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Multivariate and geostatistical analyses of the sources and spatial distribution of heavy metals in agricultural soil in Gongzhuling, Northeast China

Jingjing Zhang[1,2] · **Yang Wang**[1] · **Jingshuang Liu**[1] · **Qiang Liu**[1,2] · **Qiuhong Zhou**[1,2]

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Abstract

Purpose The content, source, and spatial distribution of heavy metals in soils are necessary to establish quality standard on a regional level, to assess the potential threat of metals to food safety and human health and to target policies of environment friendly and significant economic benefits.

Materials and methods The surface horizons of 166 agricultural soils in Gongzhuling, a representative agricultural area in the black soil region, Northeast China, were sampled, and the total contents of Cu, Ni, Zn, Pb, Cr, and Cd were analyzed. Multivariate statistics and geostatistical analysis were combined in characterizing spatial distribution of heavy metals and determining their sources in this study.

Results and discussion The mean values of the heavy metal concentrations were 19.61±6.23, 27.16±11.85, 57.82±14.28, 28.34±8.91, 53.04±19.27, and 0.106±0.048 mg kg^{-1} for Cu, Ni, Zn, Pb, Cr, and Cd, respectively, slightly higher than their background values of Siping topsoil, but lower than the guideline values of Chinese Environmental Quality Standard for soils with the exception of individual samples of Ni and Cd. Multivariate and geostatistical analyses suggested that Pb and Cd were related to anthropogenic activities, such as the atmospheric deposition of industrial soot, dust and aerosols and coal burning exhausts, the application of fertilizers, livestock manures and agrochemicals, and the disposal of anthropogenic wastes, whereas Cr and Zn were mainly due to the parent materials, and Cu and Ni displayed a mixed origin of both lithogenic and anthropogenic origin.

Conclusions The analyses of content and sources of heavy metals in agricultural soils are basis for undertaking appropriate action to protect soil quality.

Keywords Agricultural soil · Black soil region · Geostatistical analysis · Heavy metal · Multivariate analysis

1 Introduction

Soil contamination with heavy metals is of increasing concern because of its potential threat to food safety, human health, and its detrimental effects on soil ecosystems (Cui et al. 2004; Lu et al. 2012). Soils, where rock, air, and water interfaced together, can be a long-term sink for heavy metals (Li et al. 2004; Micó et al. 2006; Franco-Uría et al. 2009), and heavy metals may come from natural or anthropogenic sources. Natural contents of heavy metals in soils depend primarily on composition of geological parent materials, and human activities such as industrial expansion, fossil fuel combustion, and agricultural practices influence heavy metal contents in soils (Lu et al. 2012). However, excessive accumulation of heavy metals in agricultural soils can be transferred from soil to other ecosystem components, such as underground water or crops, which can affect human health through water supply and food web (Micó et al. 2006; Sun et al. 2013). In addition, high contents of heavy metals in soils would increase the potential uptake of these metals by crops (Zeng et al. 2011), which may affect food safety and pose threat to human health because of the nonbiodegradable nature and long-biological half-lives of heavy metals for elimination from the body (Raghunath et al. 1999; Li et al. 2004; Chabukdhara and Nema 2012).

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✉ Yang Wang
wangyangw@neigae.ac.cn

[1] Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences, Changchun 130102, China

[2] University of Chinese Academy of Sciences, Beijing 100049, China

Owing to the unique natural environment such as parent material, climate, and natural vegetation characteristics (Liu et al. 2010), the black soil region in Northeast China is one of the major base for commercial grain production in China, and maize production accounts for 25 % of the total national sown area of maize and 31.9 % of the total national maize yield (He et al. 2010). However, excessive and continuous use of agrochemicals can result in the accumulation of heavy metals in soils with the increase of reclamation years and tillage intensity. Pb concentrations in all soils except for one (Sun et al. 2013) and contents of Cd and Zn in more than 60 % of the soil samples (Guo and Zhou 2006) in the black soil region were higher than the regional background levels. However, most of the studies in the black soil region were carried out on soil fertility indices such as soil organic carbon, total N, total and available P, and clay content (Li et al. 2005; Liu et al. 2010; Stockmann et al. 2013; Zhang et al. 2013; Chen et al. 2014; Wei et al. 2014). Studies on the content, source, and spatial distribution of heavy metals in typical agricultural soils in black soil region are still in need (Sun et al. 2013), as this may pose a threat to food safety and potential barriers for international trading of foodstuffs (Cui et al. 2004).

Multivariate statistical analysis provides a useful technique for classifying the interrelation of elements (Rodríguez Martín et al. 2006; Reimann et al. 2012), reducing the initial dimension of data sets and facilitating its interpretation (Castellano et al. 2007; Franco-Uría et al. 2009), which have been widely applied to identify natural or anthropogenic sources in soils (Facchinelli et al. 2001; Micó et al. 2006; Huang et al. 2007; Luo et al. 2007; Chabukdhara and Nema 2012). However, classical multivariate statistical approaches ignore the spatial correlations between sampling points, which may include important information (Korre 1999; Lin 2002). For example, data points that are spatially close to each other are more likely to show similar values, which is termed spatial autocorrelation, and it may lead to a number of biases such as pseudoreplicates and estimates based on unweighted data if not taken into account adequately (Maas et al. 2010). GIS is a system for managing, manipulating, analyzing, and presenting geographically related information (Li et al. 2004), and geostatistical tools are mainly applied to estimate and map soil attributes in unsampled areas (Reimann 2005; Rodríguez Martín et al. 2006). Thus, the combination of multivariate statistics and geostatistical analysis can be a useful tool in characterizing spatial distribution of heavy metals and determining their sources and are still in need (Lu et al. 2012; Sun et al. 2013).

The present work was conducted as part of a large research project aiming at assessing the environmental baseline values of agricultural producing area in Jilin province, which was financed by the World Bank. Gongzhuling, with the title of the hometown of China's corn, was in a leading position of the grain output. The aims of this study were (1) to determine contents of Cu, Ni, Zn, Pb, Cr, and Cd in soils; (2) to define their natural or anthropogenic sources using multivariate analysis; and (3) to produce geochemical maps of the heavy metals and identify possible hotspots of elevated concentration of metals using GIS approaches. Such research will provide a basis for establishing proper management strategies to protect soils from long-term accumulation of heavy metals and to improve the sustainability and safety of intensive farming activities.

2 Materials and methods

2.1 Study area

Gongzhuling County (43° 11′–44° 9′ N, 124° 2′–125° 18′ E) is located in the northeast of Siping, Jilin province, Northeast China (Fig. 1). The study area is in the North Temperate Zone, with a continental monsoon climate. Average annual temperature is 5.6 °C, with 144 frost-free days. Average rainfall is 594.8 mm, and almost 70 % of the rainfall occurs in June, July, and August. The topography in the black soil region is characterized by undulating plateau, and the soils are black soil (Luvic Phaeozem, FAO) and chernozem (Haplic Chernozem, FAO).

The study area has been traditionally associated with agricultural activities and is the base for commercial grain production. The county covers 4058 km^2, and approximately 3172 km^2 is occupied by agricultural lands. Maize (*Zea mays* L.) is the main crop in the study area; the cropping area of maize in this region is 2794 km^2, accounting for 88 % of the total agricultural area; the annual total yield is 2.8×10^6 t (Jilin Statistical Bureau 2011). The traditional cropping practice is continuous corn.

2.2 Soil sampling

A total of 166 surface soil samples (0–20-cm depth) were collected from the agricultural areas under maize cultivation in Gongzhuling in October 2011 (Fig. 1). The sampling design was based on the prevailing wind direction and the distribution of local agricultural land use. Eight samples were selected from each town, with one sample upwind of the town, three samples along the prevailing wind direction, and four samples along the two secondary prevailing wind directions. Sampling sites were chosen with the density of about one every 1 km along the wind directions and at least 200 m away from industry, traffic, and residential areas. A global positioning system (GPS) was used to locate the sampling locations throughout the sampling process.

For each sample, six subsamples were collected with 20 m away from each other and mixed thoroughly. Approximately 1.0 kg of soil was taken for each soil sample, and stones, grass, leaves, and roots present in soil samples were discarded after

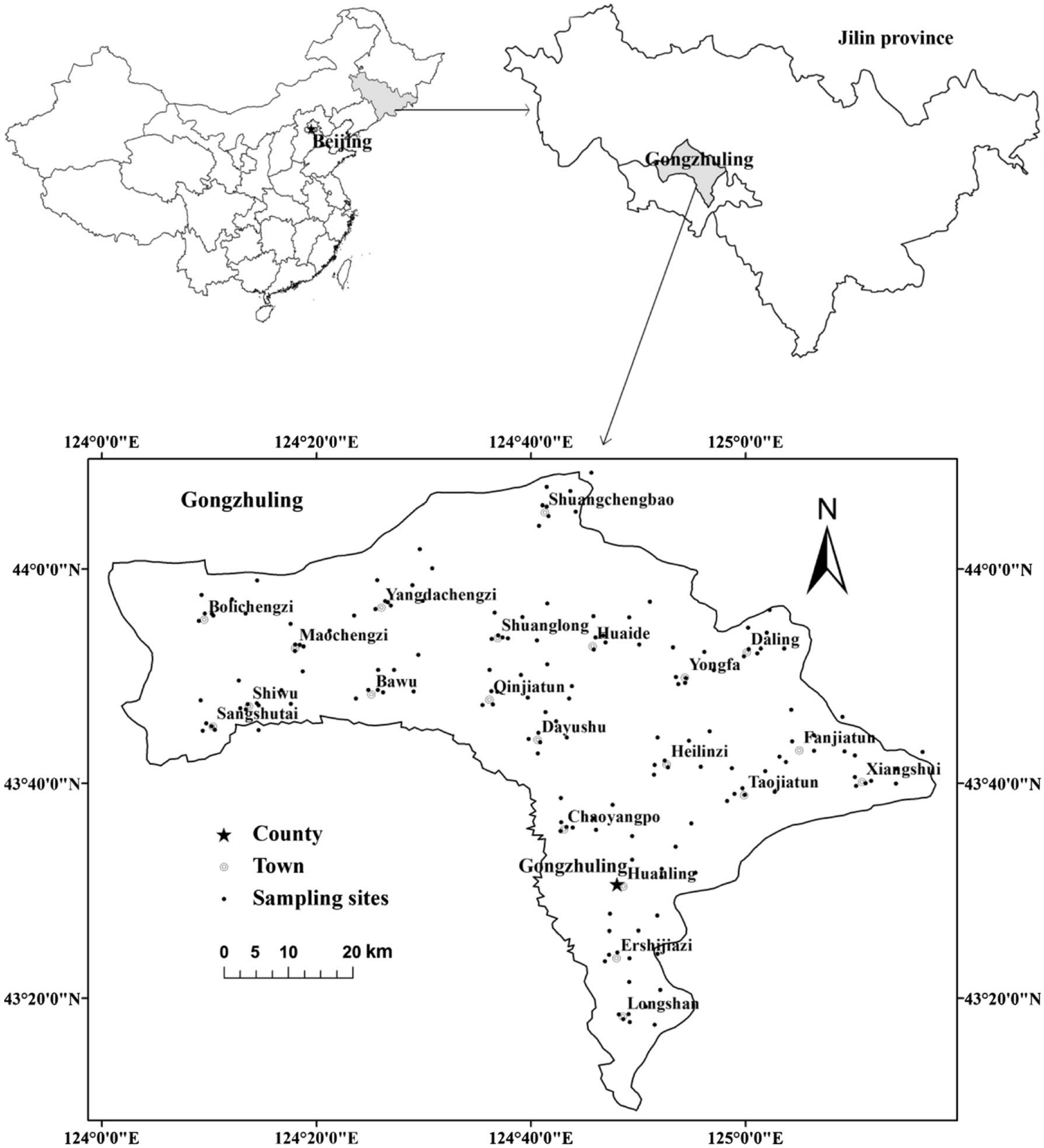

Fig. 1 Soil sampling locations in Gongzhuling County, Northeast China

gentle shaking to remove the soil attached around roots. All soil samples were air-dried at ambient temperature, crushed, and sieved to pass through a 2-mm nylon sieve. Portions of the soil samples were further ground in an agate mortar, sieved through a 0.149-mm nylon sieve, and stored in plastic bags for analysis.

2.3 Chemical analysis

Soil pH was measured in a 1:2.5 (*w*/*v*) ratio of soil to water by a pH meter (pHS-3B, Leici, Shanghai) after the soil suspension was settled for half an hour. Soil organic carbon was determined by the Walkley–Black method (Nelson and Sommers 1982).

The soil samples were digested in triplicate with the mixture of HNO_3, HCl, and H_2O_2 using Method 3050B (USEPA 1996). Concentrations of Cu, Ni, Zn, Pb, and Cr in the digestion solution were determined by flame (air-acetylene) atomic absorption spectroscopy (FAAS; AA-6300, Shimadzu, Japan). The concentrations of Cd in the soils were determined by graphite furnace atomic absorption spectroscopy (GFAAS; AA-6300, Shimadzu, Japan). The detection limits of this method were 0.055 $\mu g\ L^{-1}$ for Cd and 0.016, 0.023, 0.049, 0.071, and 0.062 $mg\ l^{-1}$ for Cu, Ni, Zn, Pb, and Cr, respectively.

Analytical reagent blanks were carried out throughout the entire sample preparation and analytical process. The accuracy of the analytical method (accuracies within ±10 %) was estimated by analyzing Standard Reference Material (GBW 07405 (GSS-5)) obtained from the Center of National Standard Reference Material of China. The certified values in GSS-5 were 144±6, 40±4, 494±39, 552±29, 118±7, and 0.45±0.06 mg kg^{-1} for Cu, Ni, Zn, Pb, Cr, and Cd, respectively. All the analyses were carried out in triplicate, and the standard deviations were within 5 %.

2.4 Statistical and geostatistical analysis

Statistical analysis was carried out using SPSS 16.0 (SPSS Inc., USA). Two multivariate analysis techniques, principal component analysis (PCA) and cluster analysis (CA), were applied to the dataset for identifying correlations between metals. In the PCA, Varimax with Kaiser normalization was used as the rotation method in the analysis. Cluster analysis (CA) was developed according to the method of the furthest neighbor linkage. The distance measure used in CA was the squared Euclidean distance. Metal–soil properties and metal–metal relationships determined by correlation matrix (CM) were employed to complete and support the results obtained by multivariate analysis. Kolmogorov–Smirnov (K-S) test for normality was also applied, with the aim of employing the adequate correlation coefficient in CM (Pearson's coefficient for normal distribution and Spearman's coefficient for non-normally distributed data).

The main application of geostatistics to soil science has been the estimation and mapping of soil attributes in unsampled areas (Goovaerts 1999; Liu et al. 2006). Semivariograms were developed to establish the degree of spatial continuity of soil properties among data points and to establish the range of spatial dependence for soil property variable. Information generated through variogram was used to calculate sample weighing factors for spatial interpolation by a kriging procedure (Liu et al. 2006). Kriging interpolation and mapping were conducted using ArcGIS 10.0 (ESRI Inc., USA).

3 Results and discussion

3.1 Descriptive statistics

Soil properties analyzed in this study are shown in Table 1. The K-S test confirmed that soil organic carbon was normally distributed while the pH values fitted an abnormal distribution.

The soil pH ranged from 4.71 to 7.77, with a mean value of 5.95. In detail, most of the soil samples were acidic, with 84 % of the soils having pH values below 7.0, and only 16 % of the soils having pH above 7.0. Compared with previous study in Gongzhuling (Li et al. 2005), significant acidification in croplands occurred during the past decade, which may be mainly due to the high-N fertilizer inputs and the uptake and removal of base cations by plants (Guo et al. 2010).

Soil organic carbon contents of all the soil samples were in a wide range from 5.40 to 28.31 g kg^{-1}, with a mean value of 11.92 g kg^{-1}. According to Stockmann et al. (2013), the contents of soil organic matter declined with the increase of reclamation years. However, the results of this study showed that the SOC contents were little affected by the reclamation of the past decade compared with Li et al. (2005), and it even increased in some sampling sites, which was due to the application of organic fertilizers like manures. Organic matter could play a significant role in the retention of heavy metals in soils due to its strong adsorption (Guo et al. 2006; Micó et al. 2006). On the other hand, the pH value could influence the cation mobility and regulate the solubility of heavy metals in soil (Kashem and Singh 2001), and most of the metals tend to be available in acid pH, with the exception of Cd (Rodríguez Martín et al. 2006). Therefore, further research was required to assess the potentially available species (e.g., extractable fraction), mobility, phytoavailability, and bioaccessibility of heavy metals to determine the probability of these metals transferring from the soil to other ecosystems, such as the underground water or crops.

The descriptive statistics of the heavy metals analyzed in this study are presented in Table 1. The mean values of the total heavy metal concentrations ranged from 0.106±0.048 mg kg^{-1} for Cd to 57.82±14.28 mg kg^{-1} for Zn. Application of the K-S test confirmed that the concentrations of Cu, Zn, Pb, and Cr were normally distributed while Ni and Cd fitted a log-normal distribution. The coefficients of variation (C.V., calculated as [standard deviation]/[mean]) of heavy metals ranged from 24.70 % for Zn to 45.28 % for Cd and decreased in the order of Cd>Ni>Cr>Cu>Pb>Zn, showing that Cd had greater variation among the soils.

It can be seen in Table 1 that heavy metal concentrations in this study area were slightly higher than the background values (13.67, 18.82, 53.51, 22.46, 44.16, and 0.087 mg kg^{-1} for Cu, Ni, Zn, Pb, Cr, and Cd, respectively) of Siping topsoils (Meng and Li 1995). This indicated that anthropogenic inputs such as long-term agricultural practices and industry activities caused the enrichment of heavy metals in soils. According to the Chinese Environmental Quality Standard for Soils (Environmental Protection Administration of China 1995), heavy metal concentrations in the soils of this study did not exceed the concentration limits (100, 50, 250, 300, 200, and 0.3 mg kg^{-1} for Cu, Ni, Zn, Pb, Cr, and Cd, respectively) with the exception of Cd in two samples and Ni in five samples. This indicated that it was still safe and suitable for agricultural production in this study area, as the concentration limits of heavy metals in the Chinese Environmental

Table 1 Descriptive statistics of heavy metal concentrations and soil properties

Parameter	Cu[a]	Ni[a]	Zn[a]	Pb[a]	Cr[a]	Cd[a]	SOC[b]	pH
Mean	19.61	27.16	57.82	28.34	53.04	0.106	11.92	5.95
Minimum	5.50	5.58	22.17	9.48	16.69	0.045	5.40	4.71
Maximum	36.89	54.12	108.95	69.81	93.49	0.455	28.31	7.77
S.D.[c]	6.23	11.85	14.28	8.91	19.27	0.048	3.20	0.79
C.V.[d]	31.77	43.63	24.70	31.44	36.33	45.28	26.85	13.28
Skewness	−0.161	0.538	0.344	0.447	0.180	3.301	0.888	0.867
Kurtosis	−0.315	−0.732	1.620	1.744	−0.980	17.887	3.324	−0.262
Background values[e]	13.67	18.82	53.51	22.46	44.16	0.087		
Standard values[f]	100	50	250	300	200	0.3		

[a] mg kg^{-1}

[b] g kg^{-1}

[c] Standard deviation

[d] Coefficients of variation (%)

[e] Meng and Li 1995

[f] The Chinese Environmental Quality Standard for Soils (Environmental Protection Administration of China 1995)

Quality Standard for Soils (Environmental Protection Administration of China 1995) were thresholds for affecting the safety of agricultural production and human health.

3.2 Multivariate statistics for source identification

3.2.1 PCA for heavy metals in soils

PCA has been widely used to identify the origin of heavy metals in the agricultural soils (Rodríguez Martín et al. 2006; Lu et al. 2012; Niu et al. 2013; Sun et al. 2013). The results of PCA for total heavy metal contents in soils are shown in Table 2. Three principal components with eigenvalues higher than 1 were extracted after the varimax rotation. Spatial representation of the three principal components is also shown in Fig. 2, where the correlations among metals can be seen. PCA leads to a reduction of the initial dimension of the dataset to three components which explained 90.28 % of the data variation. The rotated component matrix showed that Cu, Ni, Zn, and Cr were strongly associated with the first component (C1), the second component (C2) included Pb, while Cd was in the third component (C3).

The first component (C1) explained 53.47 % of the total variance, and it was considered to be both lithogenic and anthropogenic origin. This was verified by the geostatistical analysis in the present study and will be discussed later. The spatial distribution of Cu, Ni, Zn, and Cr was in a similar trend and showed a nonpoint source contamination, but there was still difference among them. Cr is geochemically associated with the major elements such as Al, Fe, and Mn, which may originate from the soil parental materials (Li et al. 2004). In general, Ni and Cr in agricultural soils were derived from the weathering of parent material and subsequent pedogenesis (Micó et al. 2006), and anthropogenic inputs of them in fertilizers, limestone, and manure were lower than the contents already present in soils (Facchinelli et al. 2001). However, the high coefficient of variation of Ni in the present study showed that Ni concentration was obviously influenced by human activities and may be from a mixed origin, which may be due to the existence of many building material factories in Gongzhuling.

Researchers have reported that Cu and Zn concentrations in soils indicate a mixed origin (Micó et al. 2006; Davis et al. 2009; Franco-Uría et al. 2009). Agronomic practices, such as the application of fertilizers (commercial fertilizer, manure, sewage sludge), pesticides, and fungicides, can increase the soil metal load in agricultural soils (Rodríguez et al. 2008). For example, Cu and Zn were supplemented as additives to animal feed for antimicrobial effects and growth promotion (Nicholson et al. 2003), and about 90 % of the Cu and Zn was excreted by animals (Dach and Starmans 2005), resulting in metal-rich manures. Luo et al. (2009) reported that livestock manures accounted for 69 and 51 % of Cu and Zn inputs, respectively, in agricultural soils. In this study area, Cu contents in about 80 % soil samples were higher than the corresponding background value of Siping topsoil, indicating the mixed origin (lithogenic and anthropogenic). Zn can have a lithogenic source as it forms a number of soluble salts (e.g., chlorides, sulfates, and nitrates) or insoluble salts (e.g., silicates, carbonates, phosphates, oxides, and sulfides) according to the prevailing pedogenic processes (Micó et al. 2006; Sun et al. 2013). However, Zn is also a minor constituent of some fungicides, such as mancozeb, that are applied to crops and vegetables (Luo et al. 2009). According to the lowest

Table 2 Total variance explained and component matrixes for heavy metals in soil

Total variance explained										Component matrix				Rotated component matrix			
Component	Initial eigenvalues			Extraction sums of squared loadings[a]			Rotation sums of squared loadings[b]			Element	C1	C2	C3	Element	C1	C2	C3
	Total	% Of variance	Cumulative (%)	Total	% Of variance	Cumulative (%)	Total	% Of variance	Cumulative (%)								
1	3.230	53.829	53.829	3.230	53.829	53.829	3.208	53.471	53.471	Cu	0.898	0.211	−0.190	Cu	0.913	0.229	0.047
2	1.386	23.101	76.930	1.386	23.101	76.930	1.172	19.529	73.000	Ni	0.915	−0.240	0.054	Ni	0.905	−0.277	−0.039
3	0.801	13.348	90.278	0.801	13.348	90.278	1.037	17.278	90.278	Zn	0.835	0.258	−0.023	Zn	0.834	0.167	0.202
4	0.334	5.558	95.836							Pb	−0.075	0.832	−0.511	Pb	−0.025	0.973	0.108
5	0.167	2.780	98.616							Cr	0.933	−0.218	0.020	Cr	0.926	−0.240	−0.051
6	0.083	1.384	100.000							Cd	0.117	0.691	0.707	Cd	0.052	0.102	0.989

[a] Extraction method: principal component analysis

[b] Rotation method: varimax with Kaiser normalization

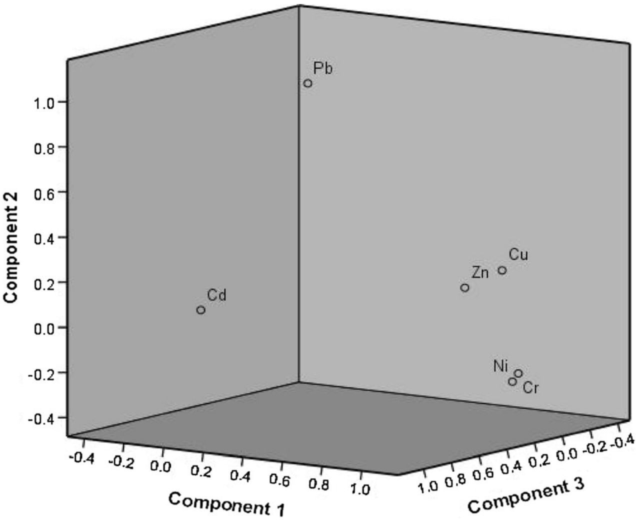

Fig. 2 Loading plot of principal component analysis based on concentrations of heavy metals

coefficient of variation among metals, anthropogenic inputs of Zn in fertilizers, manure, and fungicides may be lower than the concentrations already present in the soil.

C2 explained 19.53 % of the total variance and had a strong positive loading on Pb. It is mainly anthropogenic. Common sources of Pb in soils were vehicle exhausts, industrial fumes, manure, sewage sludge, and lead-arsenate pesticides (Facchinelli et al. 2001; Luo et al. 2007; Sun et al. 2013). According to Facchinelli et al. (2001), Pb derived from car exhausts did not extend appreciably beyond 30 m from the road, while industrial fumes, coal burning exhausts, and lead aerosols can be carried over long distances. Actually, about 67 % of China's energy needs come from coal combustion, and this status will not be changed over the next several decades (Luo et al. 2009). Thus, atmospheric deposition of industrial soot, dust and aerosols, and coal burning exhausts, which were mainly from electic power plants, metal smelters, and chemical plants, etc. may be the most important source of Pb in soils. This was verified by some plots with high Pb contents located downwind of the towns and big villages in this study. On the other hand, the continuous application of livestock manures, fertilizers, agrochemicals, and other soil amendments potentially to improve soil fertility and outputs of agricultural products may also lead to the accumulation of Pb in topsoils.

C3 only included Cd and was considered to be an anthropogenic component. Luo et al. (2007) reported that complex anthropogenic sources and heterogeneity in soil genesis may be the cause for the varied concentrations of metals among the sampling sites. Cd showed the highest coefficient of variation than the others, suggesting the largest possibility to be derived from anthropogenic sources in agricultural soils. Phosphate fertilizers, livestock manures, atmospheric deposition, agricultural activities, and anthropogenic wastes (such as sewage sludge, wastewater, or waste materials) were in general important sources of Cd entering agricultural soils (Micó et al. 2006; Nziguheba and Smolders 2008; Niu et al. 2013). Nicholson et al. (2003) reported that annual Cd inputs were 21, 4.2, 1.6, and 12 t by atmospheric deposition, livestock manures, sewage sludge, and total inorganic fertilizers in England and Wales. Luo et al. (2009) found that agricultural activities accounted for 63 % of the total annual inventory of Cd in agricultural soils. The trace metal input of Cd via fertilizers was similar to or even larger than the metal input via atmospheric deposition in European agricultural soils (Nziguheba and Smolders 2008). According to Sui et al. (2006), large amounts of phosphate fertilizers were applied in Gongzhuling in the past two decades, which may partly explain the enrichment of Cd in topsoils.

The conclusions drawn in this work are in accordance with previous studies (Micó et al. 2006; Sun et al. 2013). Cu, Ni, Zn, and Cr displayed a mixed origin while Cd and Pb were mainly controlled by human activities. For Cu and Ni, anthropogenic origin played a more important role than lithogenic origin, while anthropogenic inputs of Zn and Cr were lower than the concentrations already present in the soil. According to Rodríguez et al. (2008) and Sun et al. (2013), the association of heavy metals with the factors in a PCA can indicate the hypothetical sources of these elements (lithogenic, anthropogenic, or mixed), although it is difficult, in some occasions, to differentiate the effect of each of these factors on the soil.

3.2.2 Cluster analysis (CA) for heavy metals in soils

Cluster analysis was performed on the total concentrations of heavy metals in agricultural soils, and the results were illustrated with the dendrogram in Fig. 3. The elements were hierarchically clustered, and the distance cluster represented the degree of association between metals. The lower the value was on the distance cluster, the more significant the association was (Lee et al. 2006). A criterion for the distance cluster of between 5 and 10 was adopted in the analysis, and three distinct clusters were identified (Fig. 3).

Cluster I	contained Cu, Ni, and Pb. These elements were mainly associated with human activities and derived more from anthropogenic sources than lithogenic sources in agricultural soils.
Cluster II	contained Cd. This element was mainly derived from anthropogenic sources in agricultural soils.
Cluster III	contained Zn and Cr. The two trace elements may be geochemically associated in nature and lithogenic origin from parental materials of the soils played a more important role than anthropogenic origin.

As shown in Fig. 3, cluster III was formed at a distance criterion of about 1, indicating the significant association of Zn and Cr. Meanwhile, Cu and Ni clustered together almost at the same distance criterion of Zn and Cr, which suggested the strong association between Cu and Ni. Heavy metals of Cu, Ni, and Pb formed a cluster at a distance criterion of about 2, depicting a strong association among them.

In general, the results of the cluster analysis (CA) agreed very well with those of principal component analysis (PCA). The higher proportion of anthropogenic origin than lithogenic origin of Cu and Ni was well illustrated by strong association with Pb in CA, as Pb was mainly derived from anthropogenic sources. The anthropogenic inputs in agricultural topsoils caused significant enrichments of Pb, Cd, and partly Cu and Ni, although the origin of Cu and Ni varied between different areas depending on specific human activities that were locally relevant. The two trace elements (Zn and Cr) may be geochemically associated in nature, and lithogenic origin from parental materials of the soils played a more important role than anthropogenic origin.

3.2.3 Correlation matrix (CM) for heavy metals in soils

Relationships between concentrations of heavy metals and soil properties were investigated using Pearson correlation coefficients for normal distribution and Spearman's coefficient for non-normally distributed data. In general, correlations between metals were in agreement with the results

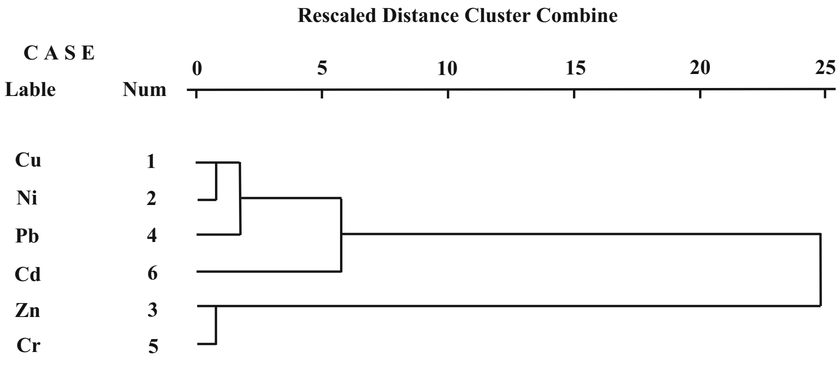

Fig. 3 Dendrogram of the cluster analysis of the agricultural soils based on their total metal concentrations

obtained by PCA and CA, and CM was useful in verifying some new associations between metals that were not clearly stated in former analyses. According to Table 3, Cu, Ni, Zn, and Cr were closely related, which might suggest a common source. Cd did not present any correlation with other metals except for Pb, which were mainly due to anthropogenic sources. Pb was also correlated to Cu, Cr, and Ni. This was due to that copper sulfate may contain significant concentrations of Pb as impurity, and the past use of these fungicides might partially contribute to the presence of these metals in soils currently (Franco-Uría et al. 2009). Wei and Yang (2010) reported that the sources of Pb, Cu, and Ni in the agricultural soils may also be derived from industrial sources such as power plant, band steel factory, and leather factory. This further confirmed the mixed origin of Cu and Ni contents in soil. The CM between metals and soil properties showed that metals which originated partially from parent materials (Cu, Ni, Zn, and Cr) displayed significant correlation with SOC. On the contrary, anthropogenic metals (Cd and Pb) did not show any correlation with SOC, which was consistent with other studies (Micó et al. 2006; Franco-Uría et al. 2009). This suggests that the parent material and subsequent pedogenic processes are major factors in the amounts and distribution of lithogenic metals in these soils.

3.3 Spatial distribution of heavy metals

A variogram analysis was conducted, and the parameters and cross-validation results for the fitted variogram models are presented in Table 4. The spatial variability of soil properties was affected by intrinsic (soil formation factors, such as soil parent materials) and extrinsic factors (soil management practices, such as fertilization) (Liu et al. 2006). Nugget represents the experimental error and field variation within the minimum spacing, and the Nugget/Sill ratio can be regarded as a criterion to classify the spatial dependence of soil properties. According to Table 4, the higher Nugget/Sill ratio of Pb and Cd indicated that the extrinsic factors such as fertilization, ploughing, and other human activities weakened their spatial correlation, which further substantiated the results of the PCA.

The spatial distribution of heavy metals in Gongzhuling is presented in Fig. 4. Similar spatial distribution patterns were found for Cu, Ni, Zn, and Cr, which increased gradually from west to east and from northeast to southwest, implying a common source for their occurrence in soils. This provided a refinement and reconfirmation of the results of PCA and correlation analysis, in which strong associations were found among these metals. This result is in accordance with Zhao et al. (2002), in which the concentration of Zn and Cr in Gongzhuling area also showed the similar spatial pattern as this work. Micó et al. (2006) reported that Ni, Zn, and Cr contents were associated with parent rocks, and their spatial distribution showed a good correlation with the surface evidence of the mineralogical structure, such as organic matter, carbonates, or clay.

The spatial distribution of Pb, characterized by localized hotspot patterns, was distinctly different from metals such as Cu, Ni, Zn, and Cr. The hotspot with the highest Pb concentrations was located in Shuangchengbao town, where a large-scale furfural factory, large numbers of livestock farms, and feed mills were concentrated. The other hotspot of Pb was in Longshan town, which coincided with orchards of apple, pear, and hazelnut planting region in this study area. Therefore, the atmospheric deposition of industrial soot, dust and aerosols, and coal burning exhausts, the application of livestock manures and agrochemicals, and the disposal of solid waste were the main sources resulting in the accumulation of Pb in soils. On the one hand, industrial fumes and Pb aerosols could be transferred over long distance in the atmosphere and accumulate in soils downwind of town; on the other hand, Pb content displayed a declining trend with distance away from the source, such as the high discharge of industrial fume, coal burning exhausts, and domestic waste (Sun et al. 2013).

Cd showed a similar spatial distribution trend with Pb, and this was consistent with the above result that the Cd had significant positive correlation with Pb. The hotspot of Cd was

Table 3 Correlation coefficient matrix between metal concentrations and soil properties

	Cu	Ni	Zn	Pb	Cr	Cd	SOC	pH
Cu	1							
Ni	0.737^{**}	1						
Zn	0.748^{**}	0.748^{**}	1					
Pb	0.173^{*}	-0.304^{**}	0.101	1				
Cr	0.766^{**}	0.902^{**}	0.648^{**}	-0.224^{**}	1			
Cd	0.095	0.018	0.147	0.220^{**}	0.010	1		
SOC	0.527^{**}	0.483^{**}	0.402^{**}	−0.113	0.497^{**}	0.100	1	
pH	-0.082^{a}	$-0.165^{a,*}$	-0.092^{a}	0.039^{a}	$-0.201^{a,**}$	$0.172^{a,*}$	$0.182^{a,*}$	1^{a}

** Correlation is significant at the 0.01 level (2-tailed)

* Correlation is significant at the 0.05 level (2-tailed)

^{a} Spearman coefficient

Table 4 The parameters and the cross-validation results of the fitted variogram models

	Model	C_0	$C+C_0$	$C_0/C+C_0$	Range (km)	R^2	RMSE
Cu	Spherical	0.103	2.194	0.047	5.33	0.912	3.956
Ni	Gaussian	0.723	3.961	0.183	1.63	0.834	8.498
Zn	Exponential	0.922	10.465	0.088	10.57	0.862	11.548
Pb	Gaussian	0.329	0.949	0.347	0.20	0.645	6.403
Cr	Gaussian	1.623	10.028	0.162	1.46	0.877	12.703
Cd	Spherical	0.875	2.520	0.347	10.786	0.763	0.051

RMSE root mean square error

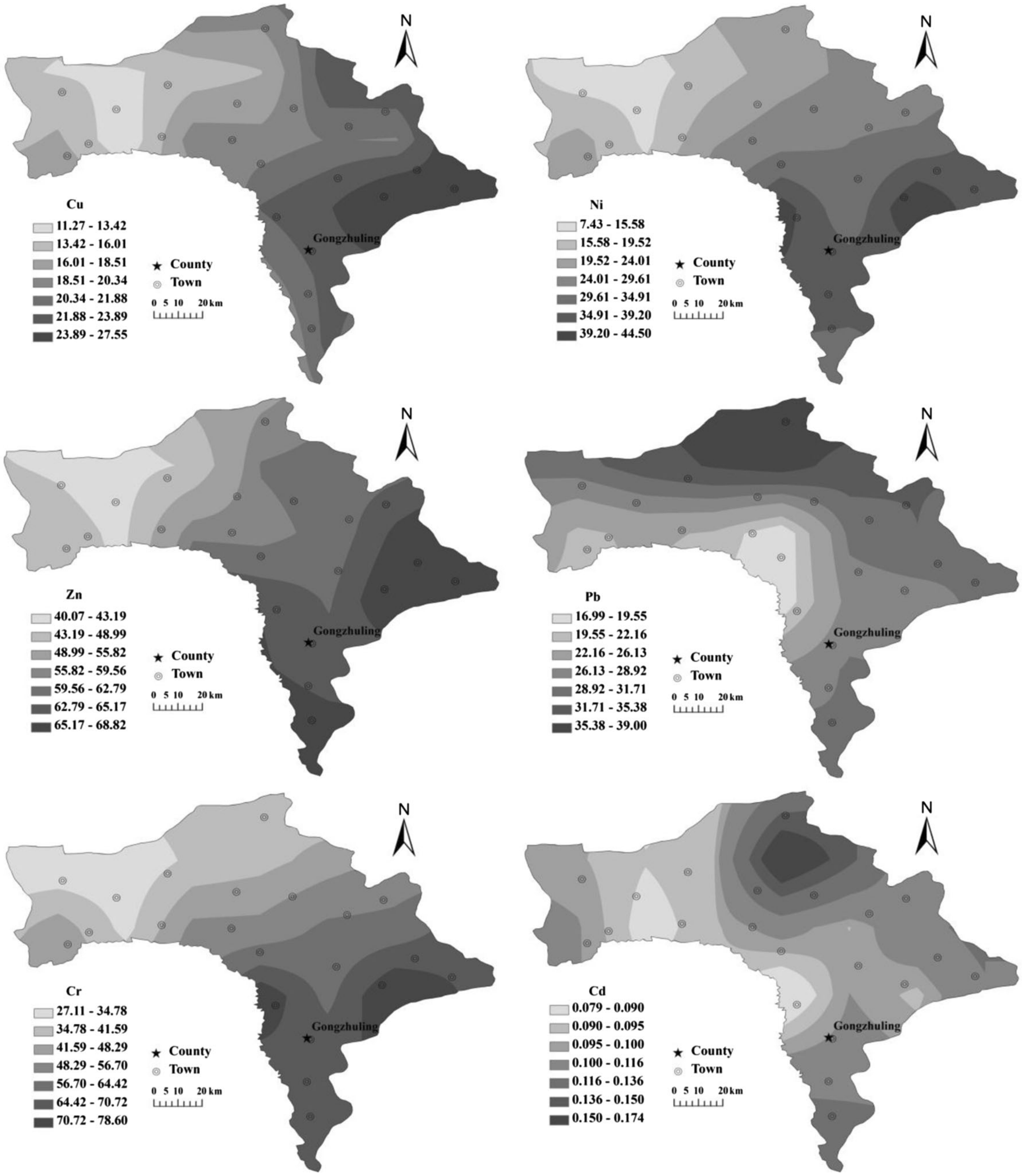

Fig. 4 Spatial distribution of soil heavy metal concentrations (mg kg^{-1}) in Gongzhuling County

located in Shuangchengbao, Shuanglong and Huaide town, where the automobile parts factories, furfural factory, liquor factory, livestock farms, vegetable farm, and processing mills were gathered. Main anthropogenic sources may be the direct discharges from local point sources, such as industrial effluents and the agricultural practices, particularly with application of fertilizer and manure. Rodríguez et al. (2008) reported that Cd was specifically adsorbed by crystalline and amorphous oxides of Al, Fe, and Mn. On the other hand, metallic (copper, lead, and zinc) and especially alkaline earth (calcium and magnesium) cations reduced Cd adsorption by competing for available specific adsorption and cation-exchange sites (Martin and Kaplan 1998). In this study, the Cd content in topsoils could be mainly controlled by the long-term anthropogenic activities rather than by soil parent rocks.

4 Conclusions

The results obtained in this study increased our knowledge of the heavy metal contents, their possible sources, and distribution in the agricultural soils in Gongzhuling. Although a slightly higher than their background values of Siping topsoil, Cu, Ni, Zn, Pb, Cr, and Cd concentrations in soils did not exceed the concentration limit affecting the safety of agricultural production and human health with the exception of Cd in two samples and Ni in five samples, indicating an insignificant contamination of these metals in this area. Among all the analyzed metals, Cr and Zn mainly come from the parent materials while Cu and Ni displayed a mixed origin. Human activities, such as the atmospheric deposition of industrial soot, dust and aerosols, and coal burning exhausts, the application of fertilizers, livestock manures, and agrochemicals, and the disposal of anthropic wastes were the main sources of Pb and Cd. This result is confirmed by the fact that lithogenic metals were better correlated with SOC, while Cd and Pb did not show any correlation with SOC. This study demonstrated that the combination of multivariate statistics and geostatistical analyses can be very useful in characterizing spatial distribution of heavy metals and in determining their sources. In addition, this work will provide basis for effectively targeting policies and implementing mitigation strategies to reduce metal inputs and to protect soils from long-term heavy metal accumulation.

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