

Monitoring and Ecological Risks of Heavy Metals of Urban Soils in Different Functional Areas Based on Plasma Technology

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open Monitoring and ecological risks of heavy metals of urban soils in different functional areas based on plasma technology

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Heavy metal pollution in soil has become a global environmental problem in recent years. This study assessed heavy metals' pollution distribution, level and ecological risk in soils from different functional areas in Shihezi City, China. Heavy metals (Cr, Cu, Pb, Zn, Ni, and Cd) were measured using atmospheric pressure discharge plasma and inductively coupled plasma mass spectrometer. The mean concentration of all heavy metals in soil was higher than heavy metals' background values. The spatial distribution of Cr is the most different, and the distribution of Cu and Zn are similar in other functional regions. The single pollution index indicated that the heavy metals in industrial, traffic, and residential areas were enriched, and the pollution of Cd was more severe than others. The Nemerow pollution index showed that the near Manas River basin coast is alert (still clean), the industrial area is moderately polluted, and all other functional areas are lightly polluted. The potential ecological risk index demonstrated that only the nearshore Manas River Basin is at a mild ecological risk level, while all other functional areas are at a moderate ecological risk level. The determinate power of DEM, temperature, and precipitation were all over 65%, which meant that the topographic and climatic factors were the main factors affecting the change of heavy metal content. Secondly, socio-economic factors are important factors to promote the change of heavy metal content in soil.

In recent years, with the rapid development of industrialization and urbanization, the number of sudden environmental pollution events caused by heavy metal pollution has increased dramatically.¹ Heavy metals enter the environment at high concentrations within a short period of time, posing a threat to human health and urban environmental quality.^{2,3} Under Heavy metals eventually sink into the soil under the action of different pollution sources and exhibit complex spatial variability.⁴ To a certain extent, the spatial variation characteristics of soil heavy metals can reflect the source and intensity of heavy metal pollution. Therefore, the study of the content of heavy metal elements in soil and their spatial distribution is a prerequisite for carrying out research related to the prevention and control of soil pollution and the early warning of soil environmental risks.⁵ The detection techniques concerning heavy metals have also shown a trend toward automated, intelligent, integrated, and accurate rapid detection. The most widely used detection methods include inductively coupled plasma mass spectrometry/atomic emission spectrometry (ICP-MS/AES), atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), laser-induced breakdown spectrometry (LIBS), etc.⁶ Furthermore, atmospheric pressure discharge plasma technology (APDP) has a promising future for detecting heavy metals in soil because it eliminates the need for a costly vacuum system, simplifies experimental equipment, and lowers production costs.⁷ Therefore, combining ICP-MS with APDP to detect heavy metal concentrations can improve the accuracy of results while also lowering the cost of testing samples.

In the practical application of conducting environmental pollution monitoring, the focus is no longer only on the specific content of pollutants at a particular location in space, but more on the spatial analysis of continuous areas.⁸ At present, a large number of studies have been conducted on the spatial distribution

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characteristics of soil heavy metals for different scales and analytical perspectives, such as heavy metal migration direction, national, provincial, functional areas, and land use patterns.^{9, 10} In the horizontal direction, by extracting surface soil samples, it was found that the content of heavy metals generally showed a trend of decreasing in concentric circles in all directions with increasing distance from the point source. In the vertical direction, by sampling the soil in layers, the soil heavy metal content basically showed a trend of gradually decreasing from the surface layer downward. Scholars from various countries have studied the sources, characteristics, distribution, and risk assessment of heavy metals in the soils of forests, plains, wetlands, coastal zones, and around different functional areas and along roads. This is in addition to more studies on the spatial distribution of heavy metal pollution in cities, farmlands, and mining areas.^{11–13} In Rizhao, China, Lv *et al.*¹⁴ investigated the relationship between heavy metals and scales at various spatial scales. They discovered the environmental elements that influence spatial variability at different scales. Besides, for the analysis of the driving factors affecting the change of heavy metal content, the geodetector is able to iterate the multi-source spatial display data with economic statistics and other attribute analysis data, and is widely used to explore the multi-factor interaction influenced by nature, society, and the economy.¹⁵ Urban soils, on the other hand, support a dense population and frequent industrial activities, with varying degrees of human activity in different functional sectors. As a result, increasing urban soil environmental quality and human habitat require a thorough examination of urban heavy metal pollution's geographic distribution, ecological risk, and pollution drivers.¹⁶

Shihezi city's heavy industrial park is adjacent to agricultural land. It has a fragile ecological environment that has changed rapidly and significantly in recent years due to human activities and natural disturbances. In light of this, this study used ICP-MS and APDP techniques to examine heavy metal concentrations (Cr, Cu, Pb, Zn, Ni, Cd) in five functional areas in Shihezi, China. The main goals were to (1) investigate the distribution patterns of heavy metals in soils from the five functional areas; (2) to assess the extent of soil heavy metal contamination and the potential ecological risks; and (3) to investigate the relationship between soil heavy metal contamination and geoenvironmental factors using a geodetector model to identify possible heavy metal sources.

Materials and methods

Overview of the study area. The studied city, Shihezi, with an area of 6,007 km², belongs to Xinjiang Uygur Autonomous Region, China. Shihezi is the central city of the economic belt on the northern slope of Tianshan Mountain. It is located at latitudes ranging from 43° 26' to 45° 20' N and longitudes ranging from 84° 58' to 86° 24' E (Fig. 1). Shihezi is the new military reclamation city's farm-based, industry-led, urban-rural, agricultural, and industrial integration. Shihezi's urban population reached 579,800 in 2018, with an urbanization rate of 83.2%, a regional Gross Domestic Product (GDP) of 53.778 billion yuan, and a per capita GDP of 82,584 yuan, according to the Shihezi Statistical Yearbook 2019. Shihezi experiences a long, cold winter and a short, hot summer. It has a typical temperate continental climate with annual mean temperatures ranging from 25.1 to 26.1°C and annual precipitation ranging from 125.0 to 207.7 mm. The city's topography is flat, and the soil is mostly grey desert soil, tidal soil, and meadow soil, with sparse native surface vegetation, primarily in the Gobi desert landscape. In recent years, new enterprises have been introduced on a continuous basis, and the combined effect of many factors has influenced the quality of Shihezi's ecological environment.

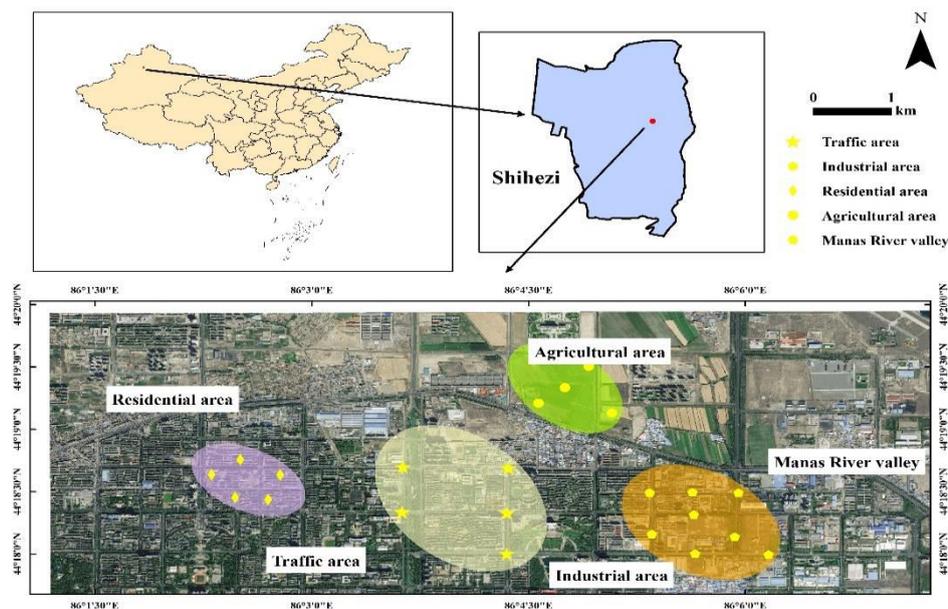


Figure 1. Map of study area and location of soil sampling sites.

Data processing and analysis methods.

Single factor pollution index (P_i). The single factor pollution index method uses measured data and standard comparative classification to evaluate the degree of pollution for a particular pollutant in the soil.²³ The basic equation is as follows:

$$P_i = \frac{C_i}{S_i} \quad C_i \leq S_a \quad (1)$$

In the formula, P_i is the environmental quality index of pollutant i in soil, C_i is the measured concentration of pollutant i (mg kg^{-1}), S_i is the evaluation standard of pollutant i (mg kg^{-1}), and the background value of soil elements in Xinjiang is selected.

Nemerow pollution index (P_N). The single factor pollution index method can only reflect the pollution degree of individual heavy metal elements. To fully reflect the pollution of the soil environment by various heavy metal elements, the Nemerow pollution index method can take into account the average value of the single factor pollution index and the highest value to highlight the role of the more polluting heavy metal pollutants.²⁴ It is defined based on the following formula:

$$P_N = \sqrt{\frac{[(P_i)_{ave} + ((P_i)_{max})^2]}{2}} \quad (2)$$

In the formula, P_N is the comprehensive pollution index, $(P_i)_{max}$ is the maximum of the single factor pollution index, $(P_i)_{ave}$ is the average of the single factor pollution index. The grading criteria of the single factor pollution index method and the Nemerow pollution index method are shown in Tab. 1.²⁵

Potential ecological risk index (RI). The Swedish scientist Hakanson proposed an index system for assessing the potential ecological risk of soil heavy metal accumulation, which can link heavy metal content in soil with synergistic effects of multiple elements, ecological and environmental effects, and toxicology according to the nature and physicochemical environment of heavy metals, in order to improve the potential ecological risk assessment of soil heavy metals.²³ The RI is computed as follows:

$$RI = \sum_i^m E_r^i = \sum_i^m T_r^i \times \frac{C_i}{S_i} \quad (3)$$

In the formula, RI is the potential ecological risk index of multiple heavy metals in soil, C_i is the measured value of a single element, S_i uses the background value of soil environment in Xinjiang as the reference standard, T_r^i is the toxicity coefficient of class i heavy metal elements ($\text{Cd}=30$; $\text{Cu} = \text{Ni} = \text{Pb} = 5$; $\text{Zn} = 1$; $\text{Cr} = 2$), E_r^i is the potential ecological hazard coefficient of heavy metals.²⁶ Based on the categorization established by Hakanson *et al.*, the risk classification of E_r^i and RI was scientifically adjusted according to the type and toxicity of the heavy metals evaluated in this study. The maximum of all T_r^i 's evaluated should be used as the initial cut-off value for E_r^i (i.e., $T_{Cd}^i = 30$). The first cut-off value for RI was obtained by taking $\sum T_r^i \times 1.13$ and taking ten integers, with the rest being twice the previous level in order.²⁷

Grade	Standard grade of single pollution index		Standard grade of comprehensive pollution index		Mean Standard grade of potential ecological risk coefficients (E_r^i) and risk index (RI)		
	Pollution index	Pollution level	Pollution index	Pollution level	Pollution index		Pollution level
1	$P_i < 1$	Clean	$P_N \leq 0.7$	Safety	$E_r^i < 30$	$RI < 60$	Mild ecological risk
2	$1 \leq P_i < 2$	Light pollution	$0.7 < P_N \leq 1$	Alert line	$30 \leq E_r^i < 60$	$60 \leq RI < 120$	Moderate ecological risk
3	$2 \leq P_i < 3$	Moderate pollution	$1 < P_N \leq 2$	Light pollution	$60 \leq E_r^i < 120$	$120 \leq RI < 240$	High ecological risks
4	$P_i \geq 3$	Heavy pollution	$2 < P_N \leq 3$	Moderate pollution	$120 \leq E_r^i < 240$	$240 \leq RI < 480$	Very high ecological risk
5			$P_N > 3$	Heavy pollution	$E_r^i \geq 240$	$RI \geq 480$	Extremely high ecological risk

Table 1. The criterion of pollution grade of soil heavy metals.

Geographical detector. Geographical detectors are a statistical method that can detect both spatial heterogeneities and test the consistency of the spatial distribution of two variables, revealing the driving forces behind them.¹⁵ Factor detectors in geographical detectors are able to determine the degree of influence of a factor on the variation of soil heavy metal content using the explanatory power of the factor.²⁸ This study used the six heavy metal contents in the study area as dependent variables and the driving factors as independent variables. The power determinant (PD) of each driving factor was obtained using a factor detector to explore the degree of influence of each driving force. The selection of the driving factors included natural factors and socio-economic factors. The natural factors include land-use type, Digital Elevation Model (DEM), soil type, soil

texture, temperature, and rainfall; the socio-economic factors include population and GDP. ArcGIS 10.3 was used to extract the heavy metal content and driver values for the spatial location of each sampling point for analysis.

The data for the required driving factors were obtained from the Chinese Academy of Sciences' Data Center for Resource and Environmental Science (<http://www.resdc.cn/>). This study reclassifies land-use types according to the primary classification and data description of the Standard for Classification of Land Use Status (GBT 21010-2017), taking into account the characteristics of the natural environment and research needs of Shihezi city. Finally, the land was classified into six categories: arable land, forest land, grassland, water areas, construction land, and bare land. All the above data points were resampled to 1 km for the experiment, and the projection was uniformly transformed into Albers.

Results and discussion

Statistics on the concentration of heavy metals in soil. The statistics on the concentrations of heavy metals in the soil of Shihezi City are presented in Tab. 2. The mean values of Cr, Ni, Cu, Zn, Pb, and Cd content were 60.93, 29.04, 32.77, 75.11, 19.84, and 0.26 mg kg⁻¹, respectively. The average values of these six heavy metals did not exceed the secondary standards in the National Soil Environmental Quality Standards (GB 15618-1995). Still, the average values of the six elements were 1.24, 1.09, 1.23, 1.09, 1.02, and 2.17 times the background values of soil elements in Xinjiang, respectively. The exceedance rates of heavy metals at individual sampling sites were greater than 57%, with the exceedance rate of Cd content as high as 93%. This result is consistent with the study of Jia *et al.*²⁹ on regional heavy metal-related soil contamination, which all showed a high enrichment of Cd. It indicates that the city's economic development has influenced the soil's heavy metal content in Shihezi.

The effect of human activities on soil heavy metal content can be expressed using the coefficient of variation. The greater the value of the coefficient of variation, the stronger the degree of disturbance to the heavy metal content and the greater the difference in spatial distribution, and vice versa, the smaller.³⁰ For all six heavy metals, the magnitude of the coefficient of variation is in this order: Cr > Cd > Cu = Zn > Ni > Pb. According to Wilding's³⁰ definition of the degree of variability, the coefficients of variation for Pb and Ni are 28% and 29%, respectively, which are moderate (15% coefficient of variation, 36%). Cr, Cu, Cd, and Zn are all highly variable (coefficient of variation > 36%), with Cr in soil having the highest (56% coefficient of variation), indicating that it is seriously disrupted by human social behavior and has the greatest regional distribution variance. The variance in their distribution could be due to pollution emissions from industrial production, agricultural production activities, and traffic exhaust.³²

Element	Minimum values (mg kg ⁻¹)	Maximum values (mg kg ⁻¹)	Average values (mg kg ⁻¹)	Standard deviation	Coefficient of variation	Background values in Xinjiang province (mg kg ⁻¹)	National Grade II standard (mg kg ⁻¹)
Cr	6.53	143.94	60.93	34.11	0.56	49.30	250.00
Ni	12.37	46.55	29.04	8.37	0.29	26.60	60.00
Cu	13.17	67.46	32.77	12.24	0.37	26.70	100.00
Zn	16.23	144.32	75.11	27.68	0.37	68.80	300.00
Pb	9.24	30.34	19.84	5.48	0.28	19.40	350.00
Cd	0.1	0.51	0.26	0.1	0.38	0.12	0.6

Table 2. Characteristics of statistical analysis of heavy metal content in soils.

The distribution of heavy metals in different functional areas. Heavy metal concentration data was loaded into SPSS software for a normal distribution test to match the requirements of the geochemical baseline and receptor models. Outliers were eliminated based on an interquartile range and histogram. According to the findings, the data for Cr, Ni, Cu, Zn, Pb, and Cd followed a normal distribution. Using ArcGIS software's inverse distance weight interpolation approach, Fig. 3 depicts the spatial distribution of six heavy metals in the soil surface layer of Shihezi City. Overall, the content of heavy metals in different functional areas varied significantly. The hot spots of heavy metal concentrations in soil were all found in the vicinity of traffic areas and industrial areas with intensive human activity in Shihezi, and the heavy metal concentrations decreased significantly with distance from the central area. This result is roughly the same as that studied by Yi *et al.*³³ regarding the distribution characteristics of soil heavy metals in different functional areas. The average contents of Cr and Cd in soil were industrial zone > transportation zone > residential zone > agricultural zone > near shore of the Manas River basin; the average contents of Ni were residential zone > industrial zone > agricultural zone > transportation zone > near shore of the Manas River basin; the average contents of Cu and Pb were transportation zone > residential zone > industrial zone > agricultural zone > near shore of the Manas River basin; the average contents of Zn were transportation zone > residential zone > agricultural zone > industrial area > near shore of the Manas River basin. The similarity of Cu and Zn in different functional areas indicates that both have similar pollution pathways caused by smelting, vehicle exhaust, and brake wear.³⁴ The highest Cd level is found in industrial regions, which is 4.5 times higher than the background value of Xinjiang soils. The residential area has the highest Ni level, which is 1.75 times the Xinjiang soil's background value. The greatest Cr, Cu, Zn, and Pb levels were found in the traffic region, which were 2.92, 2.53, 2.10, and 1.56 times higher than the background values of Xinjiang soils, respectively. This could be owing to the higher volume of traffic in this location, as well as the fact that Cr, Cu, Zn, and Pb in urban soils have been linked to transportation in studies.³⁵

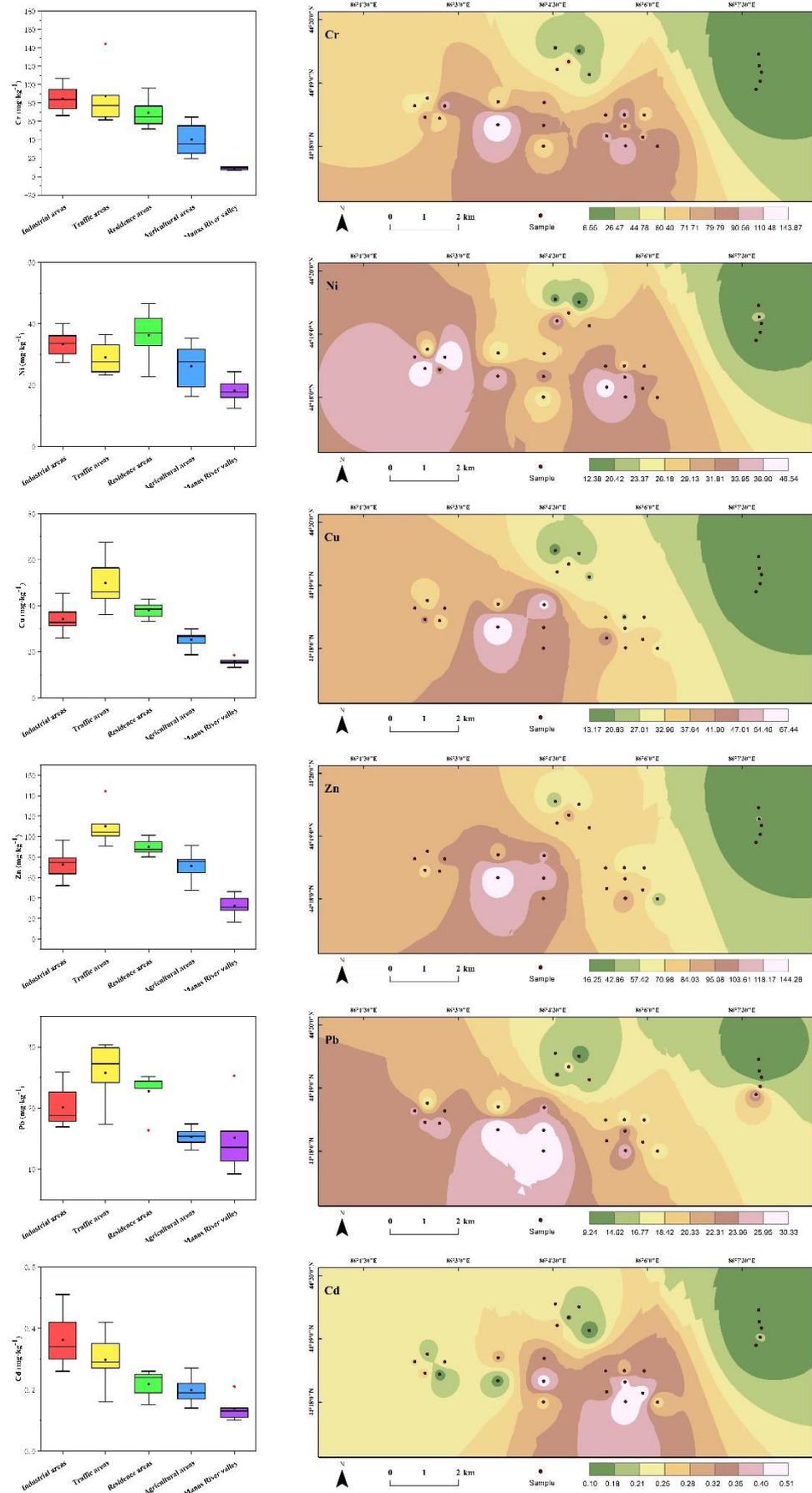


Figure 3. Spatial distribution and box line map of heavy metal content of soil in Shihezi city.

Assessment of soil heavy metal pollution in different functional areas. Using the background value of Xinjiang soil as the evaluation standard, the single factor pollution index method (P_i) and the Nemerow index method (P_N) were used to evaluate the soil heavy metal content, and the pollution index of each functional area is shown in Fig. 4. According to the P_i and P_N evaluation criteria (Tab. 1), the P_i of six heavy metal elements in industrial, transportation, and residential areas are all greater than 1, indicating that they are lightly polluted. It means that all of the heavy metals in these three functional regions have been enriched, and Cd has been severely polluted compared to other heavy metals. Only Cd and Zn are in light pollution along the near Manas River basin and agricultural areas, respectively, while all other heavy metals are in clean condition. In terms of P_N , each functional region's P_N is as follows: industrial area > transportation area > residential area > agricultural area > close shore of the Manas River basin. This result is similar to the ranking of P_N values derived by Liu *et al.*³⁶ for soil heavy metals in different functional areas of Luoyang City. The P_N of the Manas River Basin's near coast is less than 1, indicating it belongs to the alert line (still clean). The industrial area's P_N is greater than 2, meaning moderate pollution. The P_N of soil heavy metals in other functional areas is more than 1, indicating mild pollution. It shows that the environmental contamination issues caused by economic development have threatened Shihezi City's soil quality.

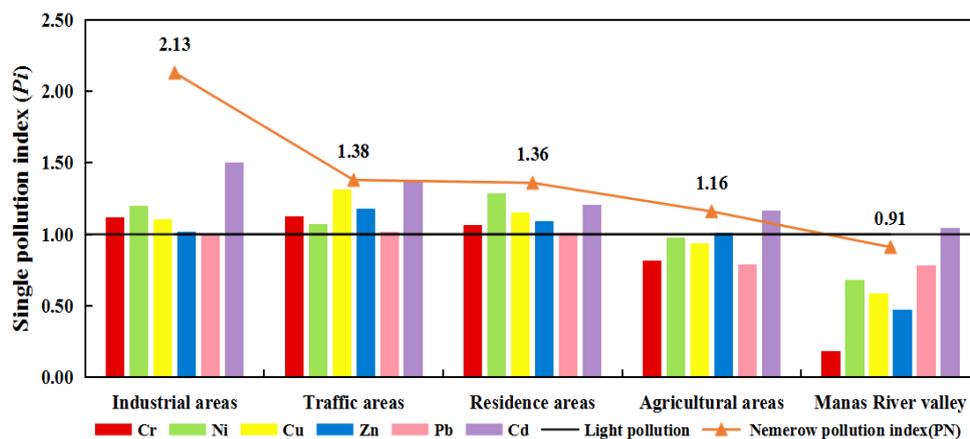


Figure 4. Evaluation index of soil heavy metal pollution in different functional areas of Shihezi city.

Potential ecological risk assessment of heavy metals in soil. The results of potential ecological risk evaluation of heavy metals in Shihezi soils are shown in Tab. 3. From the individual heavy metal potential ecological hazard index (E_r^i), the average levels of heavy metals in Shihezi are Cd > Cu > Ni > Pb > Cr > Zn. The most dominant ecological risk factor in soil was Cd, which had a moderate to high potential ecological risk level. Other heavy metals posed low ecological risks, with E_r^i values less than 30, indicating a mild ecological risk.

The mean values of RI of the potential risk index of heavy metals in the soils of different functional areas are as follows: industrial area > transportation area > residential area > agricultural area > near the shore of the Manas River basin. Among them, only the nearshore of the Manas River Basin is at a mild ecological risk level, while all other functional areas are at a moderate ecological risk level. The relatively high mean RI values in the industrial and traffic areas may be due to the highest contents of soil Cd, Cu, and Pb in this area and the high toxicity coefficients of these three heavy metals, which need to be alerted. Secondly, the soil sampling sites in the traffic area are located in a busy traffic area, where the flow of people and vehicles is high, so the mean value of RI of heavy metals in the traffic area is higher.

The spatial characteristics of potential ecological risk levels under the synergistic effect of six heavy metals are shown in Fig. 5. Combining Fig. 3 and Fig. 5, it can be seen that the spatial distribution characteristics of potential ecological risk of soil in different functional areas are similar to the spatial distribution of soil heavy metal content, showing a gradual decrease from southwest to southeast. The highest ecological risk levels are found in industrial areas and busy commercial crossroads, whereas the lowest values are found primarily near the Manas River basin. Meanwhile, the regional distribution characteristics of the potential ecological risk are nearly identical to the spatial distribution trend of Cd, showing that Cd is the primary source of soil contamination in the research area. The main causes of the most serious Cd contamination and potential ecological risk in soils may be the high levels of Cd in soot and wastewater emitted from industrial areas. In addition to industrial pollution, fossil fuel combustion and transportation are also essential sources of Cd in urban soils.³⁷

Functional	E_r^i	RI
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	Cr	Ni	Cu	Zn	Pb	Cd	
Industrial areas	3.43	6.27	6.41	1.06	5.19	90.31	112.68
Traffic areas	3.54	5.43	9.33	1.61	6.65	74.50	101.06
Residence areas	2.82	6.80	7.12	1.30	5.85	54.50	78.39
Agricultural areas	1.63	4.90	4.72	1.04	3.94	49.50	65.72
Manas River valley	0.36	3.41	2.93	0.47	3.90	34.50	45.57

Table 3. Evaluation of potential ecological risks in different functional areas of Shihezi city.

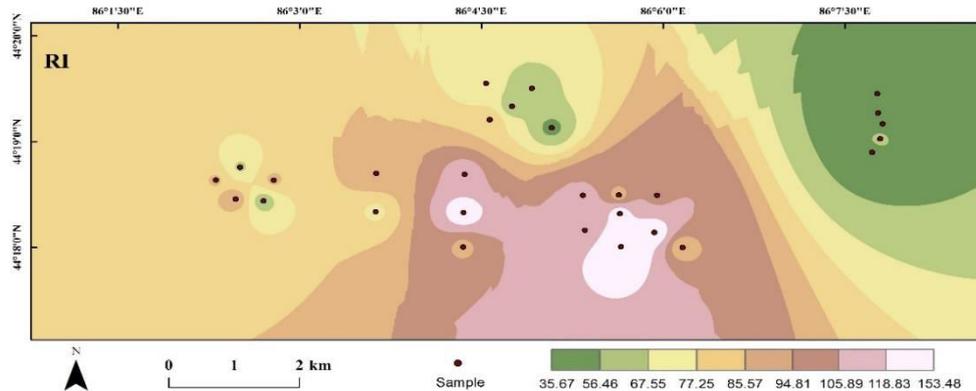


Figure 5. Spatial distribution of the heavy metals potential ecological risk index in surface soils of Shihezi city.

Driving force analysis of heavy metals in soils. The variation of soil heavy metal content in Shihezi is influenced by a combination of natural, economic, and social factors, and the data for each geoenvironmental factor (Fig. 6) was finally extracted in ArcGIS 10.3 for the corresponding sampling point values to be analyzed using Geodetector software (the results are shown in Tab. 4). Tab. 4 shows that, in terms of the overall influence of each factor on soil heavy metals, natural factors such as DEM, temperature, and rainfall had relatively strong explanatory power on the six heavy metals, all above 65%, while land use types had relatively weak explanatory power, all below 50%. For Cr, Pb, and Cd, soil type had low explanatory power, with PD values of only 28%. It appears that DEM, temperature, and rainfall are the most important elements influencing soil heavy metal changes, while land use type and soil type have little effect. Besides DEM, precipitation and temperature, population and GDP also have some explanatory power (60% ~ 82%). This indicates that socio-economic factors are important factors driving the changes in soil heavy metal content. Temperature and precipitation showed the largest explanatory power (92%) for variations in Cu concentration, while soil type had the poorest explanatory power (21%, 22%) for Cr and Pb, respectively.

Heavy metal	Land use type	DEM	Soil type	Soil texture	Population	GDP	Temperature	Precipitation
Cr	0.48	0.88	0.22	0.53	0.65	0.65	0.83	0.83
Ni	0.47	0.65	0.39	0.46	0.60	0.60	0.67	0.72
Cu	0.36	0.73	0.41	0.60	0.81	0.81	0.92	0.92
Zn	0.39	0.76	0.54	0.57	0.82	0.82	0.87	0.87
Pb	0.32	0.77	0.21	0.40	0.71	0.71	0.85	0.89
Cd	0.31	0.86	0.28	0.42	0.78	0.78	0.72	0.73

Table 4. PD values of various factors related to the evolution of heavy metal content in soils.

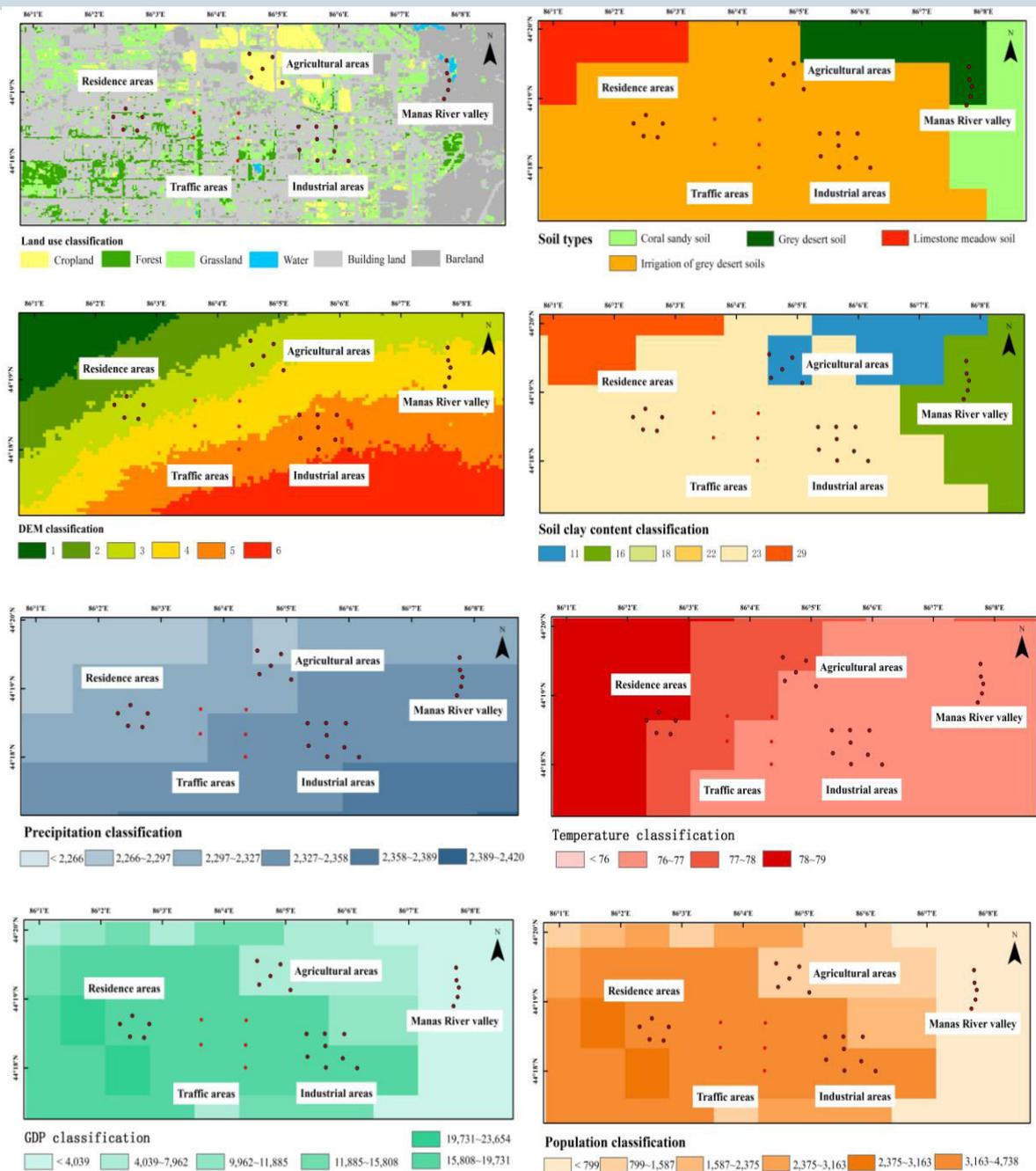


Figure 6. Geographical environmental factor (hierarchical) spatial representation.

conclusion

Although the mean values of Cr, Ni, Cu, Zn, Pb, and Cd in Shihezi did not exceed the secondary standards set forth in the National Soil Environmental Quality Standards, they were 1.24, 1.09, 1.23, 1.09, 1.02, and 2.17 times higher than the background values of soil elements in Xinjiang, respectively. Cr is seriously disturbed by human social behavior in terms of coefficient of variation, and the spatial distribution varies significantly. Different land use types have an impact on the content of soil heavy metals in general. The concentration of soil heavy metals varies greatly among Shihezi city's functional regions, while Cu and Pb levels are consistent across them. The P_N values for each functional area were as follows, in that order: industrial area > transportation area > residential area > agricultural area > close coast of Manas River basin. Cd levels were high in the industrial area; Cr, Cu, Zn, and Pb levels were high in the transportation area; and Ni levels were high in the residential area. In terms of the total potential ecological risk level, the characteristics of the spatial distribution of potential ecological risk in soils of different functional areas are similar to those of the spatial distribution of soil heavy metal content, all showing a gradual decrease from southwest to southeast. From E_r^i , the average levels of soil heavy metals in Shihezi are Cd > Cu > Ni > Pb > Cr > Zn. The average values of R_i^j of heavy metals in soils of different functional areas are industrial areas > transportation areas > residential areas > agricultural areas > near the shore of the Manas River basin, in order. Among them, only the nearshore of the Manas River Basin is at a mild ecological risk level, while all other functional areas are at a moderate ecological risk level. A combination of environmental, economic, and societal factors influenced the change in soil heavy metal content in Shihezi. The main elements impacting the change of soil heavy metal content are DEM, temperature, rainfall, and socio-economic factors. Soil type has no substantial effect on it.

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Author contributions

Meng-Ting Jin, Hao-Yuan, Li-Ping Xu and De-Zheng Yang designed the sampling plan and conducted specific sampling work. Meng-Ting Jin, Quan-Xu and Hao-Yuan performed the experiments and data analysis. Meng-Ting Jin wrote the manuscript and all authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.