The accumulation of heavy metals in agricultural land and the associated potential ecological risks in Shenzhen, China

Jiansheng Wu1,2 · Jing Song3 · Weifeng Li3 · Maokun Zheng4

Received: 8 March 2015 / Accepted: 24 August 2015 / Published online: 15 September 2015
© Springer-Verlag Berlin Heidelberg 2015

Abstract Accumulation of heavy metals in agricultural land and their ecological risks are key issues in soil security studies. This study investigated the concentrations of six heavy metals—copper (Cu), zinc (Zn), lead (Pb), nickel (Ni), and chromium (Cr) in Shenzhen’s agricultural lands and examined the potential hazards and possible sources of these metals. Eighty-two samples from agricultural topsoil were collected. Potential ecological risk index was used to calculate the potential risk of heavy metals. Principal component analysis (PCA) was applied to explore pollution sources of the metals. Finally, Kriging was used to predict the spatial distribution of the metals’ potential ecological risks. The concentrations of the heavy metals were higher than their background values. Most of them presented little potential ecological risk, except for the heavy metal cadmium (Cd). Four districts (Longgang, Longhua, Pingshan, and Dapeng) exhibited some degree of potential risk, which tended to have more industries and road networks. Three major sources of heavy metals included geochemical processes, industrial pollutants, and traffic pollution. The heavy metal Cd was the main contributor to the pollution in agricultural land during the study period. It also poses the potential hazard for the future. High potential risk is closely related to industrial pollution and transportation. Since the 1980s, the sources of heavy metals have evolved from parent rock weathering, erosion, degradation of organics, and mineralization to human disturbances resulting in chemical changes in the soil.

Keywords Soil heavy metals · Agricultural topsoil · Potential ecological risk · Principal component analysis · Pollution sources · Shenzhen, China

Introduction

Big cities are remarkable for their rates of population expansion and urban sprawls nowadays. To respond to the need of urban development, natural lands are being converted into urban areas, leading to the loss of agricultural land. As a consequence, urban roads and buildings are increasingly covering the original soil. As one of the most important components of the urban ecosystem, soil provides a growing medium, habitat, and nutrients for plants and soil microbes. It also serves as an important sink for urban pollution, helping to absorb, degrade, and reduce levels of pollutants (Sheng et al. 2012; Ayrault et al. 2013; Rota et al. 2013; Angelone and Udovic 2014). Human activities, however, have seriously affected the overall quality of soil and changed its physical and chemical conditions. One of the most significant problems is that heavy metals have begun to accumulate in the agricultural topsoil in cities, especially in areas with rapid urbanization. Heavy metal pollution has reduced both the ecological functions of soil and the activity of soil microbes, while also directly and indirectly...
affecting the health of citizens (Velea et al. 2009). Although several studies have investigated the accumulation of heavy metals in urban soils, most have focused only on industrial or outdoor urban recreation areas (Huang et al. 2003, 2007; Zhang et al. 2013). The contamination of agricultural topsoil by heavy metals at a city-wide scale has not yet been studied in detail.

In recent years, many indexes have been proposed for assessing heavy metal pollution in topsoil, including the geo-accumulation index, enrichment factor, pollution load index, and hazard quotient (Winner et al. 1980; Jackson et al. 1990; Rattan et al. 2005; Khan et al. 2008; Wei and Yang 2010). Most of these methods can only describe the current condition of pollution. However, the potential accumulation risk of heavy metals is not fully given by these indexes. Therefore, this study used the potential ecological index to analyze and evaluate the potential hazard of heavy metals.

Shenzhen is a rapidly developing city growing from a fishing village to an urban metropolis in some 30 years. The city is situated along China’s coastline and famous for tourism. In general, populated areas like Shenzhen create significant pollution (Hu et al. 2013). It is, therefore, useful to study a city like this to gain an insight into soil contamination after rapid development of tourism and other industries. The study aimed to investigate heavy metal concentrations in the surface soil of Shenzhen’s agricultural land. The potential ecological index is used to examine potential hazards to the land. Finally, the possible sources of and changes in heavy metals over the past 20 years are analyzed. The results can provide insights for rapidly developing cities like Shenzhen in controlling heavy metal sources.

Materials and methods

Site description

The chosen study area, Shenzhen (113°52′ to 114°21′ E and 22°27′ to 22°39′ N), is located in the southern part of Guangdong Province, China. Covered by hilly terrain in the southeast and flatlands in the northeast, Shenzhen consists of some 938 km² of agricultural lands within its boundary based on its land use map in 2008 (Fig. 1). Shenzhen’s geography, combined with its typical subtropical oceanic climate, makes it suitable for planting lychee and mango trees. Orchards of these fruits occupy most of Shenzhen’s agricultural lands.

Since the implementation of China’s economic reform and opening policies, Shenzhen has transformed from a small town into a modern city in some 30 years. The present Shenzhen comprises four core districts, namely Futian, Luohu, Nanshan, and Yantian. There are two suburban districts (Bao’an and Longgang) and four new management districts (Guangming, Pingshan, Longhua, and Dapeng). Shenzhen has recorded a fast industrial growth over the last three decades, which resulted from the exponential growth in a number of manufacturing plants and enterprises. A progressively complex and dense road network is developed to meet the fast-paced development. The rapid industrialization, together with the growing tourism industry, leads to traffic pollution and significantly reduces the quantity and quality of agricultural lands. These factors are considered the major sources of heavy metals in the study area (Velea et al. 2009; Paoli et al. 2013).

Fig. 1 Study area
Field sampling and analysis

The land use map of 2008 of Shenzhen was divided into 8×8 km grids with ArcGIS 10.1 (ESRI, New York, USA) prior to soil sampling. Subsequently, the map was used to predesign sampling numbers and possible locations within each grid (8×8 km grids). Sampling numbers and locations were determined by the area of agricultural land in each grid, which corresponds to the spatial aggregation of agricultural land within the whole city.

A global positioning system (GPS) was used to locate sampling points (Fig. 2). The exact locations, surrounding environment and land use conditions were recorded and photographed comprehensively during sampling. Three to five surface soil (0–20 cm) samples were collected within a distance of 10 m surrounding a specific sampling location and were then mixed. For each location, a total of 1.5 kg of soil was taken from the mixed samples using a quartile method. A total of 82 surface (0–20 cm) soil samples were collected for four types of agricultural land uses (vegetated land, orchard land, woodland, and grassland). Fifty-one of these were collected in March 2009, and 31 were collected in March 2010. Of the samples, 18 represented vegetated land, 32 were orchard land, 23 were woodland, and nine were grassland. The number of samples per district was two in Luohu, one in Futian, five in Nanshan, two in Yantian, nine in Bao’an, and 20 in Longgang. In the new management districts, 10 samples were collected in Guangming, nine in Pingshan, seven in Longhua, and 17 in Dapeng. The sample numbers were positively correlated to the types of agricultural land area within each district.

All 82 soil samples were put into vacuum bags (10×20 cm) with identifiers and taken to the laboratory. They were removed from the vacuum bags and placed on brown papers in enamel trays. All the samples were kept under room temperature from direct exposure to sunlight (lower than 40 °C). After air-drying for 6 weeks, recognizable plant debris, coarse root materials, and stones were removed, crushed, and sieved through 10- and 100-mesh screen sieves. After sieving, about 100 g of each soil sample was taken out and grounded by the machine named Mortar Grinder (Retsch, RM 200). The grounded soil samples were used to determine the chemical properties of the heavy metal components. The remaining soil of each sample was sealed into 1000-ml brown bottles with identifiers in dark places with a temperature lower than 4 °C. These storage conditions could help the concentrations of non-radioactive heavy metals of the soil samples to be permanently stored (HJ T 2004).

For the 2009 samples, all the chemical experiments were carried out by the Institute of Soil Science, Chinese Academy of Science in Nanjing of People’s Republic of China with the measurement standards provided by Environmental Protection Agency of China (1999). Samples were dissolved into a solution mixture of perchloric acid, nitric acid, and hydrofluoric acid (HClO₄–HNO₃–HF) for extraction and wet digestion. The total
concentrations of Cu, Zn, Pb, Ni, and Cr were determined using frame atomic absorption spectroscopy (FAAS), while the total concentration of cadmium (Cd) was determined using graphite furnace atomic absorption spectroscopy (GFAAS).

Ten samples, around 20% of the total samples according to the technical specification for state environmental protection administration (2004), were randomly selected for repeated measurements at a later time to reduce systematic errors. Certified standard samples (G3 and G5) were included at every stage of heavy metal analysis to make sure the data quality.

For the 2010 samples, 0.10**g of each sample was weighed by an analytical balance (0.0001 g). The total concentrations of copper (Cu), zinc (Zn), lead (Pb), nickel (Ni), chromium (Cr), and Cd in the 2010 samples were determined using inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500, Agilent, USA). Microwave digestion method was applied to extract and digest heavy metals with a solution mixture of 8 ml hydrogen peroxide (H$_2$O$_2$) and 4 ml nitric acid (HNO$_3$).

After repeated tests, the suitable steps of microwave digestion for research area’s soils were determined. Firstly, 10 min was used to heat up the digestion solution until it went up to 160 °C, and the temperature had been maintained for the following 5 min. After that, 4 min and 40 s was used to heat up the solution until it went up to 180 °C, and this temperature had been maintained for the next 10 min. Finally, 4 min and 40 s was taken to heat up the solution until it went to 200 °C, and the temperature had been maintained for another 8 min. After cooling, the solutions were accurately diluted to 250 ml with water (after repeated testing), which makes the concentrations of all the six heavy metals in this diluted solution suitable in using ICP-MS. The last step was to use ICP-MS to measure the concentrations of different heavy metals. Certified standard soil sample (G16) was included at every stage.

Six samples, around 20% of the total samples, according to the technical specification for soil environmental monitoring of China (2004) were selected for repeated measurements to reduce systematic errors. Once the relative deviation (RE%) between the two measurements of the same sample including the repeated one was out of range as presented in Table 1, another two measurements would be carried out with the same sample to make sure the group was relatively accurate. Accordingly, another group would be reexamined, and the procedure was repeated until the RE% of the two values met the requirements specified in Table 1.

Two different methods were used to measure the concentrations of Cu, Zn, Pb, Ni, Cr, and Cd in the two years due to the upgrading of experimental instruments in our laboratory. We used ICP-MS for the concentration measurements of the samples in the second year (2010), and did some investigations with reference to journal papers and books to make sure that the results gotten from these two methods can be combined. We detected that both methods were international standards for measuring concentrations of heavy metals with RE% of less than 5% compared to the certified standard samples (Moor et al. 2001; Tüzen 2003; Zhang 2010). Low relative deviations (less than 5%) of the concentration measurements by each method (compared to those of the standard samples) made it possible to consolidate the data of 2 years. Because even with a 5% (RE%) in each method, the maximum RE% between the measurements of the two methods is 5%, which met the requirements shown in Table 1. Table 2 shows a supplementary research that identified RE% for laboratory analysis of Cu, Zn, Pb, Cr, and Cd. The errors were between 0.25 and 4.5%, which met the requirements presented in Table 1 (Wen et al. 2013). For Ni (Table 3), three soil samples which were measured with the method of AAS in 2009 were remeasured (measured on 11th to 12th June, 2015) with the method of ICP-MS. The RE% of two methods were between 3.12 and 8.58% with a concentration range from 0.23 to 0.86, which also met the requirements shown in Table 1.

Heavy metal accumulation is a cumulative process. The effects of contamination are usually not detectable in the two consecutive years unless the soil is contaminated with an extremely high concentration of pollutants. Through an investigation of the relative news, Shenzhen statistical yearbooks (2009–2010) about the industries and websites$^1$ of the contaminative factories in Shenzhen, this trend was not observed. Therefore, it was reasonable to combine the data from 2009 and 2010.

### Potential ecological risk assessment

The potential ecological risk index is an effective, quantitative method in calculating the potential ecological risk of heavy metals in soil (Hakanson 1980). This method considers both

---

$^1$ http://ny.atobo.com.cn/Companys/s-p8-s135-k58885/, http://gsxt.saic.gov.cn/xwqy/mirco/info_detail?organId=100000&infoId=000000004e2d7ef8014e2ee4e9700002

---

| Table 1 | Relative deviation (RE%) requirements of measurements |
|---------|--------------------------------------------------|
| Content range (mg/kg) | ΔC>100 | 10<ΔC≤100 | 1.0<ΔC≤10 | 0.1<ΔC≤1.0 | ΔC≤0.1 |
| Relative deviation (RE%) | ±5 | ±10 | ±20 | ±25 | ±30 |

Note: $RE\% = \frac{|x_i - \bar{r}|}{\bar{r}}$, where $x_i$ is a single measurement value and $\bar{r}$ is the average measurement value of the two measurements. $|x_i - \bar{r}|$ is the absolute value of the difference between the a single measurement value and the average measurement value. $\Delta C$ is the content range of the two measurements.

Source: The technical specification for soil environmental monitoring (HJ/T166-2004) (H J T 2004)
concentrations of heavy metals and ecological factors, thus determining potential ecological risk more accurately. The potential ecological risk index can be calculated using the following equations (Hakanson 1980):

\[ c_i^f = \frac{c_i}{c_{0i}} \]

\[ E_r = T_r \times c_i^f \]

\[ RI = \sum E_r = \sum T_r \times c_i^f = \sum T_r \times \left( \frac{c_i}{c_{0i}} \right) \]

where \( i \) is the topsoil sampling site number and \( r \) indicates the heavy metal. For this study, \( i \) ranges from 1 to 82.

**Table 2** The relative deviation (RE%) between AAS and ICP-MS for laboratory analysis of Cu, Zn, Pb, Cr, and Cd

| Items       | Methods | Cu  | Pb  | Zn  | Cd  | Cr  |
|-------------|---------|-----|-----|-----|-----|-----|
| Sample 1    | AAS     | 69.43| 122.78| 325.44| 8.68| 50.49|
|             | ICP-MS  | 70.30| 120.30| 321.50| 8.79| 48.90|
|             | \( \Delta C \) | 0.43| 1.24| 1.97| 0.05| 0.80|
|             | Average | 69.87| 121.54| 323.47| 8.74| 49.70|
| Relative deviation (%) | 0.62| 1.02| 0.61| 0.63| 1.60|
| Sample 2    | AAS     | 125.58| 215.56| 356.25| 12.50| 78.20|
|             | ICP-MS  | 132.20| 214.50| 325.60| 13.20| 80.20|
|             | \( \Delta C \) | 3.31| 0.53| 15.33| 0.35| 1.00|
|             | Average | 128.89| 215.03| 340.93| 12.85| 79.20|
| Relative deviation (%) | 2.57| 0.25| 4.50| 2.72| 1.26|
| Sample 3    | AAS     | 66.42| 136.48| 280.56| 8.47| 50.84|
|             | ICP-MS  | 65.50| 135.50| 275.80| 8.58| 48.50|
|             | \( \Delta C \) | 0.46| 0.49| 2.38| 0.05| 1.17|
|             | Average | 65.96| 135.99| 278.18| 8.53| 49.67|
| Relative deviation (%) | 0.70| 0.36| 0.86| 0.65| 2.36|

Note: \( RE(\%) = \frac{|x_i - \bar{x}|}{\bar{x}} \times 100 \), where \( x_i \) is a single measurement value and \( \bar{x} \) is the average measurement value of the two measurements. \( |x_i - \bar{x}| \) is the absolute value of the difference between the a single measurement value and the average measurement value. \( \Delta C \) is the content range of the two measurements. Source: adapted from Wen et al. (2013)

c\(_i^f\) is the contamination factor which is calculated by the ratio of the measured concentration of a single heavy metal (\( c_i^f \)) to the standard preindustrial reference level of heavy metal (\( c_{0i} \)). For this study, the values provided by Tao (1990) in the 1980s were used as the standard preindustrial reference level of heavy metal (element background values).

\( E_r \) (Hakanson 1980; Zheng et al. 2009; Amuno 2013) is the potential ecological risk factor for a single heavy metal. It is calculated by multiplying the toxic-response factor \( T_r \) to the contamination factor (\( c_i^f \)). \( E_r \) has five levels (very low, low, moderate, high, and very high). \( T_r \) is the toxic-response factor for a single heavy metal. Based on Hakanson (1980), the \( T_r \) of Cu, Zn, Pb, Ni, Cr, and Cd was \( T_{Cd} = 30 > T_{Cu} = T_{Pb} = 5 > T_{Ni} = 5 > T_{Cr} = 2 > T_{Zn} = 1 \).

\( RI \) (Hakanson 1980; Zheng et al. 2009; Amuno 2013) is the potential ecological risk factor for multiple metals. It is an integrated value of several contaminants and includes four levels (low, moderate, considerable, and high). The

**Table 3** The relative deviation (RE%) between AAS and ICP-MS for laboratory analysis of Ni

| Sample Items | Methods | Sample 1 | Sample 2 | Sample 3 |
|--------------|---------|----------|----------|----------|
| Ni           | AAS     | 3.44     | 2.61     | 26.59    |
|              | ICP-MS  | 3.90     | 3.10     | 28.30    |
|              | \( \Delta C \) | 0.23| 0.25| 0.86|
|              | Average | 3.67| 2.86| 27.45|
| Relative deviation (%) | 6.27| 8.58| 3.12|

Note: \( RE(\%) = \frac{|x_i - \bar{x}|}{\bar{x}} \times 100 \), where \( x_i \) is a single measurement value and \( \bar{x} \) is the average measurement value of the two measurements. \( |x_i - \bar{x}| \) is the absolute value of the difference between the a single measurement value and the average measurement value. \( \Delta C \) is the content range of the two measurements. Source: author

**Table 4** Classification criteria for the potential ecological risk index

| Ecological risk index | The degree of ecological risk |
|-----------------------|------------------------------|
|                       | Low | Moderate | Considerable | High | Very high |
| \( E_r \)             | <40 | 40–80   | 80–160     | 160–320 | >320 |
| \( RI \)              | <150 | 150–300 | 300–600   | >600    |

Source: adapted from Zhang et al. (2005), Guo et al. (2010), and Zhu et al. (2012)
terminology used to describe the risk factor based on several relevant studies (Zhang et al. 2005; Guo et al. 2010; Zhu et al. 2012), is shown in Table 4.

Principal component analysis

Chemical fractionation studies are usually carried out using univariate procedures (element-to-element or sample-to-sample), but multivariate methods, such as principal component analysis (PCA), can provide further interpretation of results (Jolliffe 2005; Lawless and Heymann 2010). PCA is a data-reduction procedure which aims at providing a simple visualization of the relationships between variables for large or complex datasets (Lawless and Heymann 2010). Many studies have used this method for analyzing the possible sources of heavy metals (e.g., Zhou et al. 2014). Similarly, it was applied in this research to convert a set of possibly correlated heavy metals into a set of values for linearly uncorrelated variables (principal components or PCs) in order to explore the grouping of metals according to their similarities (Jolliffe 2005; Abdi and Williams 2010; Shan et al. 2013). Then, through the grouping results, the possible pollution sources could be determined. In this research, PCA was performed using SPSS 16.0 software.

The first principal component, PC 1, is the linear combination of sample values whose scores have maximum variation. The scores of the second component, PC 2, are uncorrelated with those of PC 1. The third component, PC 3, is defined as the particular linear combination with the maximum variation of those combinations whose scores are uncorrelated with the scores of the first two components. Subsequent components are defined analogously (Pop et al. 2009).

Kriging

Geostatistics was first put forward by Matheron in 1960s based on predecessors’ research (Matheron 1963; Bachi 1999). In its simplest form, geostatistical analysis is a two-step process: (1) defining the degree of autocorrelation among the measured data points, and (2) interpolating values between measured points based on the degree of autocorrelation encountered. Autocorrelation is calculated by means of semivariance. Once spatial or temporal dependency is calculated, the values of points not measured can be interpolated with the known point values based on the semi-variogram parameters and Kriging algorithms (Robertson 1987).

There are eight forms of Kriging algorithms, named ordinary Kriging, simple Kriging, universal Kriging, indicator Kriging, probability Kriging, disjunctive Kriging, co-Kriging, and logistic normal Kriging (Stein 2012). Geographic information system (GIS) is one of the softwares with these Kriging algorithms in the module of its spatial analyst tools. GIS provides the operational environment for data interpolation based on the calculating of semi-variogram with the given sample data (Robertson 1987).

The function of Kriging in GIS is an advanced geostatistical procedure that produces an estimate of the underlying surface (usually assumed to be smooth) with a weighted average of the data. The weights decline with the distance between the point at which the surface is estimated and the locations of the data points. The exact nature of the decline is based on modeling the covariation between data at various spatial locations. Data points and the associated surface at nearby locations are assumed to be more similar to each other than are data points at locations distant from each other (Liu et al. 2006; Martin et al. 2006). The general formula for the interpolator is formed as a weighted sum of the data (Robertson 1987):

$$Z(x_0) = \sum_{i=1}^{N} \lambda_i Z(x_i)$$

where, $Z(x_0)$ is the predicated value based on the measured values at the location $x_0$; $Z(x_i)$ is the measured value at the $i$th

Table 5 Statistical analysis of metal concentrations in Shenzhen’s soil

| Item                      | Cu/mg/kg | Pb/mg/kg | Cd/mg/kg | Zn/mg/kg | Cr/mg/kg | Ni/mg/kg |
|---------------------------|----------|----------|----------|----------|----------|----------|
| Minimum                   | 0.73      | 4.34     | 0.00     | 6.13     | 0.17     | 0.00     |
| Maximum                   | 143.90    | 206.30   | 6.02     | 175      | 181.49   | 49.89    |
| Mean                      | 19.89     | 51.21    | 0.51     | 62.26    | 43.96    | 12.60    |
| Soil element background   | 10.8      | 38.9     | 0.067    | 59.00    | 27.80    | 10.60    |
| Assess standard           | 100       | 100      | 0.3      | 200      | 200      | 60       |
| Median                    | 14.56     | 42.43    | 0.11     | 53.30    | 31.34    | 8.99     |
| Std. deviation            | 20.77     | 33.75    | 1.03     | 38.02    | 42.30    | 11.12    |
| Mean/background            | 1.84      | 1.32     | 7.61     | 1.06     | 1.58     | 1.19     |
| Mean/standard             | 0.20      | 0.51     | 1.70     | 0.31     | 0.22     | 0.21     |

Note: the Grade II Soil Environment Quality Standard (GB15618-1995) was chosen as the assessment standard, and Tao’s (1990) research results on the concentrations of heavy metals in Shenzhen’s topsoil in the 1980s was used to establish background values. Source: author.
location; $\lambda_i$ is an unknown weight for the measured value at the $i$th location; $x_0$ is the prediction location; and $N$ is the number of measured values.

In this research, Kriging was applied to estimate and map of the potential ecological risks of heavy metals in no sampling areas of agricultural land in Shenzhen. How and why to select the specific form of Kriging algorithms from the eight forms is based on the data statistical distribution results, which will be described in detail in the “Results” section of this paper.

**Results**

**Accumulation status of heavy metals in agricultural topsoil**

Descriptive statistics for heavy metal concentrations in agricultural topsoil are presented in Table 5. The average concentrations of Cu, Pb, Cd, Zn, Cr, and Ni in the research area were 19.89, 51.21, 0.51, 62.26, 43.96, and 12.60 mg/kg, respectively. In this research, randomly selected soil samples and standard soil samples were used to control results of chemical analysis. Therefore, the average concentrations were the mean of the 82 soil samples’ values for each heavy metal. The Grade II Soil Environment Quality Standard (GB15618-1995) was chosen as the assessment standard, and Tao’s (1990) research results on the concentrations of heavy metals in Shenzhen’s topsoil in the 1980s was used to establish background values.

From the statistical results, most soil samples were low in heavy metal accumulation compared with the study standard, except in the case of Cd, the mean concentration of which was 1.70 times the assessed standard. The concentrations of all six heavy metals, however, were higher than their background values. Specifically, the mean concentrations of Cu, Pb, Cd, Zn, Cr, and Ni were 1.84, 1.32, 7.61, 1.06, 1.58, and 1.19 times their background values, respectively. The results indicate that these six heavy metals accumulated to a degree, but not to serious levels, in Shenzhen agricultural topsoil.

**Potential ecological risk of heavy metals in soil**

The results of potential ecological risk and risk levels for heavy metals in different districts of Shenzhen are shown in Table 6. The spatial distribution of the potential ecological risk of multiple metals ($RI$) was determined using ArcGIS 10.1 and is shown in Fig. 3.

According to the results for the individual contamination factor ($E_i$), most heavy metals presented little potential ecological risk, with the exception of Cd. In some districts of Shenzhen, potential ecological risk levels of

| Sampling area risk level | $E_i$ | Zn | Cr | Ni | Cd | Pb |
|--------------------------|------|----|----|----|----|----|
| Luohu                    | 4.99 | 0.96 | 5.26 | 8.70 | 10.31 | 4.37 | 34.58 |
| Risk level               | Low  | Low | Low | Low | Low | Low |
| Futian                   | 5.18 | 1.40 | 2.26 | 7.39 | 3.20 | 7.24 | 26.67 |
| Risk level               | Low  | Low | Low | Low | Low | Low |
| Nanshan                  | 2.18 | 0.72 | 0.25 | 1.00 | 32.88 | 6.95 | 43.99 |
| Risk level               | Low  | Low | Low | Low | Low | Low |
| Yantian                  | 2.87 | 0.36 | 0.23 | 0.90 | 13.90 | 3.25 | 21.51 |
| Risk level               | Low  | Low | Low | Low | Low | Low |
| Bao’an                   | 17.90 | 1.20 | 2.09 | 5.61 | 57.54 | 6.06 | 90.39 |
| Risk level               | Low  | Low | Low | Moderate | Low | Low |
| Longgang                 | 12.60 | 1.12 | 5.54 | 8.80 | 322.56 | 6.80 | 356.92 |
| Risk level               | Low  | Low | Low | Very high | Low | Considerable |
| Guangming                | 11.41 | 1.20 | 3.54 | 7.44 | 88.68 | 8.23 | 120.50 |
| Risk level               | Low  | Low | Low | Considerable | Low | Low |
| Longhua                  | 5.25 | 0.65 | 3.46 | 5.72 | 254.31 | 6.16 | 275.55 |
| Risk level               | Low  | Low | Low | Low | High | Low | Moderate |
| Pingshan                 | 6.79 | 1.17 | 2.37 | 4.55 | 461.03 | 5.78 | 469.57 |
| Risk level               | Low  | Low | Low | Very high | Low | Considerable |
| Dapeng                   | 5.86 | 1.12 | 1.66 | 4.15 | 302.00 | 6.72 | 321.51 |
| Risk level               | Low  | Low | Low | High | Low | Considerable |

Source: author
Cd reached moderate, considerable, high, and in some places, even the very high level. Therefore, compared with other heavy metals, the potential accumulation risk of Cd was relatively remarkable. The sampling sites with such high values were mainly located in the industrial districts of Bao’an, Longgang, Longhua, Pingshan, and Dapeng, which have traditional and high-tech industries (Fig. 4).

Fig. 3 Spatial distribution of RI values of heavy metals in Shenzhen’s agricultural topsoil

Fig. 4 Spatial distribution of industrial parks and road networks in Shenzhen
In terms of the potential ecological risk factor of multiple metals (RI), six of the 10 districts in Shenzhen were within the level of low potential risk. The other four districts exhibited potential risk of multiple metals to a degree, with a relatively low RI value of 275.55 (moderate) in Longhua and a relatively high RI value of 480.99 (considerable) in Pingshan. The spatial distribution of districts with high RI values was consistent with that of traditional and high-tech industries in Shenzhen, also displayed in Fig. 4. Predictably, the RI values exhibited a similar trend of change with the $E_{Cd}$ values of different districts, demonstrating that the dominant contaminant in the research area was the heavy metal Cd. Based on these results, this metal should receive attention from governmental decision-makers considering its high concentrations and the associated future potential ecological risk.

Table 7 Statistics for 82 RI values of soil samples in Shenzhen’s agricultural topsoil

| Statistics                  | Value |
|------------------------------|-------|
| N valid                      | 82    |
| Missing                      | 0     |
| Skewness                     | 3.223 |
| Std. error of skewness       | 0.266 |
| Kurtosis                     | 11.691|
| Std. error of kurtosis       | 0.526 |

Source: author

The heavy metals’ RI values within the entire agricultural land of Shenzhen were mapped using the Kriging method (ArcGIS) based on the results from the 82 sample sites. Data and its distribution (normal or non-normal distribution) are essential for choosing the specific form of Kriging algorithms to do the spatial distribution estimation. From the statistical results (skewness value and kurtosis value) of 82 samples’ RI values presented in Table 7, the statistic distribution of 82 RI values does not belong to the normal distribution (skewness ≠ 0 and kurtosis ≠ 0). Therefore, indicator Kriging can be applied to do the spatial distribution prediction for its operation does not need the original data to obey the normal distribution. Therefore, the heavy metals’ RI values were mapped using the indicator Kriging method with ArcGIS 10.1 based on the results from the 82 sample sites. The spatial distribution result, as shown in Fig. 3, indicates some degree of potential ecological risk for most agricultural land in Shenzhen, especially in the northern part of Longgang and the new districts of Pingshan, Longhua, and Dapeng. For these districts, the potential risks have reached the considerable level (RI>300), and in some places, including the northern parts of Longgang and the western part of Dapeng New District, they have even reached the high level (RI>600). Examining the spatial distribution of Shenzhen’s industrial parks and main road networks (Fig. 4), high potential risks were generally found to be concentrated around overlapping regions with developed industries.
traditional and high-tech industries and places with dense road networks.

From the interpolation of results within the city, Dapeng New District was an area clearly requiring attention. This district is almost entirely made up of agricultural land and is known for its beautiful coast with many tourist attractions. An initial assumption of this district would be that it contains less pollution with greater natural beauty. However, this area actually exhibited a relatively high potential risk for heavy metals in its agricultural land. Excluding any interpolation errors, most samples from Dapeng had high measured values of heavy metals, especially Cd, Pb, and Zn. From the detailed enlarged-scale map of this district and its industries (Fig. 5), it is clear that the area serves as an important electronic equipment and chemical base in Shenzhen. In addition, there are several special industries, including the Daya Bay Nuclear Power Station and liquefied natural gas (LNG) factories. There are also three terminals in this district: Chengjiaotou liquefied natural gas (LNG) port, heavy cargo terminal, and the Shenzhen Moon Bay yacht public terminal for tourism. Tankers coming to the ports and vehicles brought by tourism represent potential hazardous sources of heavy metals in this area.

Source analysis of heavy metals in agricultural topsoil

PCA (performed in SPSS 16.0) was applied to the collection of data listed in Table 8 to explore possible similarities in the behavior of the six metals. In this study, PCA was conducted using the covariance matrix with pure concentration data (82 samples) of different heavy metals. The obtained factors were rotated using a varimax normalized algorithm, which allows for easier interpretation of the principal component loadings and maximization of the variance explained by the extracted factors (Maiz et al. 2000; Wang et al. 2005). Based on similar research, 80 % or over 80 % was chosen as a constraint of dimensionality reduction to group the possible sources of heavy metals in topsoil. Finally, three factors, accounting for 81.58 % of total variation and with three eigenvalues higher than 0.9 (before and after rotation), were achieved with the extracted results (Table 8). According to the rotated results of PCA (Table 9), the original variables (six heavy metals) could be reduced to three components (PC1, PC2, and PC3).

The three principal components were extracted, together explaining approximately 81.58 % (PC1: 35.29 %, PC2: 28.86 %, and PC3: 17.43 %) of the variance in the information contained in the initial variables. As shown in Tables 8 and 9, Cu, Cr, and Ni were mainly distributed in PC1; Pb and Zn were mainly in PC2; and Cd was mainly in PC3.

PC1 was characterized by high levels of Cu, Cr, and Ni. Based on field surveys and data collection (Cheng 2003; Zheng et al. 2009; Xie et al. 2010), the spatial heterogeneity of Cu, Cr, and Ni in this research area is affected by structural factors, such as parent materials and soil type, and these heavy metals share a strong environmental geochemistry engineering relationship.

PC2 was characterized by high levels of Pb and Zn. Pb and Zn are reduced to the same component, which suggests that they may have similar pollution sources. According to

| Component | Initial eigenvalues | Extraction sums of squared loadings | Rotation sums of squared loadings |
|-----------|---------------------|-----------------------------------|---------------------------------|
|           | Total               | % of variance | Cumulative % | Total               | % of variance | Cumulative % | Total               | % of variance | Cumulative % |
| 1         | 2.55                | 42.45       | 42.45        | 2.55                | 42.45        | 42.45        | 2.12                | 35.28        | 35.29        |
| 2         | 1.39                | 23.21       | 65.66        | 1.39                | 23.21        | 65.66        | 1.73                | 28.86        | 64.15        |
| 3         | 0.96                | 15.92       | 81.58        | 0.96                | 15.92        | 81.58        | 1.05                | 17.43        | 81.58        |
| 4         | 0.63                | 10.57       | 92.13        |                     |              |              |                     |              |              |
| 5         | 0.33                | 5.43        | 97.57        |                     |              |              |                     |              |              |
| 6         | 0.15                | 2.43        | 100.00       |                     |              |              |                     |              |              |

Extraction method: principal component analysis. Source: author
previous studies on the possible sources of these two heavy metals, both can be attributed to traffic pollution (Day et al. 1975; Miguel et al. 1997; Jiries et al. 2001; Zanders 2005; Paoli et al. 2013). Pb has long been linked primarily to traffic activities due to the utilization of leaded gasoline (Day et al. 1975; Paoli et al. 2013). Additionally, traffic activities also contribute to the concentration of Zn in soil. It has been reported that tire wear contributes significantly to Zn in the agricultural topsoil in cities (Zanders 2005). According to Jiries et al. (2001), Zn may be derived from the mechanical abrasion of vehicles; thus, Zn in Shenzhen agricultural topsoil may be related, in part, to vehicular movement. Zn compounds have also been employed extensively as antioxidants (e.g., zinc carboxylate complexes and zinc sulphonates) and as detergent/dispersant improvers for lubricating oils (Miguel et al. 1997). Thus, PC1 mainly comprises the heavy metals from traffic pollution, offering an explanation for why the overlapped regions with developed industries and dense road networks are more seriously polluted by heavy metals. Furthermore, ports with tankers and tourism resulting in more vehicles in Dapeng New District are also potential sources of Pb and Zn accumulation. Although Pb and Zn pollution in Shenzhen has not yet exhibited a high level of potential risk, based on the descriptive statistics of heavy metal concentrations, these metals have accumulated to some degree compared with their background values. Accordingly, they should be monitored, and their sources should be regulated.

PC2 is characterized by a high level of Cd. Cd usually comes from industrial activity, especially battery industries (Velea et al. 2009). The mean concentration of Cd was higher than its background value in Shenzhen during the 1980s, and its ECd values and RI values also indicated a very high potential ecological risk. The concentration of Cd has been greatly influenced by human activity since the 1980s. Based on photos, descriptions, and GPS information recorded during sampling, the samples with higher ECd values were mainly collected in Dapeng New District and along the boundary between Longgang and the city of Huizhou. This area is located near factories, including auto centers, circuit plants, LNG receiving stations, power plants, and chemical plants. From the spatial distribution of Cd, we can conclude that most of this contaminant was due to the atmospheric deposition of heavy metals by these plants.

Changes in pollution sources over a 20-year period

In the late 1980s, after considering the main parent materials, types, and spatial distribution of soil in Shenzhen, Tao (1990) set up 83 different sites in the city, taking into account topography, vegetation, transport conditions, and other factors. PCA was used to analyze the sources of heavy metal accumulation. The results indicated that such accumulation in agricultural soil was mainly due to rock weathering, leaching, and a series of geochemical processes occurring naturally in the soil without human disturbance. However, with rapid urbanization over the past 20 years, heavy metal accumulation is now more attributable to human activities. The current main accumulation sources are traditional and high-tech industries, transportation, and industries that involve an increase in vehicular travel, such as tourism.

Conclusions and discussion

Through the use of different techniques, this study attempted to describe the problem of agricultural topsoil contamination with heavy metals, the resulting potential ecological risks, and the sources of change in contamination levels. The study, importantly, offers a quantitative assessment of the potential contamination status of heavy metals in topsoil, which may be applied to or replicated in other contexts.

In this research, the case city of Shenzhen exhibited some degradation in soil quality in terms of the accumulation of heavy metals. Specifically, results indicated that Shenzhen’s soils, particularly the surface topsoil, are now more enriched with six heavy metals (Cu, Zn, Pb, Ni, Cd, and Cr) than in the past. Fortunately, most heavy metals’ concentrations have not reached the Grade II Soil Environment Quality Standard, except in the case of Cd, indicating that, in most agricultural areas of Shenzhen, the soil’s environmental quality is under control and suitable for agricultural use. The heavy metal Cd does require attention, as it has seriously accumulated in the agricultural topsoil in Shenzhen.

From the results of the potential ecological risks analysis, Cd presents quite a high potential ecological risk for Shenzhen, especially in the industrial districts of Bao’an, Longgang, Longhua, Pingshan, and Dapeng, which have concentrated traditional and high-tech industries. From the interpolation results of the entire city’s potential ecological risk values, overall heavy metal concentrations or enrichment may pose low potential ecological risk, except in the northern parts of Longgang and the western part of Dapeng New District near the chemical plants, such as LNG stations, power plants, and electronics production plants. The dominant contributor to this potential risk is the heavy metal Cd, whose sources should be urgently regulated.

This research also aimed to determine the sources of different types of heavy metals in Shenzhen’s agricultural topsoil. The PCA analysis results determined the three main sources of heavy metal accumulation in Shenzhen agricultural topsoil: geochemical processes, industrial pollutants, and traffic pollution. Since the 1980s, the sources of heavy metals have evolved from parent rock weathering, erosion, degradation of organics, and mineralization to industrial and traffic pollution. These changes have been caused by industrial and
traffic pollution, as well as the development of traditional and high-tech industries and tourism.

However, due to the limited number of samples collected, it may not be possible to determine completely the exact sources of different heavy metals in topsoil at this stage. Therefore, the next steps should involve selecting additional accurate methods for the determination of the exact sources. Furthermore, this study does not clearly highlight the necessity of immediate control measures for the exceptionally severe heavy metal accumulation in the study area, which is another future task of our work.

Acknowledgments The work described in this paper was financially supported by the National Natural Science Foundation of China (41271101) with the title, “The ecological effects of the dynamics of landscape patterns and the landscape multifunction in coastal area—a case study of Shenzhen city.” We thank Priscilla Lynne Young (senior lecturer in Peking University HSBC Business School), and a native speaker and professional editor at Editage, a division of Cactus Communications for reading an earlier draft of this article and for their many helpful suggestions.

Conflict of interest We declare that we have no financial or personal relationships with other people or organizations that could inappropriately influence our work, and there is no professional or other personal interest of any nature or kind in any product, service, and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled “The accumulation of heavy metals in agricultural land and the associated potential ecological risks in Shenzhen, China”.

References

Abdi H, Williams LJ (2010) Principal component analysis. Wiley Interdiscip Rev Comput Stat 2:433–459. doi:10.1002/wics.101
Amuno S (2013) Potential ecological risk of heavy metal distribution in cemetery soils. Water Air Soil Pollut 224:1–12. doi:10.1007/s11270-013-1435-2
Angelone M, Udovic M (2014) Potentially harmful elements in urban soils. PHEs, Environ Hum Health 221–251. doi:10.1007/978-94-017-9865-3_6
Aymuh S, Catimon M, Boudouma O et al (2013) Street dust: source and sink of heavy metals to urban environment. Paper presented at the EJS Web of Conferences. doi:10.1051/e3conf/20130120001
Bachi R (1999) New methods of geostatistical analysis and graphical presentation: distributions of populations over territories. Springer Science & Business Media
Cheng S-P (2003) Heavy metal pollution in China: origin, pattern and control. Environ Sci Pollut Res 10:192–198. doi:10.1065/espr.2002.11.141.1
Day J, Hart M, Robinson M (1975) Lead in urban street dust. Nature 253:343–345. doi:10.1038/253343a0
Environmental Protection Agency of China (1999) Monitoring and analytical methods of environment. Chinese Environ. Sci. Press, Beijing (in Chinese)
Facchinelli A, Sacchi E, Mallen L (2001) Multivariate statistical and GIS-based approach to identify heavy metal sources in soils. Environ Pollut 114:313–324. doi:10.1016/S0269-7491(00)00243-8
Guo W-H, Liu X-B, Liu Z-G et al (2010) Pollution and potential ecological risk evaluation of heavy metals in the sediments around Dongjiang Harbor, Tianjin. Procedia Environ Sci 2:729–736. doi:10.1016/j.proenv.2010.01.084
Hakanson L (1980) An ecological risk index for aquatic pollution control—a sedimentological approach. Water Res 14:975–1001. doi:10.1016/0043-1354(80)90143-8
Hu B-Q, Li G-G, Li J et al (2013) Spatial distribution and ecotoxicological risk assessment of heavy metals in surface sediments of the southern Bohai Bay, China. Environ Sci Pollut Res 20:4099–4110. doi:10.1007/s11356-012-1332-z
Huang X-P, Li X-D, Yue W-Z et al (2003) Accumulation of heavy metals in the sediments of Shenzhen Bay, south China. Environ Sci 24:144–149 (in Chinese)
Huang J-M, Huang R-Q, Jiao J-J et al (2007) Speciation and mobility of heavy metals in mud in coastal reclamation areas in Shenzhen, China. Environ Geol 53:221–228. doi:10.1007/s00254-007-0636-7
Jackson RB, Manwaring JH, Caldwell MM (1990) Rapid physiological adjustment of roots to localized soil enrichment. Nature 344:58–60. doi:10.1038/344058a0
Jiries AG, Hussein HH, Halaseh Z (2001) The quality of water and sediments of street runoff in Amman, Jordan. Hydrol Process 15:815–824. doi:10.1002/hyp.186
Jolliffe IT (2005) Principal component analysis, 2nd edn. Springer, New York
Khan S, Cao Q, Zheng Y-M et al (2008) Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. Environ Pollut 152:686–692. doi:10.1016/j.envpol.2007.06.056
Lawless HT, Heymann H (2010) Data relationships and multivariate applications. In: Lawless HT (ed) Sensory Evaluation of Food. Principles and practices. Chapman & Hall, New York, pp 433–449
Li X, Poon C, Liu P-S (2001) Heavy metal contamination of urban soils and street dusts in Hong Kong. Appl Geochem 16:1361–1368. doi:10.1016/S0883-2927(01)00045-2
Liu X-M, Wu J-J, Xu J-M (2006) Characterizing the risk assessment of heavy metals and sampling uncertainty analysis in paddy fields by geostatistics and GIS. Environ Pollut 141:257–264. doi:10.1016/j.envpol.2005.08.048
Maiz I, Arambbarri I, Garcia R et al (2000) Evaluation of heavy metal availability in polluted soils by two sequential extraction procedures using factor analysis. Environ Pollut 110:3–9. doi:10.1016/S0269-7491(99)00287-0
Martin JAR, Arias ML, Corbi JMG (2006) Heavy metals contents in agricultural topsoils in the Ebro basin (Spain). Application of the multivariate geostatistical methods to study spatial variations. Environ Pollut 144:1001–1012. doi:10.1016/j.envpol.2006.01.045
Matheron G (1963) Principles of geostatistics. Econ Geol 58:1246–1266. doi:10.2113/gsecongeo.58.8.1246
Miguel E, Llamas JF, Chacón E et al (1997) Origin and patterns of distribution of trace elements in street dust: unleaded petrol and urban lead. Atmos Environ 31:2743–2740. doi:10.1016/S0010-0753(97)00101-5
Moore C, Lymberopoulou T, Dietrich JV (2001) Determination of heavy metals in soils, sediments and geological materials by ICP-AES and ICP-MS. Microchim Acta 136:123–128. doi:10.1007/s006040170041
Paoli L, Munzi S, Fiorini E et al (2013) Influence of angular exposure and proximity to vehicular traffic on the diversity of epiphytic lichens and the bioaccumulation of traffic-related elements. Environ Sci Pollut Res 20:250–259. doi:10.1007/s11356-012-0893-1
Pop HF, Einaix JW, Sárbus C (2009) Classical and fuzzy principal component analysis of some environmental samples concerning the
pollution with heavy metals. Chemom Intell Lab Syst 97:25–32. doi:10.1016/j.chemolab.2008.06.006

Rattan RK, Datta SP, Chhonkar PK et al (2005) Long-term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater—a case study. Agric Ecosyst Environ 109:310–322. doi:10.1016/j.agee.2005.02.025

Robertson GP (1987) Geostatistics in ecology: interpolating with known variance. Ecology 68:744–748. doi:10.2307/1938482

Rota E, Caruso T, Monaci F et al (2013) Effects of soil pollutants, biogeochemistry and microbiology on the distribution and composition of enchytraeid communities in urban and suburban holm oak stands. Environ Pollut 179:268–276. doi:10.1016/j.envpol.2013.04.026

Shan Y, Tysklind M, Hao F et al (2013) Identification of sources of heavy metals in agricultural soils using multivariate analysis and GIS. J Soils Sediments 13:720–729. doi:10.1007/s11368-012-0637-3

Sheng J-J, Wang X-P, Gong P et al (2012) Heavy metals of the Tibetan top soils. Environ Sci Pollut Res 19:3362–3370. doi:10.1007/s11356-012-0857-5

State Environmental Protection Administration (2004) The technical specification for soil environmental monitoring. Beijing, China (in Chinese)

Stein M L (2012) Interpolation of spatial data: some theory for kriging: Springer Science & Business Media

Tao S (1990) Trace element contents in soils from Shenzhen. Chinese EPA Report, China pp 75–60 (in Chinese)

Tüzen M (2003) Determination of heavy metals in fish samples of the middle Black Sea (Turkey) by graphite furnace atomic absorption spectrometry. Food Chem 80:119–123. doi:10.1016/S0308-8146(02)00264-9

Velea T, Gherghıţ L, Predica V et al (2009) Heavy metal contamination in the vicinity of an industrial area near Bucharest. Environ Sci Pollut Res 16:27–32. doi:10.1007/s11356-008-0073-5

Wang X-S, Qin Y, Sang S-X (2005) Accumulation and sources of heavy metals in urban topsoils: a case study from the city of Xuzhou, China. Environ Geol 48:101–107. doi:10.1007/s00254-005-1270-x

Wei B-G, Yang L-S (2010) A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. Microchem J 94:99–107. doi:10.1016/j.microc.2009.09.014

Wen X-Y, Hu H, Hao X et al (2013) Comparison study on determination of heavy metals in soil. 2013 Chinese environmental science annual conference symposium (the fourth volume), 2079–2081 (in Chinese)

Winner RW, Boesel MW, Farrell MP (1980) Insect community structure as an index of heavy-metal pollution in lotic ecosystems. Can J Fish Aquat Sci 37:647–655. doi:10.1139/f80-081

Xie J, Wu J-S, Zheng M-K et al (2010) Evaluation of the heavy metal pollution in different agricultural soils of Shenzhen City. Asian J Ecotoxicol 5:202–207 (in Chinese)

Zanders JM (2005) Road sediment: characterization and implications for the performance of vegetated strips for treating road run-off. Sci Total Environ 339:41–47. doi:10.1016/j.scitotenv.2004.07.023

Zhang F (2010) An approach to the method for determination of heavy metal contents in soil. Shanghai Environ Sci 02:74–77 (in Chinese)

Zhang L-X, Ren S, Cai J (2005) Enrichment of heavy metals in the surface sediments from the three regions of random dumping in East China Sea and assessment of their potential ecological risk. Mar Sci Bull 24:92–96 (in Chinese)

Zhang H-L, Chen Y-H, Qi J-Y et al (2013) Characterization of heavy metals in the surrounding of Municipal Solid Waste Incinerator (MSWI) and health risks assessment via inhalation in Shenzhen Nanshan, China. Adv Mater Res 790:425–428 (in Chinese)

Zheng M-K, Xie J, Wang Y-L et al (2009) Heavy metal accumulation characters and risk assessment in the soil of agriculture and forest of shenzhen area. Asian J Ecotoxicol 4:726–733 (in Chinese)

Zhou L-L, Yang B, Xue N-D et al (2014) Ecological risks and potential sources of heavy metals in agricultural soils from Huanghuai Plain, China. Environ Sci Pollut Res 21:1360–1369. doi:10.1007/s11356-013-2023-0

Zhu H-N, Yuan X-Z, Zeng G-M et al (2012) Ecological risk assessment of heavy metals in sediments of Xiawan Port based on modified potential ecological risk index. Trans Nonferrous Metals Soc China 22:1470–1477. doi:10.1016/S1003-6326(11)61343-5