Metals are well known for their 'non-biodegradability', which enable them be present in the environment for very long time. These vicious characters of metals coupled with the high cost to remediate contaminated soils make the risk evaluation necessary, especially for the agricultural soils located near mining sites and industry areas, which are more susceptible to the metal pollution. Identifying the metal sources, clarifying the pathways of dispersion and preventing further movement to the surrounding areas are essential for the environmental and human health concern. In recent years, geostatistic has been extensively applied in the soil science to quantify the spatial features of soil parameters and enable spatial interpolation, by which soil attributions in unsampled area can also be estimated and mapped (Goovaerts 1999). Geostatistic, together with geographic information system (GIS) has been proved to be a useful tool in the study of spatial distribution pattern and hazard assessment (Steiger et al. 1996; Matín et al. 2006).

The metal contamination risk resulted from the mining activity has been well presented (Navarro et al. 2008; Ngoc et al. 2009). The present study area – Jiuhuashan (32°2′47–32°4′57″N, 119°3′36–119°5′46″E) is situated in the north-eastern of Tangshan town, Jiangning District, Nanjing City, China, covering about 11.2 km^2. This region has a typical subtropical humid climate. North/south-east wind prevails through the whole year. The weather is characterized by dry and chilly in winter, and hot and rainy in summer, with an annual temperature of 15.4°C and an annual average rainfall of 1,060 mm. This site is dominated by yellow-brown soil. This area experienced an intense mining activity during the past four decades, and the mining operations ceased just several years ago. The skarm deposits are mainly composed of copper, accompanied by associated elements, such as Zn, Fe, S, Mo and Ag. Waste materials from the mining were deposited onto a tailing dump located west of the mining site. A previous metallurgy plant was located south of the mining site, and

C. Qin · Y. Chen · Z. Shen
College of Life Sciences, Nanjing Agricultural University, Nanjing 210095, China

C. Luo (✉)
Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
e-mail: clluo@gig.ac.cn

now it has been transformed for other functions. In recent years, agriculture is booming in this region. Rice and vegetables are main crops being planted, which form an important part of the diet for the local residents. The present study is focused on the investigation of the metal contamination in the agricultural soils around the abandoned copper mine. The spatial distribution pattern of metals is revealed using multivariate statistics, geostatistics and geographic information system (GIS) techniques. Valuable information on potential contamination assessment can be generated for future soil management and decision support.

Materials and Methods

A total of 155 agricultural soil samples were collected on a grid sampling system at intervals of 200 m. Composite samples for each plot consisted of 8 top soil (0–15 cm) taken from within a 10 × 10 m area using a wood spade with the central point giving the defined position for this sampling plot. All the soils were air-dried and sieved to pass a 2 mm mesh after removing the plant remains and stones. A representative sample of each soil was grinded with an agate mortar to 0.15 mm for the following metal analysis.

The total concentrations of metals were determined by atomic absorption spectroscopy (AAS400, Analytic Jena) after strong acid digestion (4:1 concentrated HNO_3 and $HClO_4$ (v/v); Luo et al. 2005). A certified standard reference material NIST (SRM 2709) of the National Institute of Standards and Technology, U.S.A., was used in the digestion and analysis as part of the QA/QC protocol. Reagent blank and analytical duplicates were also used where appropriate to test the accuracy and precision of the analysis. The recovery was around 90 % ± 8 % for all of the metals in the soil reference material (NIST SRM 2709).

Geostatistic method is used in the soil science to characterize the regionalized variables by developing semivariograms and provides the input parameters for the spatial interpolation of kriging. The basic theory of kriging is the data is intrinsic stationary. Real data often violate this assumption, so the data that were not normally distributed were logarithmically transformed in this study. Semivariograms are generated to ensure the data fit this criterion prior to estimation by kriging.

Semivariance, $\gamma(h)$, is computed as half the average squared difference between the components of data pairs (see Eq. 1; Goovaerts 1999):

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i}^{N(h)} [Z(x_i) - Z(x_i + h)]^2 \quad (1)$$

where N(h) is the number of data pairs separated by a distance h, and Z represents the measured value for soil property, and x is the position of soil samples.

Several standard models like spherical, exponential, Gaussian, linear and power models are developed to fit the experimental semivariogram. In the present study, the best fitted model for Cu, Zn and Cr was spherical model (see Eq. 2); for Pb, the best one was found to be Gaussian model (see Eq. 3); and for Cd and Mn the best fitted one was exponential model (see Eq. 4).

$$\gamma(h) = \begin{cases} C_0 + C[1.5(h/A_0) - 0.5(h/A_0)^3] & \text{for} \quad h \le A_0 \\ C_0 + C \quad h > A_0 \end{cases} \quad (2)$$

$$\gamma(h) = C_0 + C[1 - \exp(-h^2/A_0^2)] \quad (3)$$

$$\gamma(h) = C_0 + C[1 - \exp(-h/A_0)] \quad (4)$$

where $\gamma(h)$ stands for semivariance for interval distance class h, h is lag interval, C_0 presents nugget variance ≥0, C presents structural variance $\ge C_0$, and A_0 is range parameter.

The fitted model provides information about the spatial structure as well as the input parameters for kriging interpolation. The software employed here are GSt (Gamma Design 2004) and ArcGIS 9.2 (ESRI Co, Redlands, USA).

The Nemero Synthesis Index evaluation method was adopted to assess the potential contamination risk. The synthesis index can be computed by Eq. 5:

$$P = \sqrt{\frac{\left(\frac{C_i}{S_i}\right)_{max}^2 + \left(\frac{C_i}{S_i}\right)_{ave}^2}{2}} \quad (5)$$

where P is the synthesis evaluation score corresponding to each sample, C_i is the measured value of certain a element at each sample point, i is an element, and S_i is the evaluation criterion of the ith kind of element. In this study, the evaluation criterion is based on local soil background value. The evaluation process was performed in the same procedure of Chen et al. (2008): the synthesis index of each sample was firstly evaluated based on Eq. (4). Integrated pollution distribution was achieved using Kriging. According to the Chinese Farmland Environmental Quality Evaluation Standards for Edible Agricultural Products (SEPA 2006), the pollution distribution was graded into five categories and illustrated in the evaluation map.

Results and Discussion

The summary statistics of the data set for six metals are given in Table 1. The mean concentrations of Cu, Pb, Zn, Cd, Cr and Mn were 147, 53.8, 158, 0.32, 73.1 and

Table 1 The descriptive statistics of metals in soil (n = 155; units in mg/kg)

Heavy metal	Mean	SD	C.V. (%)	Median	Min.	Max.	Skewness	Kurtosis	Background values[b]	Number exceeding background values
Cu	147	284	194	39.5	6.70	1,500	1.30[a]	3.90	32.2	96
Pb	53.8	36.1	67.2	44.5	12.9	373	1.48[a]	2.50	24.8	152
Zn	158	148	93.8	119	34.1	1,180	1.69[a]	6.93	76.8	143
Cd	0.32	0.12	37.8	0.30	0.12	0.92	0.47[a]	5.13	0.19	146
Cr	73.1	18.4	25.2	72.6	34.8	170	0.03[a]	3.26	59	117
Mn	457	374	81.8	373	113	3,050	0.85[a]	5.01	511	38

SD standard deviation, *C.V.* coefficient of variation

[a] Log-transformed data

[b] Soil element background values in Nanjing City, Jiangsu Province (The Group of Natural Background Values of Soil, Academia Sinica. 1979)

[c] Detection limits of metals (mg/L): Cu, 0.2; Pb, 0.2; Zn, 0.2; Cd, 0.01; Cr 0.2), and Mn, 0.2

457 mg kg^{-1}, respectively, all of which were above the background value of Nanjing City with the exception of Mn (see Table 1). The maximum value of the six metals reached 1,500, 373, 1,180, 0.92, 170 and 3,050 mg kg^{-1}, respectively, which was more than 4.8-fold of the corresponding background level except Cr (2.8 of the background value). Noticeably, the highest Cu even reached 46-fold of the background level. All the data indicated the soils were severely contaminated on some plots. The coefficients of variation of Cu were 194 % and higher than those of Pb (67.2 %), Zn (93.8 %) and Mn (81.8 %), suggesting that Cu had greater variation among the soils. Cd and Cr owned the lowest coefficient of variation being 37.8 % and 25.2 %, respectively. As mentioned earlier, the investigated area was close to an abandoned copper mine. The elevated Cu in the soils is reasonably contributed to the mining activities in the past decades. Potential leakage and dust from the mining site and waste materials dump can bring large amounts of Cu and other metals to the surrounding area. Zn, as an accompanying element in the mine, could also be released in these processes. Fume dust and wastewater from the smelting plant used to irrigate some agricultural areas can become a major common source of Cu, Pb, Zn and Cd. Several roads including Ninghang freeway pass through this region and the vehicle exhaust probably constituted another origin for Pb (Li et al. 2004). Phosphate fertilizer has been used for many years in this region to enhance agricultural production. It is thought to be another important source of metals entering soils, especially Cd (Luo et al. 2005; Micó et al. 2008). Other agronomic practices like the usage of manure, sewage sludge, Cu-based pesticide and the release of domestic waste over the years consist of possible inputs of the metals. The metals in the soils could also be influenced by the activities in the surrounding area. A waste incineration station is on the south edge of the study area. In addition, there is an industry base bordering on the south and a military training field in the east. Heavy populated residential district of Tangshan Town is located in the west side. It is conceivable that the occurrence in the study region could be partly ascribed to the activities in the surrounding district.

The attributes of the semivariograms for each metal are given in Table 2. The Nug/Sill ratio expressed in percentage can be regarded as a criterion to classify the spatial dependence of soil properties, in which <25 %, the variable being strong spatial dependent; 25 %–75 %, the variable being moderate spatial dependent; and >75 %, the variable being only weak spatial dependence (Chien et al. 1997; Matín et al. 2006). Lithogenic and anthropogenic factors can affect the spatial variability of soil properties. It is thought that strong spatial dependence of soil properties

Table 2 Parameters of models of the theoretic semivariogram

Variable	Transformation	Model	C_0	$C_0 + C$	$C_0/(C_0 + C)$	a (km)	R^2	RSS
Cu	Log (Cu)	Spherical	0.065	0.306	0.211	2.62	0.980	1.585E−03
Pb	Log (Pb)	Gaussian	0.021	0.046	0.463	2.72	0.972	2.292E−05
Zn	Log (Zn)	Spherical	0.020	0.065	0.407	2.37	0.971	7.483E−05
Cd	Log (Cd)	Exponential	0.007	0.029	0.256	5.71	0.949	1.420E−05
Cr	Log (Cr)	Spherical	0.004	0.013	0.330	1.55	0.946	4.360E−06
Mn	Log (Mn)	Exponential	0.029	0.058	0.499	0.96	0.744	9.325E−05

are due to lithogenic factor, and weak spatial dependence can be attributed to anthropogenic factors (Cambardella et al. 1994). Semivariograms showed that Cu, Zn and Cr were all fitted for spherical model. Cd and Mn were all best fitted for an exponential model. However, Pb was best fitted for a Gaussian model. The Nug/Sill ratios of six metals were between 21.1 % and 49.9 %, which indicated the metals were moderate spatial dependent. In addition,

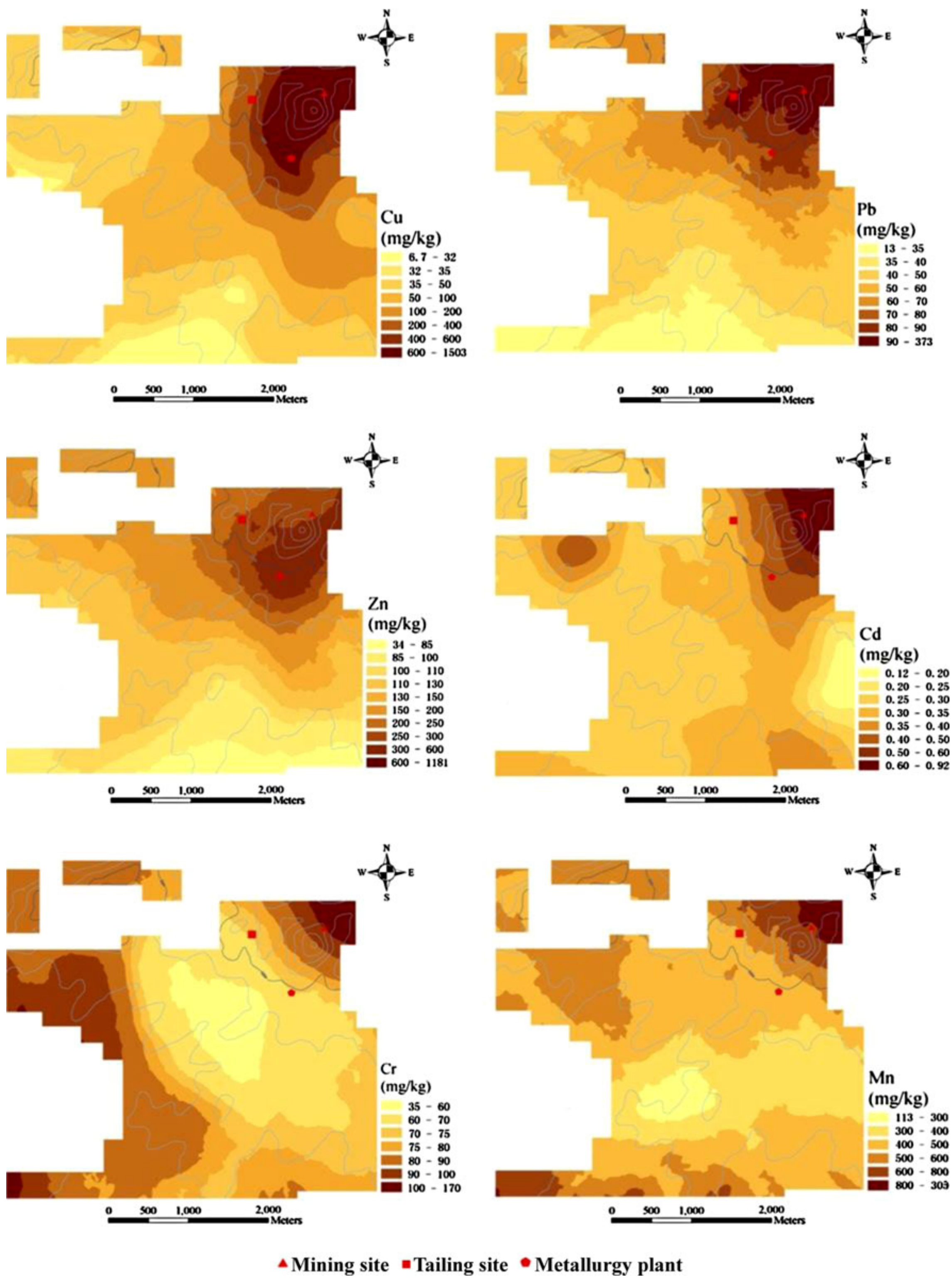

Fig. 1 Filled contours map of soil trace elements

their ranges were between 960 and 5,710 m which meant that the length of the spatial autocorrelation was much longer than the sampling interval of 200 m. Hence, the current sampling design is appropriate for this study, and it is expected that a good spatial structure can be achieved on the interpolated map.

The spatial patterns of soil metals generated from their semivariograms are presented in Fig. 1. It can be seen that the high metal content are located around the copper mine indicating the profound influence of Cu mining activities. The spatial distribution maps for Cu, Pb, Zn and Cd showed similar geographical trends, especially for soil Zn and Pb, with high concentrations surrounding the copper mine and gradually decreased along the increasing distance from the mining site and down the altitude. The two distinct patterns can be related to the topographic character of this region, which is high on the north and east sides, and gradually low in the south and west directions. The waste from the mining site and process plant can disperse along the land and wastewater was also used for the irrigation of the agricultural soils down the hill, which facilitate metal dispersion in soils. This region has prevailing NE/SE wind, in combination with the lower altitude in the west side, flue gas dust from the waste dump and mining site can move towards west with the aid of wind, which could be another reason for the this spatial distribution. As far the Cr and Mn are concerned, although the content of Cr and Mn was high near the mining site, their spatial distribution pattern was different from other elements, which implied the possible different source and pathway. Cr was high on the both sides of east and west with low concentrations in the middle; whereas for Mn, it was found to be high on the north and south part and low in the middle area.

Regarding the distribution of metals around the mine area in the north part of the study area, more specifically, metals showed distinct distribution pattern in different functional part of the mine. The highest Cu appeared around the mining site and metallurgical plant with low level near the tailing dump. The highest Pb was observed around the mining site and the tailing dump. For Cd, Cr and Mn, the highest value was located surrounding the mining site. The highest Zn was observed around metallurgical plant. For Cd, Cr and Mn, the highest value was located surrounding the mining site. In addition, a high Cd was also presented in the northwest part of the study area, which was possibly related to a factory activity there. Generally, the distinct distribution of metals in the mine area illustrated the association between metals with distinct mine-related activities.

The Nemero Synthesis Index evaluation results are presented in Table 3. It can be seen that severely and moderated contaminated soils covered 18.4 % of the total study site, which mainly concentrates on sites surrounding mining location, metallurgy plant and tailing dump. In addition, low contaminated soils accounted for 40.2 % of the study area. When these soils are grown with rice or various vegetables, the metal contents in these crops and potential health risk associated with these crops need to be critically evaluated. As discussed earlier, the severely contaminated site is located in the north part with high altitude which facilitates the dispersion of metals to the surrounding with surface run-off during rainfall and potential air deposition. For the benefit of the local community, imperative and efficient soil management and remediation action may be required. Conventional soil remediation methods usually are expensive and not applicable on a large scale, phytoremediation may be as a good alternative under this situation. On the heavily and moderately contaminated sites, trees with deep roots and high metal resistant capacity or metal hyperaccumulating plants can be introduced to prevent soil erosion and metal leaching to the surrounding environment. Some crops with metal tolerant character can be grown in the low contaminated soils, meanwhile, chemicals like lime which usually work as stabilizer to reduce metal availability can be applied to improve plant growth. Therefore, certain economic income can be generated. Critical quality assessment on the agricultural products should be involved.

Table 3 The evaluation standard and results of soil trace elements

Grade level	p[a]	Pollution Grade	Percent
1	$p \le 0.7$	Safety	4.78
2	$0.7 < p \le 1$	Guard	29.94
3	$1 < p \le 2$	Low pollution	40.22
4	$2 < p \le 3$	Moderate pollution	6.67
5	$p > 3$	Severe pollution	18.39

[a] The synthesis evaluation scores, which were graded into five categories based on the Chinese Farmland Environmental Quality Evaluation Standards for Edible Agricultural Products (SEPA 2006)

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