Short communication

An investigation on the distribution of eight hazardous heavy metals in the suburban farmland of China

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1. Introduction

The evaluation of soil environmental quality can provide some science warranty for proper land use, soil contamination control and eco-environmental construction, whose precondition depends on realizing the spatial distribution of soil heavy metal contents. The problems associated with the characterization of heavy metals in the majority of sites are often due to multiple sources of pollution. Soil heavy metal information has undoubtedly implications for agriculture product and food safety [1]. Hazardous soil heavy metals have been a very useful indicator of environmental quality worldwide and been the subject of much attention because of their peculiar characteristics. The suburban farmland is a spatial transition zone between urban and rural, which plays an important role in providing regional food security to urban and local residents and protecting environment or ecosystem, and currently it experiences a rapid growth of industrialization than in rural areas in China. Soil heavy metals in suburban farmland may have deposited and accumulated as a result of the urban rapid industrial development. Heavy metal contents are influenced by natural and anthropogenic factors including parent materials, land use, application of pesticides and fertilizers etc. Such heavy metals can accumulate in crops and may lead to the damage and alteration of animal or human physiological functions by food chain [2,3]. Understanding the spatial distribution of heavy metals is critical for environmental management and agricultural production [4,5].

Geostatistics has successfully been applied in investigating and mapping hazardous soil heavy metals [6–8]. The spatial variability of soil heavy metals is an important part of environmental supervision and ecosystem evaluation. Taihang Piedmont Plain as a dominating area for agricultural production of Hebei Province, but little attention has been paid to the spatial variability of soil heavy metals in this region. Zhengding County is the typical suburban farmland in Taihang Piedmont Plain and its spatial variability of eight hazardous heavy metals (Cu, Zn, Cr, Ni, Pb, Cd, Hg and As) was investigated by statistics, geostatistics and geographical information system (GIS) techniques, in order to find out the spatial distribution maps and provide efficient estimates for soil environ-
mental monitoring and valuable information for the regional soil quality management [9–12].

2. Materials and methods

2.1. Sample collection

A total of 100 soil samples were collected by the simple random sampling method, whose sampling points are an irregular grid that can represent cultivated areas and allow geostatistical treatment. Actually the density of sampling varies within small limits due to difficult sampling conditions in the study area. Each sample mixed by five topsoil cores (0–20 cm in depth, approximately 200 g of total weight) was taken from within a 20 m × 20 m area and recorded by the central point position with GPS device.

2.2. Laboratory analysis

All soil samples were air-dried at room temperature and ground in an agate mortar to pass through a 100-mesh plastic sieve. The soil pH was measured by a glass electrode in a 1:5 soil/water suspension. Cu, Zn, Cr, Ni, and Pb were extracted by aqua regia digestion (HNO₃, HCl and H₂O₂) of the soil fraction in a microwave (Milestone Ethos 900 plus Mod. 44062) in accordance with the ISO 11466 procedure [International Organization for Standardization, 1995], then the total concentrations of Cu, Zn, Ni, Cr and Pb were measured by flame atomic absorption spectrometry (AAS), and Cd and Pb by graphite furnace AAS, as well as As and Hg was determined by atomic fluorometry (Agricultural Chemistry Committee of China 1983)[12].

2.3. Spatial structure analysis

Common descriptive statistics and histograms do not incorporate the spatial locations of data into their defining computations. The four main operations of linear geostatistics (variances of estimation and dispersion, regularization and kriging) involve only the structural function of the random function (covariance or variogram). Thus, every geostatistical study begins with the construction of a model designed to characterize the spatial structure of the regionalized variable studied.

Soil heavy metals are typical regionalized variables. The presence of a spatial structure where observations close to each other are similar than those that are far apart (spatial autocorrelation) is a prerequisite to the application of geostatistics [11]. The experimental semivariogram measures the average degree of dissimilarity between sampled values and a nearby data value [12], and thus can depict autocorrelation at various distances.

Geostatistics uses the technique of semivariogram to measure the spatial variability of a regionalized variable, and provides the input parameters for the spatial interpolation of kriging [13]. The value of the experimental semivariogram for a separation distance of h (referred to as the lag) is half the average squared difference between the value at Z(xᵢ) and at Z(xᵢ+h).

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

where \(N(h)\) is total number of pairs of sample points separated by the lag distance h. For irregular sampling, it is rare for the distance between the sample pairs to be exactly equal to h, therefore, the lag distance h is often represented by a distance band. Z(xᵢ) is measured sample value at point i, Z(xᵢ+h) is measured sample value at point i+h. The variogram model is chosen from a set of mathematical functions that describe spatial relationships. The appropriate model is chosen by matching the shape of the curve of the experimental variogram to the shape of the curve of the mathematical function.

The fitted model provides information about the spatial structure as well as the input parameters such as nugget, sill and range for kriging interpolation. By fitting the appropriate variogram model, the distance-dependent coefficients can be estimated and graphically interpreted. In this study, the fitted spherical model and gaussian model were selected.

Raw data were analyzed with different software packages. The descriptive statistical parameters were calculated with SPSS 11.0. The geostatistical analyses and the probability calculation were carried out with VarioWin 2.2. The maps of eight elements spatial distribution pattern were produced using ArcGIS 8.3 software by kriging interpolation.

### Table 2

<table>
<thead>
<tr>
<th>Soil Metal</th>
<th>Model</th>
<th>Nugget ((C₀))</th>
<th>Sill ((C + C₀))</th>
<th>(C₀/(C + C₀))</th>
<th>Range (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>Spherical</td>
<td>0.0006096</td>
<td>0.0016</td>
<td>43.23</td>
<td>3.28</td>
</tr>
<tr>
<td>As</td>
<td>Spherical</td>
<td>0.657</td>
<td>2.35</td>
<td>27.96</td>
<td>11.63</td>
</tr>
<tr>
<td>Cr</td>
<td>Spherical</td>
<td>39.29</td>
<td>77.00</td>
<td>51.03</td>
<td>7.76</td>
</tr>
<tr>
<td>Cu</td>
<td>Spherical</td>
<td>6.86</td>
<td>11.51</td>
<td>59.60</td>
<td>7.37</td>
</tr>
<tr>
<td>Hg</td>
<td>Spherical</td>
<td>0.0021</td>
<td>0.0035</td>
<td>59.04</td>
<td>9.31</td>
</tr>
<tr>
<td>Ni</td>
<td>Linear</td>
<td>10.71</td>
<td>21.00</td>
<td>51.00</td>
<td>10.08</td>
</tr>
<tr>
<td>Pb</td>
<td>Spherical</td>
<td>8.48</td>
<td>15.41</td>
<td>55.03</td>
<td>3.42</td>
</tr>
<tr>
<td>Zn</td>
<td>Gaussian</td>
<td>37.14</td>
<td>51.76</td>
<td>71.75</td>
<td>8.92</td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1. Statistic descriptive parameters and normality test

To evaluate the raw data, the descriptive statistical parameters of soil heavy metals are presented in Table 1. The results showed that Cu, Zn, Ni, As had passed the Kolmogoro–Smirnov normality test (K-S p < 0.05), but other variables such as Pb, Hg, Cr and Cd had not passed. Since further geostatistic analysis need data to follow a normal distribution. Data transformation was carried out prior to the next analysis. At last, all eight heavy metals followed normal distribution or lognormal distribution (Table 1).

![Graphs showing semivariograms for Cd, As, Cr, Pb, Cu, Hg, Ni, and Zn](image)

Fig. 1. Semivariograms model of topsoil heavy metals.

The maximum observation values of every heavy metal except for Zn were more than double the minimum values, which exhibited large spatial ranges. The average content plus standard deviation of Cd is $0.15 \pm 0.04 \text{mg kg}^{-1}$. The value is much higher than the background values that can be used to assess metal contamination in soil, indicating possible pollution at few locations of the study area, which are probably caused by anthropogenic activity such as fertilizers and pesticides, vehicle exhausts and industrial fumes, and burning of coal. The Zn, Hg, Cu, Cr, Ni, Pb and As (mean ± S.D.) exhibited lower contents than the background values that probably caused by weathering and lithogenic of rich parent materials.
According to the Standard of Chinese Environmental Quality for Soils (GB 15618-1995) [State Environmental Protection Administration of China, 1995] [11], the study area soils are feeble alkaline with an average pH value of 8.05. All heavy metals in the surface soil are lower than the guidance values established for cultivated areas, indicating that soil environmental quality in study area was little threaten in terms of environment and human health.
The coefficient variation (C.V.) values of eight heavy metals in the study ranges from 0.10 to 0.75 indicating that they had moderate variations. The C.V. of Hg was 0.75, which is the highest of the eight heavy metals, suggesting that Hg has the greatest variation among the soil samples and thus would have the highest possibility of being influenced by the extrinsic factors such as human activities. The lowest C.V. of the eight heavy metals was Zn with a score of 0.1, suggests that Zn has a weak variation and its content was almost constant across the county (Table 1).

3.2. Spatial structure of soil heavy metals

Semivariograms were used to establish the degree of spatial continuity and the range of spatial dependence. The experimental semivariogram represents the variance of the sample value at various separation distances. Each of the experimental semivariograms can be described on three parameters: nugget, sill and range. Experimental semivariograms suggested that the theoretical spherical model is in reasonable agreement with the data. The Zn and Ni were fitted with the gaussian model and the linear model (Fig. 1), respectively.

The largest nugget effect of Cr (C_0 = 39.29) indicated a strong random variance at short distance. The smallest nugget effect is Cd (C_0 = 0.000696), which showed relative variance and the sampling density is adequate to reveal the spatial structures. All soil heavy metals showed positive nugget, because of the sampling error, shorter distance variability, and random and inherent variability. More attention has been paid to the spatial correlation distance, as they play more important role in kriging estimation.

The range of heavy metal contents varied from 3.28 to 11.63 km. The As had the largest range 11.63 km, which indicated that As was the smallest range 3.28 km, which implies that the length of the spatial autocorrelation is much longer than the sampling interval of 1.5 km. Therefore, the current sampling design is appropriate for this study and it is expected that a good spatial structure will be shown on the interpolated map. These results are inconsistent with the previous reports [6–9] that the correlation length is from 6.27 to 85.75 km. These results may indicate that the range of autocorrelation is influenced by different study scales.

The C_0/(C_0 + C_S) ratio (Table 2) can be regarded as a criterion to classify the spatial dependence of soil properties. If the ratio is less than 25%, the variable has strong spatial dependence. If it is between 25% and 75%, the variable has moderate spatial dependence. With a ratio of greater than 75%, the variable shows only weak spatial dependence. With ratio between 25% and 75%, have moderate spatial dependence. Without the sampling error, shorter distance variability, and random and inherent variability. More attention has been paid to the spatial correlation distance, as they play more important role in kriging estimation.

The coefficient variation (C.V.) values of eight heavy metals in the study ranges from 0.10 to 0.75 indicating that they had moderate variations. The C.V. of Hg was 0.75, which is the highest of the eight heavy metals, suggesting that Hg has the greatest variation among the soil samples and thus would have the highest possibility of being influenced by the extrinsic factors such as human activities. The lowest C.V. of the eight heavy metals was Zn with a score of 0.1, suggests that Zn has a weak variation and its content was almost constant across the county (Table 1).

3.3. Spatial distribution maps of soil heavy metals

ArcGIS is a valuable tool for interpreting spatial variability and environmental monitor. Information generated through semivariogram (nugget, sill, range) was used to calculate sample weighing factors for spatial interpolation by the simple point kriging procedure, using the nearest eight sampling points and a maximum searching distance equal to the range distance of the variable. In particular, mapping the conditional probabilities of a soil property is of importance for management decisions, which are based on threshold values of this property, such as delineating safe or hazardous areas and identifying zones that are suitable for crop growth and those that must be treated.

Fig. 2 is the spatial distribution map generated based on the semivariograms of all heavy metals gathered from the study area. The maps showed similar geographical trends, especially for Cu, Zn, Ni and Cd, with both high contents at centre and northeast edge part of the County. At the other place, their concentrations are relatively low. Apart from the northwest and southeast directions, Zn values are generally high. It is concluded that the explanation for higher uncertainty is most likely attributed to land use. Similar to the grade in Fig. 1, it shows no risk of Pb in this study area. On the other hand, high content of Ni distribution was found on the top of the study area. Hg is a dangerous metal, the higher soil Hg concentrations are found in the south edge of the bottom and the highest Hg area is the smallest. Ni and Hg exhibit apparent variance from north to south, while Zn and As display most variance from the northeast to southwest.

Generally, anthropic inputs of Cr and Ni in fertilizers, limestone and manures are lower than the concentrations already present in the soil; Cu and Zn are common ingredients of some pesticides; Common sources of Pb in soils are manures, sewage sledge, vehicle exhausts and the burning of coal. Cd is a highly mobile and toxic element. In addition, using coal for heating during the winter period could have resulted in high Zn, Pb and Hg in the air fallout [13–16]. Cu, Zn, Pb, Cr, As, Cd except for Hg, indicating that they were from the same origin as their soil parent materials and of the same soil formation factors. The local anomaly had been found with Cd, which is probably linked to anthropic and industrial activities [14–18].

The study results demonstrated that the spatial variability of eight heavy metals in suburban arable area was apparent in the Zhengding County. Such studies could help validate procedures of spatial predictions that have limited measured data. This may be suitable for many problems in soil monitoring where heavy metal changes are relatively small and slow. All heavy metal contents are less than the guidance values. Thus, even these eight elements are unlikely to exhibit a risk to the environment or a threat to human health at present, but the results are helpful for improving agricultural and forest ecosystem in the region [1–6,15–18].

Acknowledgments

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References


