Chemical Characteristics of Coil Heavy Metal Elements and Ecological Security Risks Caused by Fertilization

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In order to investigate the effects of fertilization on soil chemical characteristics and ecological security, the chemical characteristics and ecological security risk analysis of heavy metal elements in a certain soil caused by fertilization were proposed. The contents of Ni, V, Cr, As, Cd, Pb, Zn, and Hg in 1,065 surface soil samples collected in a district of a city in the southwest agricultural area were tested and analyzed. Multivariate statistical analysis and spatial analysis were used to clarify the geochemical distribution characteristics of these heavy metals, and the possible main sources were also discussed. The results showed that the eight heavy metals could be divided into three categories. The first category included Ni, V, Cr, and As, whose content was lower than the background value in Beijing. And the distribution was mainly affected by natural factors such as parent materials of soil formation. The second category included Cd, Pb, and Zn, whose average content was higher than the background value. And the content was the highest in residential areas. In addition to the parent material inherited from the soil, the distribution characteristics of these elements were greatly affected by human activities. And Cd was significantly more affected by human activities than Pb and Zn. The third category included Hg, and it was inferred that atmospheric deposition was the main factor affecting the distribution of Hg. It was concluded that the Hakanson method was used to evaluate the ecological risk of heavy metals in soil, and the results showed that the potential ecological risk index was low in the area.

1. Introduction

With the development of the social economy, the impact of human activities (industrial and agricultural production, transportation, etc.) on the urban natural environment tends to be strong. With the development of the city's industrial and transportation, the original inheritance of urban soil has changed in a certain intensity. The soil is widely distributed in the suburban areas, urban rivers, leisure venues, stadiums, roads and waste plant, and abandoned factories around or covered by industrial and building facilities [1]. With the acceleration of global urbanization, there are more and more heavy metals such as cadmium (Cd), and copper (Cu). Nickel (Ni), lead (Pb), zinc (Zn), mercury (Hg), chromium (Cr), iron (Fe), manganese (Mn), molybdenum (Mo), and cobalt (Co) entering the soil through various ways. At present, all countries in the world are polluted by soil heavy metals to varying degrees, thus damaging the normal function of the ecosystem. More seriously, heavy metals will also enter animals, plants, and human bodies through the food chain and water, affecting their normal survival, which is a potential “chemical time bomb.” If the human body absorbs them excessively, it will also lead to a variety of endemic diseases and even endanger human life and health. In addition, soil heavy metal pollution also has the characteristics of latency, lag, and accumulation [2, 3]. If the soil is seriously polluted by heavy metal elements, it requires a large amount of money and a long treatment cycle. The harm caused by it is more serious than the harm caused by air and water pollution and is more difficult to eliminate. In recent decades, the research on soil heavy metal pollution has attracted the attention of many scholars at home and abroad, but the focus is generally on agricultural soil. However, there are relatively few researches on heavy metal pollution in...
urban soil. Therefore, the ecological and environmental effects brought by the drastic environmental changes caused by human activities should gradually become a scientific issue of concern as shown in Figure 1.

2. Literature Review

Wang and Ji used multivariate statistics and Fourier sum spectral analysis to analyze the sources of heavy metals in the surface soil samples of vegetables in a certain area and conducted safety warning research on the content of lead in soil and vegetables. The results showed that lead pollution in local vegetables may be caused by human activities (such as industrial wastewater discharge and gasoline combustion) [4]. Alobaidi et al. investigated the ecological geochemical characteristics of lead in a certain area and concluded that there was no significant relationship between lead geochemical characteristics and the cause of liver cancer prevalent in the area [5]. Sun et al. investigated the current situation of heavy metal element pollution in rural soil of the Pearl River Delta and showed that in addition to the pollution sources such as chemical fertilizer, pesticides, and livestock and poultry, industrial and other pollution also had a great impact. In addition, the industrial soil in the research area is dominated by excessive Cu, while the planting soil is dominated by excessive Cd [6]. Mukeba et al. investigated the spatial distribution and source analysis of 12 heavy metals on the surface of Lianyuan, a typical coal mining city, and the results showed that most heavy metals were related to human activities. Based on the PMF model, the influence of natural sources, atmospheric deposition, industrial activities, and agricultural activities on the source and distribution of 12 heavy metals in Lianyuan soil was 33.6%, 26.5%, 23.44%, and 16.91%, respectively. Some people also conducted quantitative research on different sources of soil heavy metals in Beijing [7]. Fouladi et al. used the MCR-WALS model to calculate quantitatively that contribution rates of atmospheric deposition, fertilizers and pesticides, and natural sources to soil heavy metals accounted for 15.5%–16.4%, 5.9%–7.7%, and 76.0%–78.6%, respectively, indicating that natural sources dominated soil heavy metals in Beijing as a whole [8]. Jwad and Abbas investigated the soil heavy metals (Cd, Hg, Cu, and Zn) in a vegetable base in North China, and showed that the average content of each heavy metal in this area did not exceed the second-level soil quality standard. Through the calculation of exposure risks in three ways, it was found that non-carcinogenic and carcinogenic risks were low and would not cause harm to human health [9].

In the research, combined with agriculture area agriculture in southwest district neighborhood of heavy metals in the soil, which was the research object, the geochemical characteristics of eight heavy metals in soil (Ni, V, Cr, As, Cd, Pb, Zn, and Hg) were analyzed. Combined with multivariate statistics and spatial analysis discrimination, the main source of heavy metal was judged. The soil’s environmental quality and its potential ecological risk were evaluated according to the relevant standards.

3. Research Methods

3.1. Sample Collection and Analysis. In this research, sampling grids were divided into 0.5 km × 0.5 km in the research area. In order to reduce the random error, 5 surface soil samples were collected in each grid; the sampling depth was 0–20 cm; and each sample weighed about 1.0 kg. After mixing, a mixed sample was prepared, and a total of 1,065 samples were collected. GPS recorded the actual coordinates of sampling points. The collected soil samples were dried by air and ground, then passed through a nylon sieve with a diameter of 70 mesh, and then crushed through a 100-mesh sieve with an agate-grinding bowl without pollution. In order to avoid the volatilization of metal Hg, the soil samples were stored in a cool environment for future use.

The samples were analyzed and determined by National Geological Experimental Testing Center in reference to national soil environmental quality standards. The contents of Ni, V, Cr, Pb, Zn, SiO₂, Al₂O₃, and Fe₂O₃ were measured by x-ray fluorescence spectrometry (RS-1818, HORNG JAAAN). The contents of Cd were determined by graphite furnace atomic absorption spectrophotometry (AA6810SONGPU), and the contents of Hg and As were determined by atomic fluorescence spectrometry (XGY-1011A). In order to ensure the accuracy of the data, the National Geological Experimental Testing Center took the relevant quality assurance and quality control (QA/QC)
measures, and the recovery rate of each standard sample was between 92% and 108%. The standard deviation of 20% of the samples was less than 5%.

3.2. Data Processing. Geochemical statistical analysis and multivariate statistical analysis are effective tools to identify pollution sources. These methods were used to identify the main sources of heavy metals in soil. Kriging interpolation method in MapGis 6.7 was used for spatial mapping [10]. Data were analyzed by Pearson correlation analysis, principal component analysis (PCA), and cluster analysis (CA) in SPSS16.0, in which the maximum variance rotation method was adopted for principal component analysis (PCA).

3.3. Assessment Methods. The single factor index method is widely used to evaluate the pollution of single heavy metal elements in the soil. The calculation formula is as follows:

\[ P(i) = \frac{C_i}{S_i} \]  \hspace{1cm} (1)

where \( P(i) \) is the environmental quality index of pollutants (\( i \) is an element) in soil, \( C_i \) is the measured concentration of heavy metals in soil, and \( S_i \) is the assessment standard value of heavy metals in soil. In the research, the soil background value of a city was used as the assessment standard of heavy metals in soil. The segmented assessment criteria of \( P(i) \) value were as follows: \( P(i) \leq 1 \) means no pollution, \( 1 < P(i) \leq 2 \) means light pollution, \( 2 < P(i) \leq 3 \) means moderate pollution, and \( P(i) > 3 \) means heavy pollution.

In addition, the potential ecological hazard index method proposed by Swedish scholar Hakanson in 1980 was used to evaluate the soil environmental risk. The Hakanson index method comprehensively considered the synergistic effect of multiple elements, toxicity level, pollution concentration, and environmental sensitivity to heavy metal pollution. It could reflect the impact potential of heavy metals on the ecological environment comprehensively and was suitable for the assessment and comparison of sediment and soil in a large regional range. The calculation formula is as follows:

\[ E(i) = T_i \times \left( \frac{C_i}{C_0} \right), \]  \hspace{1cm} (2)

where \( E(i) \) is the potential ecological risk coefficient of a single heavy metal and \( T_i \) is the toxicity response coefficient of a single heavy metal, and the toxicity coefficients of each metal are: \( \text{Ni} = \text{Pb} = 5, \text{Cr} = \text{V} = 2, \text{As} = 10, \text{Cd} = 30, \text{Zn} = 1, \text{and} \text{Hg} = 40 \). \( C_i \) represents the concentration of heavy metals in soil. \( C_0 \) is the assessment standard value of heavy metals in soil. In the research, the soil background value of a city was used as the assessment standard of heavy metals.

The sum of the potential ecological risk coefficient \( E(i) \) of each element is the potential ecological risk index (RI) of this region. The calculation formula is as follows:

\[ \text{RI} = \sum E(i). \]  \hspace{1cm} (3)

According to the potential ecological risk coefficient of each element and the comprehensive potential ecological risk index, soil quality can be divided into five grades: mild ecological pollution, moderate ecological pollution, intense ecological pollution, very intense ecological pollution, and extremely intense ecological pollution (see Table 1).

4. Result Analysis

4.1. Characteristics of Heavy Metal Content in Soil. The enrichment coefficient is the ratio of the average content of heavy metals in soil to the background value in this area, and the enrichment ratio is the proportion of the samples exceeding the natural background value to the total samples. The average value, enrichment coefficient, and local background values of each metal element in the research area are listed in Table 2.

The results showed that the average contents of heavy metals: Ni, V, Cr, As, Cd, Pb, Zn, and Hg were 21.773 mg/kg, 70.642 mg/kg, 55.476 mg/kg, 6.957 mg/kg, 0.144 mg/kg, 24.285 mg/kg, 67.724 mg/kg, and 0.046 mg/kg, respectively. The average values of Ni, V, Cr, As and Hg were slightly lower than the background values of a city. And the enrichment coefficients (EF) of these elements were less than 1, which were 0.88, 0.89, 0.91, 0.90, and 0.78, respectively. The average values of Cd, Pb, and Zn elements were greater than the background value of a city, and the enrichment coefficients were greater than 1, which were 1.21, 1.03, and 1.18, respectively.

Box diagrams and histograms of elements are commonly used to represent the distribution characteristics of elements (see Figure 2). Some researches have shown that in the natural state; if there is no other external source, the element is normally distributed. As shown in Figure 2, Ni, V, Cr, and As are approximately normally distributed. And it is speculated that they are mainly affected by natural factors and less by exogenous factors. However, Cd, Pb, Zn, and As are not normally distributed, which means that these elements may have external input [11]. In addition, the box diagram shows that Ni, V, Cr, and As are distributed symmetrically except for a few outliers. However, Cd, Pb, Zn, and Hg elements not only have an obvious trend to the right but also appear partial outliers at both ends of the box diagram.

4.2. Spatial Distribution of Heavy Metals in Soil. The geochemical map of heavy metal element content can provide effective information for the source and pollution range of elements. In the research, the cumulative frequency method was used to classify the elements, and the Kriging interpolation method was used to draw the spatial distribution map of each element’s content combined with the location of sampling points. The contents of Ni, V, Cr, and As were low in the west but high in the east and north. The enrichment proportions of these four elements were low, which were 30.89%, 29.86%, 32.2%, and 26.67%. The vast majority of the research area was covered by Quaternary sediments, with
only a small range of limestone and dolomite exposed in a few areas in the north and east [12]. Because the weathering degree of rocks was controlled by environmental factors, topographic conditions, and exposure time, the more thoroughly the weathering degree is, the higher the enrichment degree of Si, Al, Fe, and other elements is. Among them, Al2O3/SiO2 is a commonly used index to calculate the weathering degree, which can indirectly explain the weathering degree of rock. The higher the Al2O3/SiO2 ratio is, the higher the weathering degree is. Fe2O3, as a product of rock weathering into the soil, is an important component of soil, and Fe2O3 can adsorb heavy metals in soil by affecting the charge properties of the soil surface so that Cr, As, and other elements in the surrounding soil of mountainous areas present significant high values. Similar researches have been reported in the southern area of a city. According to the spatial distribution of Fe2O3 and Al2O3/SiO2, it can be seen that the weathering degree of rocks in the northern and eastern parts of the research area is relatively high. The area with high Ni, V, Cr, and As contents is consistent with the area with a high degree of rock weathering, indicating that these four elements are mainly affected by rock weathering.

Compared with the above four elements, the enrichment proportion of Cd, Pb, and Zn elements was 66.29%, 45.63%, and 63.38%, respectively. The maximum content was found in a few areas in the central and northwest regions. The middle part of the research area was the area with the largest population concentration density in a county. G101 and highway ran through the area. And there were many well-known scenic spots and leisure resorts in the northwest of the research area. It was speculated that these three elements may be affected by local human activities. The enrichment proportion of Hg in soil samples in the research area was 14.37%, and the highest content was found in the central residential area. Because Hg was volatile and could be widely exchanged between soil and air, it formed unique distribution characteristics.

4.3. Principal Component Analysis and Cluster Analysis. The principal component analysis is a method that converts multiple indexes into a few comprehensive indexes to reflect
the original data information, which is used to distinguish various metal sources in soil research. Elements with a high load on the same principal component may have similar sources [13]. Principal component analysis of heavy metal elements in the research area showed that 3 principal components were extracted from the eight heavy metal elements (see Table 3). These three groups of principal components could explain 78.51% of the total variance, which should be considered the main component. The variance of other components was less than 10%, so these three groups of factors were mainly discussed in the research.

The variance of the first principal component accounted for 43.34% of the total variable variance. Although the variance of the first principal component did not exceed 50%, the variance of the first principal component was the largest among the three principal components, indicating that the first principal component obviously affected the behavior characteristics of soil heavy metals in this area. The Ni, V, Cr, and As elements had higher loading on the first principal component, and the enrichment coefficient of the above four elements was low. The histogram showed that the Ni, V, Cr, and As elements had normal distribution and the spatial distribution of element content showed that the high values of Ni, V, Cr, and As elements appeared in the areas with high weathering degrees. These results indicated that these elements were less affected by exogenous substances and were mainly controlled by soil parent materials in this area, which was consistent with the above conclusion.

The second principal component accounted for 23.74% of the variance of the total variables. Cd, Pb, and Zn elements had a high load on the second principal component. The average values of these three elements all exceeded the background values, and their enrichment coefficients were high. The histogram showed that they were not normally distributed. The spatial distribution diagram of element content showed that the above elements had high values in the central and northwestern regions of the research area. Local agricultural activities such as planting crops and raising livestock were the main factors affecting Cd, Pb, and Zn elements in the soil. Large orchards and vegetable gardens may have been planted in the research area in order to provide an urban area with quality and sufficient agricultural products, and fertilizers and pesticides may have been used. Cd and Zn were the main additives of phosphate fertilizer and zinc fertilizer because of their insecticidal and growth-promoting effects. The application of chemical fertilizer was one of the main factors affecting the heavy metal Cd and Zn in soil. The use of Pb insecticides also significantly increased Pb content in orchard growing areas. It was very common for local agricultural planting to use plastic film, and the residual plastic film in the soil also led to the increase of Cd content in the soil [14]. In the research area, animal husbandry was developed, and livestock manure was considered to be a good supply source of soil Zn. Long-term application of organic fertilizer could increase the content of Zn in soil by 5%–30%. Other researches showed that Zn content in soil would also show a trend of accumulation with the increase of the planting years of greenhouse vegetable plots [15]. In addition, anthropogenic disturbances in scenic spots and leisure resorts could also enrich elements. In addition to the inheritance from the parent materials, the above three elements were obviously interfered with by human factors.

The third principal component of Hg accounted for 11.43% of the variance of the total variable. Hg was different from other elements because of its volatility, so it was divided into a separate category. Building facilities and medical facilities in densely populated areas greatly increased the Hg content in the environment. Meanwhile, the lifestyle of local residents such as sewage irrigation and garbage incineration was also one of the important factors affecting Hg content.

The first principal component (F1) included Ni, V, Cr, and As, which were high in the northern and eastern parts of the research area due to the influence of rock weathering and soil parent material. The second principal component (F2), including Cd, Pb, and Zn, was higher in densely populated areas of the research area and was greatly affected by human activities. The high value of Hg in the third principal component (F3) was mainly affected by atmospheric deposition in the research area.

Cluster analysis is a method to classify variables according to the degree of intimacy between variables. Through cluster analysis, variables with similar characteristics and behaviors can be grouped into a group, which has been widely used in statistical analysis [16]. The application of cluster analysis in earth science can cluster the elements from the same material source into one class and distinguish the elements from different material sources. The distance of cluster analysis represents the closeness degree between elements. The closer the clustering distance is, the closer the relationship between elements is. In this research, eight heavy metal elements were divided into three groups according to the standard distance of 15–20. The results of cluster analysis and principal component analysis were similar.

Category I: Ni, V, Cr, and As elements. The distribution of the four elements in soil samples accorded with normal distribution, and the enrichment coefficient was less than 1. They have a higher load in the first principal component, and higher values only appear in the area with a higher weathering degree of rock. This indicates that the distribution of elements Ni, V, Cr, and As in the study area is relatively uniform. The categories of heavy metals were mainly influenced by natural factors and derived from soil parent material formed by weathering of local rocks.

Category II: Cd, Pb, and Zn elements. The histogram showed that the above three elements were not normally distributed and the enrichment coefficient was greater than 1, which occupied a high load in the second principal component. This kind of element was the most seriously polluted element in soil. And the pollution of this kind of element has been reported in many literature.

Heavy metal elements Pb and Zn are known as traffic pollution elements. The closer the road is, the higher the content of Pb is. And the accumulation of Pb content is closely related to traffic flow. Pb is considered a landmark element of vehicle pollution, and vehicle exhaust becomes one of the important sources of Pb in soil due to the
combustion of leaded gasoline. Although the use of leaded gasoline has been banned in China since 2000, the high content of Pb in this area obviously reflects the severity of Pb gasoline pollution in the past because of its strong stability and difficulty in degradation [17]. Pb and Zn elements in the environment have very similar sources. The driving of motor vehicles, the oxidation of motor lubricating oil, the wear of brakes and tires, and the shedding of paint all affect the accumulation of Zn in the soil. Cd is a typical element introduced into the environment by human activities. Industrial activities such as metal smelting, production of plastic stabilizers and additives and batteries, burning of fossil fuels, and production of industrial wastes in the research area can affect the content of Cd in soil [18].

Category III: Hg element. The use of coal for heating in the Beijing-Tianjin-Hebei region has increased significantly in recent decades, and Hg released by coal combustion is directly discharged into the environment, which also makes Hg remain in the soil in the form of atmospheric deposition [19].

4.4. Ecological Risk Assessment. The single pollution index and ecological hazard index of eight heavy metal elements were calculated. The potential ecological risk coefficient of each element and the number of samples under different single pollution levels were calculated. The results were listed in Table 4. The results showed that most of the sampling sites of the eight elements were not polluted, and the single pollution index \( P(i) \) of a few sampling sites of a few heavy metals was slightly greater than the range of moderate pollution. Among them, the mean value of the single pollution index of Cd element was the largest \( \left( P(\text{Cd})_{\text{mean}} = 1.21 \right) \), followed by Zn \( \left( P(\text{Zn})_{\text{mean}} = 1.18 \right) \) and Pb \( \left( P(\text{Pb})_{\text{mean}} = 1.03 \right) \). Previous researches reached similar conclusions [20, 21]. The average pollution indexes of the other five elements were all less than 1 \( \left( P(\text{Cr})_{\text{mean}} = 0.91, P(\text{As})_{\text{mean}} = 0.90, P(\text{V})_{\text{mean}} = 0.89, P(\text{Ni})_{\text{mean}} = 0.88, \right) \) and \( P(\text{Hg})_{\text{mean}} = 0.78 \). It indicates that the soil was not contaminated. According to the mean value of single factor pollution index, the order was \( \text{Cd} > \text{Zn} > \text{Pb} > \text{Cr} > \text{As} > \text{V} > \text{Ni} > \text{Hg} \).

The potential ecological risk of eight heavy metal elements in the research area was evaluated by the Hakanson assessment method, and the potential ecological risk coefficient \( E(i) \) and potential ecological risk index \( RI \) of eight heavy metal elements were calculated. The results showed that the \( E(i) \) values of the eight heavy metals were all lower than 40, indicating that the single factor ecological pollution risk was low. Combined with the sampling points, the potential ecological risk index map could be drawn. RI values of more than 94% of the sampling points in the research area were lower than 150, indicating that the potential ecological harm index of local heavy metals was low and below the level of mild ecological pollution [22]. A very small number of high values occurred in local residential areas, indicating that the current soil environmental protection was good. It was suggested to maintain the current soil protection measures and create a good living environment [23–25].

5. Conclusions

In the research, 1,065 soil samples were collected in the southwest of a city and 8 heavy metals were analyzed. Spatial analysis and multivariate statistics were used to clarify the distribution characteristics of heavy metals in soil, and the main factors affecting the distribution characteristics were discussed. The results showed that the average value of Ni, V, Cr, and As elements was lower than the background value of the city. The histogram was normal distribution, and it had a high load on the first principal component of principal component analysis. The spatial distribution diagram of element content showed that the contents of Ni, V, Cr, and As elements were higher in the northern and eastern areas of the research area with a high degree of rock weathering. It showed that its distribution was mainly affected by the parent material of soil formation. Cd, Pb, and Zn element background value was higher compared to the average content of the city region. The enrichment coefficient was greater than 1. The content of the histogram did not obey the normal distribution, and the principal component analysis of the load on the second principal components was relatively high. And the three elements in densely populated and range larger regional content was higher; it may be affected by artificial factors such as local traffic, agriculture, and tourism. Hg had a non-normal distribution and was independently divided into the third principal component. Due to its volatility, its distribution characteristics were mainly affected by atmospheric deposition.

By calculating the single pollution index, potential ecological risk coefficient, and potential ecological risk index of each heavy metal element in a certain area, it could be concluded that all indexes of heavy metal elements in the local soil were low and below the level of mild pollution. However, long-term human activities may lead to continuous accumulation of heavy metals, which may pose a threat to the soil quality in the future. Therefore, attention should be paid to soil quality safety and prevention.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.
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