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Original Research

Ecological Risk Evaluation of Heavy Metal Pollution in Soil Based on Simulation

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Abstract

Heavy metals pollution of surface soils is a major global issue. To assess the ecological risk caused by heavy metals, 280 samples were collected in Chiping, Shandong Province, China. Eight different heavy metals in surface soils (Cu, Pb, Cd, Cr, Hg, Ni, Zn, and As) were analyzed in this study. The author got the realization of the eight kinds of heavy metals respectively based on sequential simulation methods. Next, the ecological risk of the region of heavy metals was assessed using the Hakanson potential danger index. The result showed that Hg was the main heavy metal problem in ChiPing. The potential ecological risk caused by Hg amounts to 200 on the Hakanson potential danger index, which was classified as 'high.' Cd has a potential ecological risk of nearly 72, which was classified as 'medium.' The comprehensive potential ecological risk caused by all eight different heavy metals was 278.34. Therefore, the heavy metal pollution of the study area was associated with a 'medium' potential ecological risk. Finally, the result was analyzed based on the land use map. We found that the highest integrated potential ecological risk area was located in plough land.

Keywords: ecological risk assessment, heavy metal, pollution, spatial variability, soil, simulation

Introduction

Air, water, and soil are the most important components of the living environment for human beings. In recent years, with the quick development of urbanization and industrialization, the contamination of soil by heavy metals has become an increasing public concern [1-4]. The pollution caused by heavy metals in agricultural soil can affect food quality and safety. To date, various potentially toxic elements (PTEs) have been identified, such as arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn), which are known to influence human disease by their respective deficiency or toxicity [5]. Heavy metal contaminants in the soil can enter the human body through various means. Highly toxic heavy metals may result in serious ecological risks [6]. It is necessary to monitor heavy metal contamination in the soil, access the potential ecological risk of heavy metals, and then take remediation measures on affected soil. Such approaches have been described by such publications as the "Guide to Strengthening Food Safety from the Health and Family Planning Commission," "Opinions on Deepening Rural Reform," and "Acceleration of the Modernization of Agriculture" by the State Council of China [7].

Many studies have been carried out regarding heavy metal pollution. The usual method is to collect soil samples, extract the various heavy metals, and then assess

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the soil pollution and potential ecological risk [8-15]. Most of the research was based on the samples directly. However, the number of sample points is often limited in terms of representing the real status of the entire study area. To address this problem, the paper made use of the Geostatistics method to simulate the attributes of heavy metals at unsampled points. Then the assessment was carried out based on the 1,000 given realizations of the whole area.

Geostatistics has been widely used in the field of soil science [16-17]. Goovaert [18] summarized the application of Geostatistics in soil science, including the description of spatial patterns, quantitative modeling of spatial continuity, spatial prediction, and uncertainty assessment. In this paper, the author made use of the 'bin' variogram to quantify the spatial distribution of heavy metal concentrations, and the 'simulated' map to represent the different pollution status of heavy metals in the study area. It is well known that there are two different methods in Geostatistics: Kriging and simulation. Kriging methods tend to get more 'accurate' and 'smoothed' values of the unsampled points. The results are based on the condition of the minimum local error variance [19]. However, methods of simulation pay more attention to the detailed spatial pattern of the sampled points. They reproduce the statistics drawn from sampled points, such as the histogram or the semivariogram model [20]. Thus the maximum and the minimum value will be reserved in the map, which is very important for the discovery of the pollution sources. The paper selected the sequence Guassian simulation method to realize the spatial prediction of heavy metal pollution in Chiping, China. In a future study, the uncertainty of risk assessment can be accessed based on the uncertainties in the spatial distribution of attribute values, and government may take different remediation scenarios according to the level of probability.

Materials and Methods

Sampling and Analysis

Chiping is located west of Shandong Province, China. It covers an area of 1,003.37 km^2 and has 542,000 inhabitants. It is an important cotton growth region both in the province and in China. The paper designed 2×2 km uniform grids for sampling across the whole study area. 280 topsoil samples (0-20 cm) were collected from each grid center. The central point position was recorded using GPS. Fig. 1 shows the locations of sample sites. Approximately 1 kg of soil sample was collected at each location using a stainless steel spade and stored in self-sealing plastic bags.

Soil samples were air-dried, ground, and a 2 mm nylon sieve was used to remove rough materials and other debris. Each digested sample was analyzed by inductively coupled plasma atomic absorption spectrometry (ICP/AES) for the following heavy metals: As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn. All the crushed and dried samples were introduced into a plasma (at a temperature in the order of 6,000-10,000 k). The elements were converted to gaseous atoms (then ions). A spectrometer was used to separate the different light emitted by different elements [21]. Quality assurance and quality control was made based on standard reference materials obtained from the Center of National Standard Reference Materials of China [22]. One blank and one standard sample were inserted with every 10 samples. The relative standard deviations were all less than 10%. All samples were analyzed in duplicate. When the relative standard deviation was within 5%, the results were accepted. The results met the accuracy demand of the Technical Specification for Soil Environmental Monitoring HJ/T 166-2004 [23].

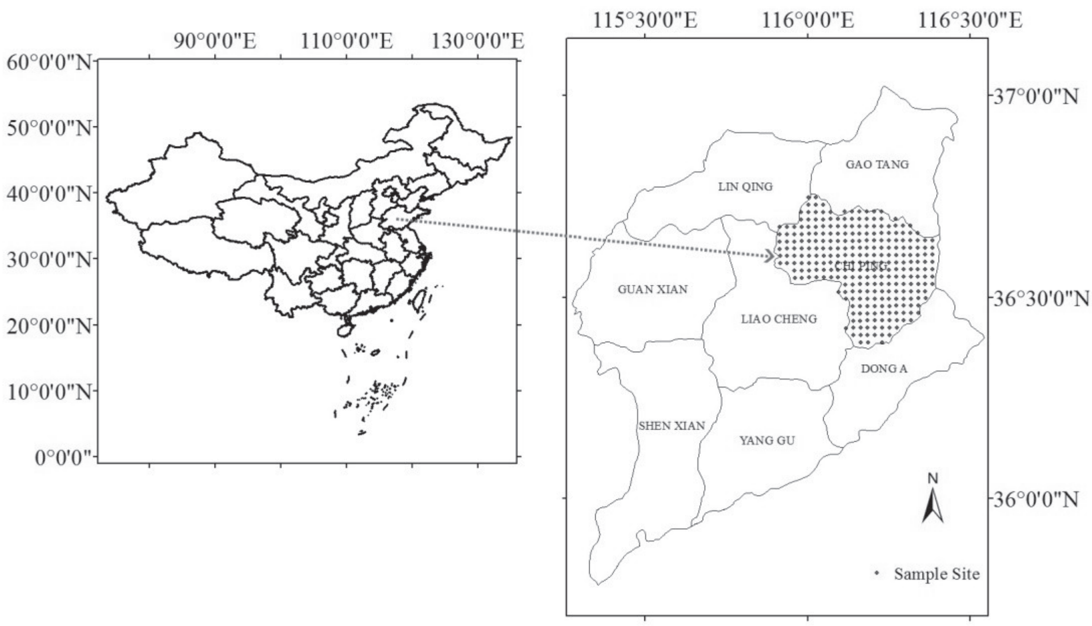

Fig. 1. Study area.

Data Processing

Sample data was processed using geostatistical methods. First was testing the distribution of all the heavy metals with a histogram. Then, semivariogram model selections and model cross-validation were carried out. The main parameters in theoretical models included nugget (C_0), sill (C_0+C), range (Range), nug/sill ratios (C_0/ (C_0+C)), and coefficient of determination (R^2). The nug/sill ratios are often used for spatial heterogeneity and reflect the influence of regional factors (nature) and the role of non-regional factors (human factors). Soil is generally contaminated by heavy metals from two main sources: natural factors such as weathering, erosion of parent rocks, atmospheric deposition and volcanic activities; and anthropogenic activities such as sewage irrigation, addition of manures, fertilizers, and pesticides [24-27]. When C_0/ (C_0+C) < 0.25, the variable space mutation gave priority to the structural variation (nature), and the variables have a strong spatial correlation. When , the variables have a moderate spatial correlation. When , the variables are random and the variables of spatial correlation are very weak. Finally, GS+ (v.9) software was used to perform the geostatistical analysis of the data. Sequential Gaussian simulation method was used to estimate the unobserved points.

Assessment Method

The potential ecological risk of heavy metals in soil can be accessed by a potential ecological risk index [28]. Based on concentrations of heavy metals and ecological factors, the method can provide a quantitative result. The equations to compute the potential ecological risk of each heavy metal and the integrated potential ecological risk are as follows:

$$\mathrm{E_r^i} = \mathrm{T_r^i} \times \mathrm{C_f^i}$$

$$\mathrm{IR} = \sum_{\mathrm{i=1}}^{\mathrm{N}} \mathrm{E_r^i} = \sum_{\mathrm{i=1}}^{\mathrm{N}} \mathrm{T_r^i} \times \mathrm{C_f^i}$$

...where T_r^i is the toxic response factor of different heavy metals; the corresponding values of Hg, Cd, As, Pb, Ni, Cu, Cr, and Zn are 40, 30, 10, 5, 5, 5, 2, 1; $C_f^i = C_i/C_r^i$ is the pollution coefficient of each heavy metal; C_i is the concentration of each heavy metal; and C_r^i is the recommended value of heavy metal concentration in soils [29]. The paper selected the recommended values for Shandong Province (Table 1) [30]. The presence of various different heavy metals would result in a higher comprehensive potential ecological risk. The classifications defined by Hakanson are listed in Table 2.

The result of total potential ecological risk was analyzed in ArcGIS. When overlaid with the land use map in the study area, we can roughly identify the source of heavy metal pollution.

Table 1. Commended values of heavy metal concentrations in soil (mg/kg).

Element	Background values of Shandong	Background values of China	Global soil median
Cu	24.0	22.6	30
Zn	63.5	74.2	90.0
Pb	25.8	26.0	35.0
Cd	0.084	0.097	0.350
Cr	66.0	61.0	70.0
Ni	25.8	26.9	50.0
Hg	0.019	0.065	0.060
As	9.3	11.2	6.00

Table 2. Classification of potential ecology risk by Hakanson.

Potential ecological risk					
	Slight	Medium	High	Higher	Highest
E_r^i	<40	40-80	80-160	160-320	>320
IR	<50	150-300	300-600		≥600

Results and Discussion

Explore Data Analysis

To make use of the simulation method, the prerequisite is that the spatial data distribution satisfied the assumption of multivariate normality. The histograms of each heavy metal were used to test the distribution of heavy metals. Cd, Cr, Ni, and Pb had almost normal distributions, with low skewness and kurtosis values close to 3. The other four heavy metals values were log transformed to satisfy requirements for normal distribution.

Four theoretical models were used to fit the semivariance function models: the exponential model, the Gaussian model, the spherical model, and the linear model (Fig. 2). The fitted results of the soil heavy metal semivariance function (Table 3) show that the nug/sill ratios C_0/ (C_0+C) of As and Hg were smaller than 0.25. This suggested that the spatial variation of the two elements mainly arises from the soil parent materials, topography, and other structural variations. This result also shows that the nug/sill ratios of Cd, Cr, Ni, Zn, Pb, and Cu were between 0.25 and 0.75, indicating a medium spatial correlation. In the analysis of semivariance, we found that the sampling schedule was very important. The uniform 2 km grid sampling was limited to provide information of short-distance spatial variation. For example the nugget of Hg is forced to zero in Fig. 2, where this was not backed up by the data.

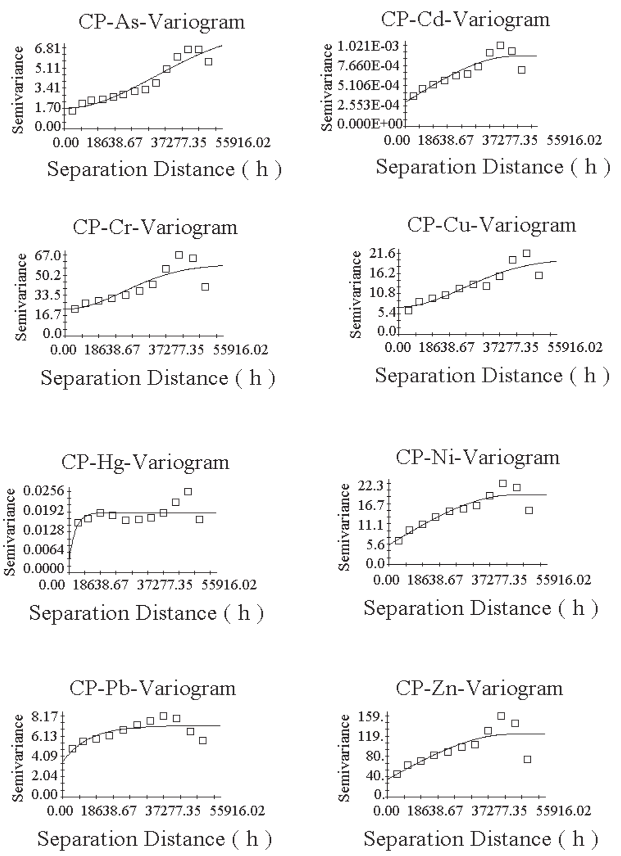

Fig. 2. Semivariogram of heavy metal in Chiping.

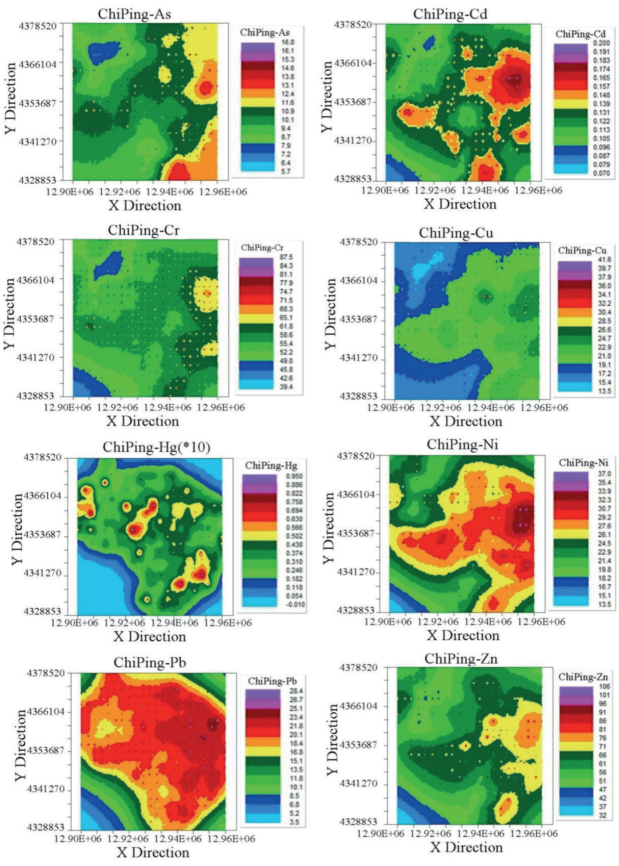

Fig. 3. Spatial distribution of heavy metal in Chiping.

Table 3. Semivariograms fitting of heavy metals in soils from Chiping.

	Model	C_0	Sill	Range	$C_0/(C_0+C)$
As	Gaussian	1.73	8.469	81,752	0.204274
Cd	Spherical	0.000302	0.000884	48,500	0.341629
Cr	Gaussian	22.2	59.03	53,000	0.37608
Ni	Spherical	5.37	19.07	45,800	0.281594
Pb	Exponential	3.52	7.202	28,800	0.488753
Zn	Spherical	34.5	123.1	45,500	0.28026
Cu	Gaussian	7.26	20.13	58,370	0.360656
Hg	Exponential	0.00344	0.01898	7,500	0.181243

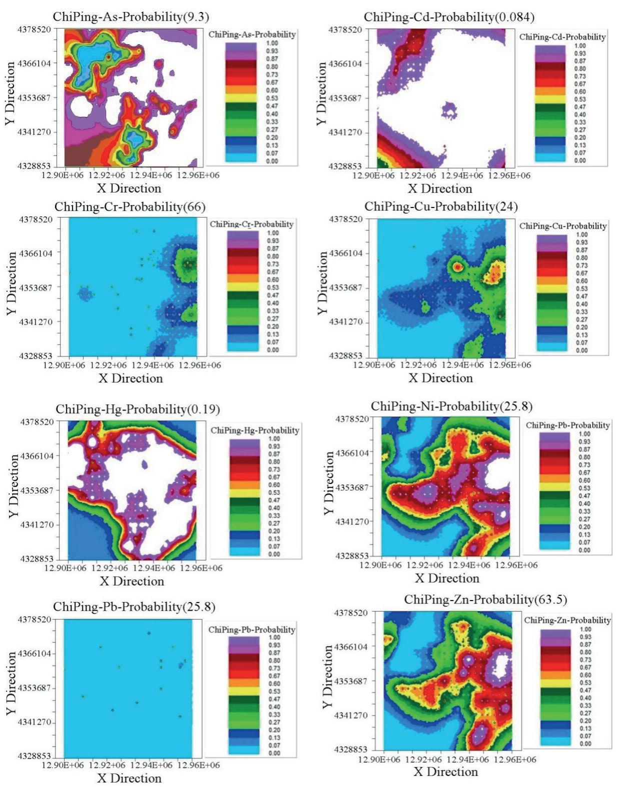

Fig. 4. Probability map of heavy metal in Chiping.

Spatial Distribution and Probability Map of Heavy Metals

The result spatial distributions of the eight heavy metals were based on the 1,000 realizations of simulation. The paper took the upper limit of the background value of heavy metals in soil established by the local government as the standards (Table 1). The legend of each heavy metal was set up to more than 10 intervals to extract the details of spatial distribution (Fig. 3).

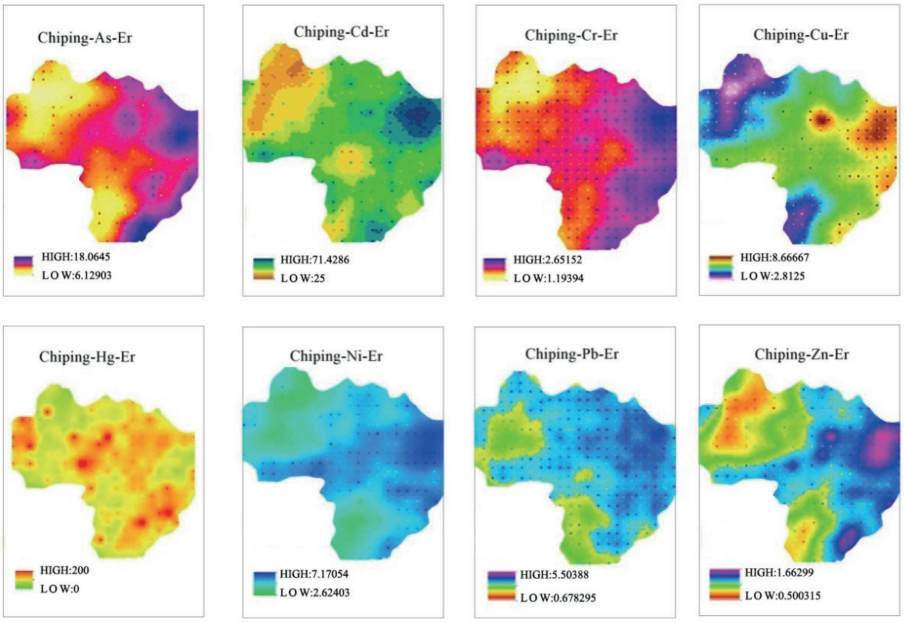

Fig. 5. Potential ecological risk of heavy metal in Chiping.

According to the spatial distribution of each heavy metal, the paper found that there were no detectable Pb, Cr, and Cu present in the simulation results. The Zn- and Ni-contaminated area was about one third or half of the whole area. However, Cd, Hg, and As pollution were spread widely across the whole area. High accumulation was found in the middle of the eastern and in the southern parts of the study area.

In addition, the probability map of each heavy metal was made with the corresponding background threshold values listed in Table 1. Pb, Cr, and Cu had little probability of exceeding the threshold value (Fig. 4). Some areas for Zn and Ni had probabilities >50% for exceeding the threshold value. For Cd, Hg, and As, almost 80% of the total area had a probability > 90% of exceeding the threshold value. The background value is the normal value of each element in soil. The high probability to exceed the threshold represented the contamination of soil. These results were the same as those from the spatial distribution analysis.

A strong relationship was found between some of the heavy metals, for example Cu and Zn. Including cross-correlations in the simulation method maybe improve the precision of the results. The paper would take it as the further study content in the near future.

Potential Ecological Risk of Heavy Metals

The evaluation of the Hakanson potential ecological risk was carried out for each heavy metal. So did the comprehensive risk based on all the heavy metal-integrated contamination. The results showed that Hg was the main

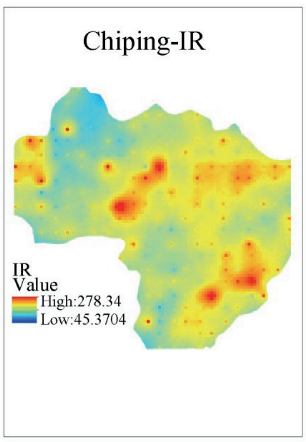

Fig. 6. Integrated potential ecological risk of heavy metal in Chiping.

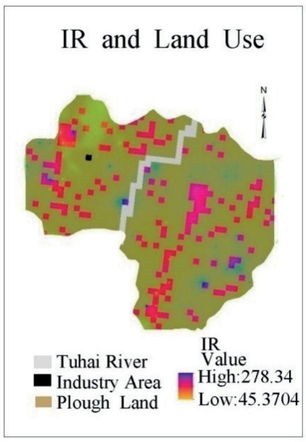

Fig. 7. Overlaid map of integrated potential ecological risk with land use map.

heavy metal contamination problem in Chiping. The maximum potential ecological risk caused by Hg is 200, which represented a ‘high’ classification. The maximum potential ecological risk of Cd contamination is nearly 72, which represented a ‘medium’ classification (Fig. 5). The comprehensive potential ecological risk caused by all eight examined heavy metals is 278.34. Therefore, the heavy metal pollution across the study area is classified as ‘medium’ potential ecological risk (Fig. 6).

The result of integrated potential ecological risk was overlaid with the land use map of the study area (Fig. 7). As we can see, plough land is the primary land use type in the study area, amounting to 63.25% [31]. In Fig. 7, we can find that most of the highest-integrated potential ecological risk area was located in plough land. Meanwhile, two parts of them were along the Tuhai River. The distribution of the industrial area was limited in Fig. 7, which implied little effect of heavy metal contamination caused by local industry.

Conclusions

Eight different heavy metals (Cu, Pb, Cd, Cr, Hg, Ni, Zn, and As) in surface soils were analyzed in Chiping, China. The variogram analysis showed that As and Hg had a strong spatial correlation. The variable space mutation prioritized the soil parent materials, topography, and other structural variations. The other six heavy metals were more likely to be sourced from human activities. Based on the sequential simulation methods, this paper got the different realizations of the eight different heavy metals. Next, the ecological risk of the “simulated region” of heavy metals was assessed using the Hakanson potential danger index.

The pollution of heavy metal in soil may be further transferred to underground water and plants [32]. This would be a long-term threat to human health, plant growth, and the total environment. The potential ecological risk caused by most of the heavy metals is slight, except for the main heavy metal contamination caused by Hg. As a result, the whole study area was faced with the “medium” integrated ecological risk. To analyze the source of heavy metal contamination, the paper overlaid the land use map with the integrated ecological risk map. The result showed that the highest ecological risk caused by heavy metal were scattered in plough land, along with the Tuhai River. It can be concluded that the contamination in Chiping was not caused by industry. The main pollution of heavy metal in the study area was caused by Hg, which perhaps originated from the soil parent materials. Essential measures and remediation should be taken within these areas to prevent further deterioration.

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