Spatial Distribution Characteristic and Assessment of Total and Available Heavy Metals in Karst Peri-Urban Vegetable Soil

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Abstract. The purpose of this study was to investigate the total and available concentration of Cu, Zn, Pb and Cd in the vegetable soil from typical Karst peri-urban and to analysis the spatial distribution characteristic of heavy metal and to assess their potential ecological risk in Guiyang city, southwest China. The mean value of Cu, Zn, Pb and Cd was higher than their background values of Guizhou topsoil and show a certain accumulation phenomenon. Furthermore, the concentration of available Cu, Zn, Pb and Cd were shown moderate spatial variability and had a complex pollution tendency. Based on semivariance function and Kriging's geostatistics, the total and available Cu, Zn, Pb and Cd were essentially showing the pattern of patch-like distribution and high of heavy metal concentration are mainly distributed in southwest of this area. The potential ecological hazard trend is Cd>Pb>Cu>Zn from the average values of the total and availability of heavy metals. According to the current ecological risk assessment, vegetable soil in the peri-urban of the karst area is subjected to the ecological harm of the Cd and should be paid enough attention.

1. Introduction
Karst topography in China are mainly concentrated in the southwest area, where exposed carbonate rock on the surface and distributed many peaks, depression, stone, basin, valley, ditch, cave and buried river, so the ecological environment is very fragile[1]. Guizhou is a typical karst province where has shallow and poor soil and less available land, due to topography and soil parent material, the background values of Pb, Cd, Zn, Mn, Ni and As is usually higher than other soil parent of development[2]. In addition, high temperature and rainy climatic characteristics and complex spatial hydrological systems have also provided favorable conditions for the migration and diffusion of heavy metals[3]. Compared with the non-karst area, the heavy metal pollution in the karst area is characterized by small capacity and flexible migration (mainly refers to the migration of the surface and groundwater), which is widespread and difficult to control. As a result, the agricultural productivity of the karst mountainous soil is seriously affected.

A large urban population of cities had led to a rapid expansion of the peri-urban interface, where domestic and industrial modifications of the environment interact strongly with agricultural production[4]. Vegetable production in the areas is now a key sector of the regional agricultural economy.
However, the large urban population generates a lot of waste, some of which is applied to surrounding lands, and the intensive year round peri-urban vegetable production creates pressures to use large quantities of organic wastes, fertilizers, pesticides and contaminated irrigation water. In addition, many factories are being constructed in peri-urban areas or relocated from inner cities, posing a high risk of industrial pollution of water and air that may have a direct impact on public health as well as their effects via vegetable production.

In the past, the study of suburban soil was only a statistical analysis of the limited individual soil sample data, and the results reflect the discrete distribution and cannot establish the concept of regional continuity\textsuperscript{[5]}. Based on semivariance function and Kriging's geostatistics, the optimal linear unbiased estimation of the regional variables in the finite region can be obtained\textsuperscript{[6]}. Therefore, it has been widely used in soil science research, but it has little application in heavy metal of suburban soil at karst area. Moreover, the available metals are more active in the soil and their contents determines their bioavailability and environmental risk, furthermore, the proportion of the total metal can better reflect the harmful effects of pollutants on crops\textsuperscript{[7]}. Therefore, it is more practical to study the spatial distribution of soil heavy metal and its pollution risk assessment.

Therefore, we selected the typical karst area, Guiyang Huaxi District, as the research object. 1) Using geostatistics and GIS spatial analysis tools to achieve the expansion from point to surface, and study on the spatial distribution of total and available heavy metals from the regional perspective. 2) To reveal the state quo of total and available metals in karst peri-urban and to carry out potential ecological risk assessment in order to provide a reference for the karst peri-urban agricultural safety protection and production.

2. Materials and methods

2.1. Description of the study area

Huaxi district is located in south of Guiyang city, Guizhou province, southwest of China (26°11'-26°34’N,106°27'-106°52’E). This area experiences a subtropical monsoon climate, with an annual rainfall of 1178.3 mm and an annual average temperature of 14.9℃. The annual sunshine time is about 1278 h, and the frost-free period is about 270 d. The prevailing wind direction is from the southwest to the northeast throughout the year, and there is an annual average wind speed of 17m/s. The soil types mainly include yellow and calcareous soil and the average depth is about 0.8 m to 1.2 m. The vegetable planting area and yield in huaxi district of were about 1570 ha and 0.56 million tons, occupying 26% of total vegetable production of Guiyang city, and these vegetable crops are mainly produced for home consumption and sale to residential areas of urban and suburban regions of Guiyang.

![Figure 1. Location map of the study area and sampling sites of peri-urban soil from Guiyang.](image-url)
2.2. Collection and preparation of soil samples
Sixty-two composite vegetable soil samples in this study were collected from each individual vegetable fields covering an area more than 1 hm² for each field in the peri-urban of Huaxi in November 2014 (Figure 1). All vegetable field were regularly fertilized and had been used for vegetable production for over eight years. At each of sites, five repeat soil sub-samples were collected at 0-20 cm using a bamboo shovel, and mixed thoroughly. The coordinates of sample locations were recorded with a hand-held global positioning system (GPS). The samples were air-dried before analysis and sieved through a 2 mm screen, mixed and stored in the mouth-closed polyethylene bags. Sub-samples were further ground with a mortar and a pestle to pass through a 0.15mm sieve and analyzed for characterizing concentration of heavy metals.

2.3. Chemical analysis
Soil samples were digested by with a solution of HNO₃-HCl-HF-HClO₄, and Cu, Zn, Pb and Cd were determined with inductively coupled plasma atomic emission spectrometer (ICP-OES Perkin Elmer, Optima 5300v). Meanwhile, a series of soil standards were used for quality assurance and quality control(QA/QC). The geochemical reference materials were GSS-3 and GSS-4, which supplied by the National Research Center for Certified Reference Materials of China. The recoveries for the 6 observed metals were between 90% and 110% and the deviation ranged within 5%. The blank determinations were also performed in triplicate throughout all the experiments.

EDTA-extractable metals were extracted by shaking 2.5 g of soil with 25 ml of 0.05 mol l⁻¹ EDTA at pH 7 in 50 ml centrifuge tubes for 1 h[8]. Certified materials for EDTA(BCR-700) technique was included in each batch of analytical determinations to check that the analytical procedures were under control. Deviations were within ± 10% of the certified values.

2.4. Potential ecological risk index
Since early 1980, the method of evaluating the potential ecological risk index (RI) has established by the Swedish scholar L.Hakanson that he has evaluated to the heavy metal pollution and ecological risk by using the principle of sedimentation. As one of the methods of soil heavy metal research, this method divides the potential harm degree of heavy metals by quantitative method. This method is calculated using Eq (1):

\[ RI = \sum E_r' = \sum (T_r' \cdot C_r') = \sum (T_r' \cdot \frac{C_m'}{C_n'}) \]  

Where: \( C_s' \) represents the measured value of heavy metals in soil(mg·kg⁻¹); \( C_r' \) is the reference value (mg·kg⁻¹); the soil background value of Guiyang was selected as the reference value; \( T_r' \) represents single pollutant toxicity response parameter, Cd(30)>Cu(5)= Pb(5)>Zn(1). The potential ecological risk index and grading relationship of heavy metals are shown in Table 1.

| Range of potential ecological \( E_r' \) | Degree of single factor ecological risk | Range of potential ecological risk index \( RI \) | Total potential ecological risk level |
|----------------------------------------|----------------------------------------|---------------------------------------------|------------------------------------|
| \( E_r' < 40 \)                        | Low                                    | \( RI < 150 \)                               | Low                                |
| \( 40 \leq E_r' < 80 \)                | Moderate                               | \( 150 \leq RI < 300 \)                      | Moderate                            |
| \( 80 \leq E_r' < 160 \)               | Considerable                           | \( 300 \leq RI < 600 \)                      | Considerable                        |
| \( 160 \leq E_r' < 320 \)              | High                                   | \( RI \geq 600 \)                            | High                                |
| \( E_r' \geq 320 \)                    | Very high                              |                                             |                                    |

2.5. Data analysis
All statistical analysis in this study were performed using SPSS 22.0 software (IBM Inc.). Correlation analysis was performed on normalized data with log-transformation to identify the relationships
between heavy metals. The normalized data were analyzed using Arcgis 10.2 (Esri Inc.). Cokriging interpolation was used to establish the spatial distributions of heavy metals.

3. Results and discussion

3.1. Total and available concentration of heavy metals

The descriptive statistics of total and available metal levels in vegetable soil are summarized in Table 2. Total concentration of Cu, Zn, Pb, Cd and available Pb shows a normal distribution. Available Cu, Zn and Cd were shown a significant positive skew distribution and skew up to 2.04, 3.25 and 2.42, respectively, however, all of them approach a log-normal distribution. When the data satisfy the normal distribution, the arithmetic mean is taken as the mean of the data, on the contrary, the geometric mean is used\(^9\). Therefore, the average contents of Cu, Zn, Pb and Cd were 41.10, 94.65, 65.93 and 0.21 mg·kg\(^{-1}\), respectively, all of them exceeded the natural background value of the study area. The coefficient of variation was between 0.21 and 0.43, indicating that some points still have a certain accumulation phenomenon. The available concentration of Cu, Zn, Pb and Cd had a wider distribution, and the range of available Cu and Zn was 33.64 and 41.64, and the corresponding coefficient of variation was 0.70 and 0.65, respectively. The results showed that available heavy metal also had been in high accumulation situation in this study.

Table 2. Total and available heavy metals concentration in vegetable soils.

| Parameter          | Total concentration/wt (mg·kg\(^{-1}\)) | Available concentration/wt (mg·kg\(^{-1}\)) |
|--------------------|-----------------------------------------|--------------------------------------------|
|                    | Cu \(t\) | Zn \(t\) | Pb \(t\) | Cd \(t\) | Cu \(a\) | Zn \(a\) | Pb \(a\) | Cd \(a\) |
| Minimum            | 13.48    | 37.70   | 35.36   | 0.05    | 1.75     | 0.09     | 1.04     | 0.003    |
| Maximum            | 82.64    | 187.5   | 99.00   | 0.46    | 35.39    | 41.73    | 21.80    | 0.016    |
| Mean               | 41.10\(a\) | 94.65\(a\) | 65.93\(a\) | 0.21\(a\) | 9.57\(b\) | 8.90\(b\) | 11.91\(a\) | 0.006\(b\) |
| SD                 | 16.57    | 35.75   | 13.53   | 0.09    | 6.68     | 5.82     | 4.48     | 0.002    |
| CV                 | 0.40     | 0.38    | 0.21    | 0.43    | 0.70     | 0.65     | 0.38     | 0.33     |
| Kurtosis           | -0.27    | -0.17   | 0.07    | 0.42    | 5.36     | 16.22    | -0.26    | 6.09     |
| Skewness           | 0.42     | 0.71    | 0.12    | 0.81    | 2.04     | 3.25     | 0.17     | 2.42     |
| Distribution pattern | normal | normal | normal | normal | lognormal | lognormal | normal | lognormal |
| Background values \(^1\) | 25.7     | 82.4    | 29.3    | 0.133   | -        | -        | -        | -        |

Note: SD, Standard deviation; CV, Coefficient of variation; K-S, Kolmogorov-smirnov; 1)Background values of heavy metals in the soil of Guiyang

The results of Pearson partial correlation analysis (Table 3) show that the available concentration of Cu, Zn and Pb have a significantly negative correlation with pH(p<0.05). However, the correlation between Cd and pH was not obvious, which indicated that the activity of Cd might be influenced by other factors. There was a significant positive correlation between the total and available Cu, Zn and Pb (p<0.05), indicating that three elements in the study area had a common source and showed a trend of compound pollution.

Table 3. Correlation analysis between total and available heavy metals concentration and pH.

| pH  | Cu \(t\) | Zn \(t\) | Pb \(t\) | Cd \(t\) | Cu \(a\) | Zn \(a\) | Pb \(a\) | Cd \(a\) |
|-----|----------|----------|----------|----------|----------|----------|----------|----------|
|     | 1        | 0.004    | 0.230    | 0.322\(^*\) | -0.085   | -0.293\(^*\) |
| Cu \(t\) | 0.004    | 1        | 0.435\(^**\) | 0.349\(^**\) | -0.060   | -0.335\(^*\) |
| Zn \(t\) | 0.230    | 0.435\(^**\) | 1        | 0.535\(^**\) | 0.084   | -0.122   |
| Pb \(t\) | 0.322\(^*\) | 0.349\(^**\) | 0.535\(^**\) | 1        | -0.171   | -0.080   |
| Cd \(t\) | -0.085   | -0.060   | 0.084    | -0.171   | 1        | -0.067   |
| Cu \(a\) | -0.293\(^*\) | -0.335\(^*\) | -0.122   | -0.080   | -0.067   | 1        |
Zn a $-0.323^*$ $-0.012$ $0.419^*$ $-0.162$ $0.023$ $0.361^*$ $1$

Pb a $-0.281^{**}$ $0.070$ $-0.068$ $0.313^*$ $-0.077$ $0.425^{**}$ $0.320^*$ $1$

Cd a $0.175$ $0.115$ $0.096$ $-0.086$ $0.111$ $-0.162$ $-0.083$ $-0.109$ $1$

Note: ‘*’ and ‘**’ mean that the significance of difference is at 0.05 and 0.01 level, respectively.

3.2. Spatial variability of vegetable soil heavy metal

The spatial variability of soil heavy metal is fitted by semivariance function. In the semivariogram analysis, nugget values represent the variability of measured metal levels at zero distance, which is positive in this study for all heavy metals. The sill, sum of partial sill and nugget, is the maximum variance between data pairs and reflects the variations of regionalized variables in the study area\textsuperscript{[10]}. The ratio of nugget to sill is commonly used to express the spatial autocorrelation of regional variables, which also indicates the predominant factors among the natural and anthropogenic factors\textsuperscript{[11]}. If the ratio is larger than 0.75, it means that the metals in the matrix have a weak spatial autogenic; a strong spatial autocorrelation when less than 0.25, and a ratio indicates the medium spatial autocorrelation ranging from 0.25 to 0.75\textsuperscript{[12]}. This spatial random variance is caused by artificial nature of heavy metal pollution in soil, meaning that anthropogenic input is a significant source of heavy metals in peri-urban area.

According to the principle of the maximum of the coefficient of decision ($R^2$) and the least square sum of the residuals (RSS), the best spatial variation model is selected. The fitting results of the theoretical semivariogram models (Table 4) showed ideal effect that the average RSS of all models is small and the $R^2$ is more than 0.7. The ratio of nugget to sill of total and available Cd is less than 0.25, it shows strong spatial autocorrelation, viz. Dominated by a long-range structure (Table 3). This is related to the high-Cd geological background in the karst area, indicating that its content in the soil is controlled by internal factors (such as soil type, parent rock, topography, etc.); while the other metals show medium spatial auto-correlations (Table 3), which imply that they are affected by both anthropogenic and natural factors. The variance of each variable is between 2.63–20.46 km, which is greater than the actual maximum sampling interval of 2386 m, indicating that the points are in the spatial variation range and it can reflect the true variation of metals.

Table 4. Theoretical semivariogram models and their correlation coefficients of soil heavy metal.

| Model style | Nugget ($C_0$) | Sill ($C_0+C$) | Nugget/Sill ($C_0/C_0+C$) | Range ($\text{km}$) | Determine the coefficient ($R^2$) | Residual square sum (RSS) |
|-------------|----------------|----------------|--------------------------|------------------|---------------------|------------------------|
| Cu t Exponential | 0.029 | 0.043 | 0.674 | 11.39 | 0.911 | 0.284 |
| Zn t Exponential | 0.179 | 0.416 | 0.430 | 20.46 | 0.719 | 0.260 |
| Pb t Gaussian | 0.017 | 0.023 | 0.739 | 9.42 | 0.723 | 0.123 |
| Cd t Spherical | 0.012 | 0.052 | 0.231 | 6.45 | 0.720 | 0.033 |
| Lg Cu a Gaussian | 0.493 | 0.957 | 0.515 | 4.33 | 0.875 | 0.327 |
| Lg Zn a Spherical | 0.247 | 0.716 | 0.345 | 4.47 | 0.841 | 0.152 |
| Pb a Gaussian | 0.097 | 0.153 | 0.634 | 3.55 | 0.725 | 0.061 |
| Lg Cd a Gaussian | 0.005 | 0.096 | 0.052 | 2.63 | 0.766 | 0.075 |

3.3. Analysis of spatial distribution of heavy metal

Due to the high spatial variability of soil, the collected soil samples can only represent the soil quality of the sample points themselves. Under the support of GIS, the spatial structure of heavy metals in soil can be simulated by Kriging spatial interpolation method based on geostatistics, and the spatial distribution pattern of heavy metal content can be visually expressed\textsuperscript{[13]}. Hereby, we used the Kriging optimal interpolation method to estimate the value of the regionalized variables of the unampled points.
by Arcgis 10.2 software, and finally generated the spatial distribution of the total and available contents of the heavy metal in the study area.

It can be seen from Figure 2 that the spatial distribution pattern of Cu, Zn, Pb and Cd basically showing patch-like distribution in the study area. The results showed that the human activities in this area had a negative aggregation effect on the heavy metal content of vegetable soil. The spatial distribution patterns of the total of Cu, Zn and Pb are generally similar, with elevated levels from northeast to southwest. While the Cd element is distributed in the northwest and northeast of the study area. This feature is obviously different from other elements and may be related to the special geological background of the karst area. Combined with the actual situation of the sampling site, it is found that the areas with high content of heavy metals are mainly distributed in Dangwu, Qiantao, Yanlou and Maling township. With the development of urbanization and the disorderly discharge of industrial and agricultural production pollution, sewage irrigation has become an important reason for vegetable soil heavy metal pollution in Karst peri-urban area.

![Figure 2. Spatial distribution of total heavy metals in the study area.](image)

It can be seen from Figure 3 that the spatial distribution pattern of the available Cu, Zn, Pb and Cd also shows the dot-like distribution, but it does not correspond completely to the total of heavy metal. In particular, two relatively large contents or hotpots exist for the four available metal. One is located between the Huchao and Dangwu township (inside the industrial gathering area), with the highest levels. The other is located in the south part of the city and is close to the outskirts of the city. According to the existing research shows[14], the main reason for the high content of available heavy metal in soil is long planting time and long-term application of phosphate fertilizer.
3.4. Environmental Risk Analysis of Heavy Metals in Soils

The potential ecological hazards ($E'_{i}$) of heavy metals in the suburbs of karst area are shown in Figure 4. We know that the range of potential ecological hazards of the total and available Cu, Zn, Pb and Cd were as follow: $E'_{i}$ Cu: 2.62–16.08, $E'_{i}$ Zn: 0.46–2.28, $E'_{i}$ Pb: 6.03–16.89, $E'_{i}$ Cd: 12.36–104.57, $E'_{i}$ Cu a: 1.47–29.57, $E'_{i}$ Zn a: 0.01–5.39, $E'_{i}$ Pb a: 0.98–20.60, $E'_{i}$ Cd a: 24.45–118.52. Indeed, median $E'_{i}$ values for four heavy metals showed the potential ecological hazard trend is Cd > Pb > Cu > Zn.

According to the statistics on the frequency of potential hazards corresponding to the potential hazard coefficient of heavy metals in soil (Table 5). The total and available Cu, Zn and Pb live in a slight potential ecological risk, while the total and available Cd soils at the moderate risk level were 46.78% and 77.42%, and even 6.45% and 8.06% of the soil has reached a strong ecological risk level.
From the frequency distribution, it can be seen that 70.97% of the soil samples are at the mild ecological risk level and 29.03% of the soil reaches the moderate ecological risk degree, which is mainly related to the large ecological damage coefficient and high geological background of Cd in the karst area. According to the current ecological risk assessment, the soil in the suburbs of the karst area may suffer from the ecological damage of Cd, which should be paid enough attention.

Table 5. Frequencies of potential ecological hazard coefficient and potential ecological risk index

| Single ecological risk level | Cu t | Zn t | Pb t | Cd t | Cu a | Zn a | Pb a | Cd a | frequency distribution/% | RI   |
|------------------------------|------|------|------|------|------|------|------|------|--------------------------|------|
| Low                          | 100  | 100  | 100  | 46.77| 100  | 100  | 100  | 14.52| 70.97                    |      |
| Moderate                     | 0    | 0    | 0    | 46.78| 0    | 0    | 0    | 77.42| 29.03                    |      |
| Considerable                 | 0    | 0    | 0    | 6.45 | 0    | 0    | 0    | 8.06 | 0                       |      |
| High                         | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0                       |      |
| Very high                    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0                       |      |

4. Conclusions
Karst peri-urban vegetable soils from Guiyang were collected, the concentration of total and available for Cu, Zn, Pb and Cd were measured, and that spatial distribution of these metals was analyzed and their potential ecological risk were also assessed. The following conclusions are based on analytical findings: (1) The mean concentration of Cu, Zn, Pb and Cd in vegetable soils in Guiyang peri-urban were higher than reference values, the total concentration of Cu, Zn and Pb were positively correlated with the available Cu, Zn and Pb, indicating that they had a trend of compound pollution; (2)The predication map of total and available metals in vegetable soil were basically showing patch-like distribution pattern, and high concentration of metals is mainly distributed in Dangwu, Qiantao, Yان lou and Maling township; (3) The potential ecological hazard trend is Cd>Pb>Cu>Zn from the average values of the total and available of heavy metals. According to the current ecological risk assessment, the vegetable soil in the karst peri-urban area is subjected to the ecological harm of Cd element, which should pay more attention.

Acknowledgements
The authors are grateful to The Key Project of Science and Technology Foundation of Guizhou Province (Qian Sci.Co.JZ.[2014], NO.2012), Support program from Science and Technology of Guizhou Province (Qian Sci.Co.[2017], No.2580).

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