

Spatial variability characteristics and source analysis of heavy metals in soils of the Daxia River basin

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Abstract. In order to understand the influence of heavy metals on the surrounding environment in the Daxia River basin and provide a scientific basis for environmental pollution prevention and control, 30 heavy metal samples were collected and the contents of five heavy metals, As, Cd, Cr, Cu and Pb, were detected. The contribution rates of As and Cr were 98.36% and 56.14%, respectively, which were mainly influenced by agricultural activities; the contribution rates of Cu and Pb were 42.28% and 89.80%, respectively, which were more influenced by traffic factors; and the contribution rate of Cd was 35.50%, which was influenced by industrial activities. industrial activities, the estimated probabilities indicate a risk of heavy metal pollution in the northeastern part of the study area in the Daxia River basin.

Keywords: spatial variation; heavy metals; Sources of heavy metals.

1. Introduction

In recent years, the investigation and evaluation of heavy metal pollution status and change characteristics in watersheds have received increasing attention. For example, Yilmaz C H utilized metal pollution parameters such as enrichment factors and geographic accumulation indices to determine and evaluate the pollution status and distribution of heavy metals in agricultural soils, and factor analysis and principal component analysis were used to analyze the sources of pollution [1]. Therefore, this study combines Moran index, variance function theory and geostatistical methods to study the spatial distribution structure of heavy metals in Daxia River Basin and analyze the sources of heavy metals using FA-PCA-APCS-MLR model, which provides a basis for environmental protection and management of Daxia River.

2. Materials and methods

2.1 Overview of the study area

The Daxia River originates from the north and south foothills of the Dabulehka Mountain at the junction of Gan and Qing in the Gannan Plateau, located in the transition zone between the Qinghai-Tibet Plateau and the Loess Plateau (102°02'~103°23'E, 34°51'~35°48'N).

2.2 Data sources and analysis

Field sampling was conducted from 2016 to 2018, using GPS to record the location, and samples were collected from 30 sampling points in the watershed, and the soil samples were sent to the Lanzhou Institute of Chemical Physics of the Chinese Academy of Sciences for testing, As shown in Figure 1.

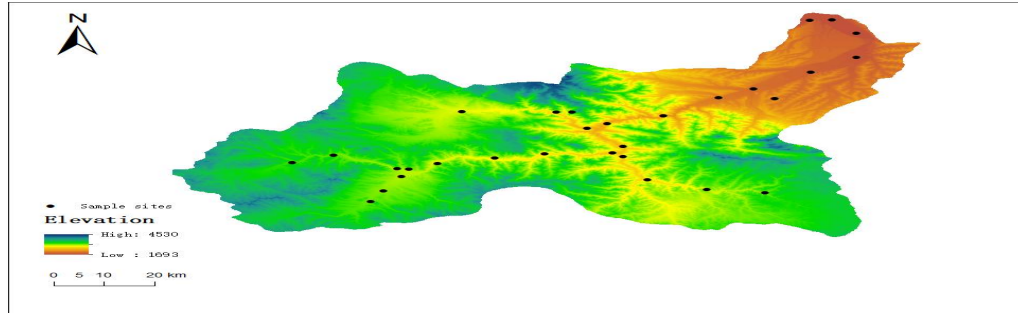


Figure 1. Distribution of points in the study area

2.3 Analysis of heavy metal sources

The basic principle of the absolute factor analysis/multiple linear regression receptor model (APCS-MLR) is to transform the principal factor scores from factor analysis into absolute principal factor scores (APCS), and each indicator content is then multivariate linearly regressed on all APCS separately, with the following equation(1):

$$PC_{mi} = \frac{|a_{mi} \cdot \overline{APCS_{mi}}|}{|b_i| + \sum_m |a_{mi} \cdot \overline{APCS_{mi}}|} \quad (1)$$

where b_i is the constant term of the multiple linear regression, $\overline{APCS_{mi}}$ is the mean absolute principal factor score, a_{mi} is the principal factor score, and $a_{mi} \cdot \overline{APCS_{mi}}$ is the contribution of factor mi to PC_{mi} .

3. Results

3.1 Statistical characteristics of soil heavy metal content

Excel and SPSS24.0 software were used to process the data of five heavy metals, As, Cd, Pb, Cu and Cr, in the soil of Daxia River basin.

Table 1. Statistical characteristic values of heavy metals

HM.	Min	Max	Mean	Medain	Skew	Kurt	SD	CV(%)	Background value
As	5.98	137.80	25.16	21.65	4.44	22.35	22.34	89	0.12
Cu	14.41	31.83	21.10	19.73	0.72	-0.59	4.87	23	24.1
Pb	10.01	21.59	15.30	14.93	0.30	1.30	2.23	15	18.8
Cr	53.22	207.06	96.28	94.32	0.10	1.56	35.11	36	62.2
Cd	0.97	2.3	1.45	1.40	1.48	2.94	0.27	19	12.6

The values of variability less than 15% are classified as less variability, between 15-35% as moderate variability, and if greater than 35% as high variability. Table 1 shows the statistical data of the heavy metal content of soils in the Daxia River basin, the coefficients of variation of Cu and Cd were 23%, 19%, and Pb were medium variability; the coefficients of variation of Cr and As were 36% and 89% were high variability. The larger the coefficient of variation, the more heterogeneous the distribution of elements, indicating that they are influenced by human activities. In Gansu Province, the mean values of As and Cr exceeded the soil background values. Specifically, the heavy metal As exceeded the background value by nearly 25 times, while Cd exceeded this value by 12 times.

3.2 Spatial correlation analysis

3.2.1 Global Moran's I Analysis.

Table 2 summarizes the Global Moran's I for the spatial autocorrelation analysis of heavy metals in the Xiahe basin. correlations were judged by normal distribution within 95% confidence interval based on the magnitude of Z-values, with a two-sided test threshold of 1.96 as the limit.

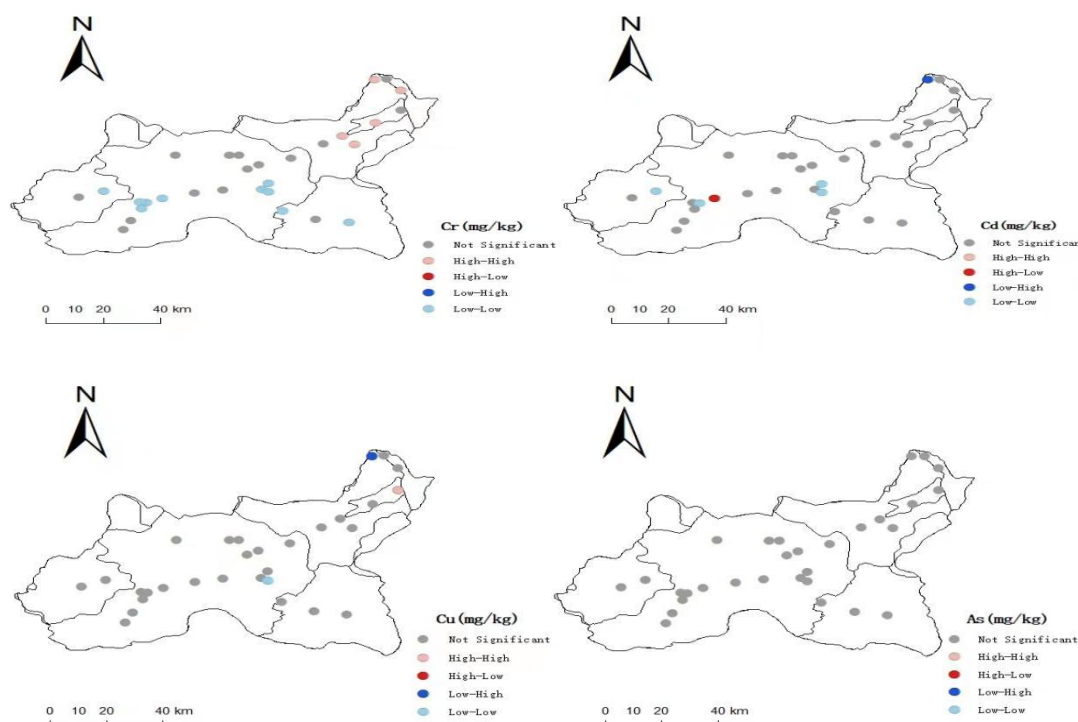
Table 2. Results of Global Moran's I analysis

HM.	Moran	Z	P
Cu	0.064	0.067	0.504
Pb	0.192	1.579	0.114
Cr	0.645	4.754	0.000
As	0.004	0.468	0.640
Cd	0.249	2.026	0.043

The results showed that the normalized spatial autocorrelation index of Cr (4.754) > 1.96, $p(0.000) < 0.05$, and the normalized spatial autocorrelation index of Cd (2.026) > 1.96, $p(0.043) < 0.05$ indicated that Cr and Cd showed positive spatial autocorrelation and the spatial distribution was clustered. the Z values of As, Pb and Cu ranged from 0 ~ 1.96, $p > 0.05$, indicating that the spatial autocorrelation of As, Pb, and Cu was not significant and showed a random spatial distribution. It indicates that the distribution of this element is influenced by anthropogenic factors

3.2.2 Anselin Local Moran's I Analysis.

Anselin local Moran's I analysis was performed using ArcGIS software [2]. As shown in the figure 2, there are five high-value clusters for Cr, one high-value cluster for Cu, and two high-value clusters for Pb. Most of the five heavy metals in the Daxia River basin show non-significance in most areas, while the distribution of Cr, Cd, and Cu have lower levels of heavy metals mostly clustered in the upper and middle reaches of the basin.



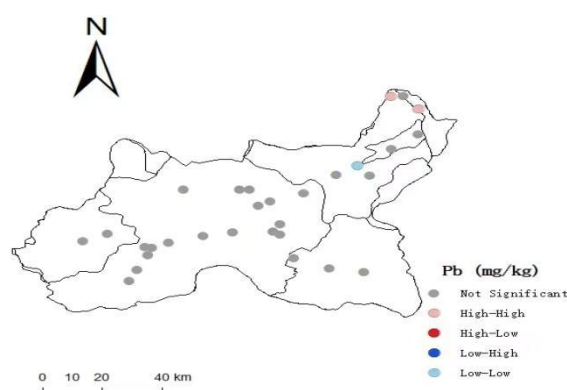


Figure 2. Results of Anselin local Moran's I analysis

3.3 Spatial variation analysis

3.3.1 Structural characteristics analysis of heavy metal content.

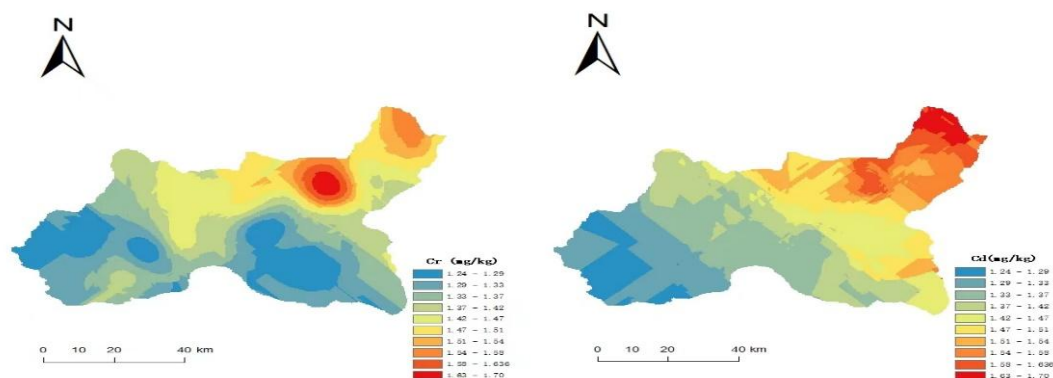
The K-S test of SPSS24.0 software was used to calculate the significance test values of the data. The data that did not conform to normal distribution were log-transformed. The content of each heavy metal in the soil except As basically obeyed normal distribution, so the transformation of As was required. GS + 9.0 software was used to analyze the variance functions of the five heavy metal elements. Before the analysis, the geographic coordinates of the sampling points had to be converted to projection coordinates and the parameters of the variation function had to be established. The results are shown in the table: the R^2 indicates the goodness of fit of the model and the RSS represents the residual sum of squares of the model fit. As shown in Table 4, As, Cr, and Pb indicators showed moderately strong spatial autocorrelation, and Cd and Cu parameters showed weak spatial variability.

Table 4. Eigenvalues of semi-covariance function of soil heavy metals

HM.	Models	C_0	$C_0 + C$	$\frac{C_0}{C_0 + C}$	R^2	RSS	Range	MSE	RMSE
As	Spherical	0.001	3.143	0	0.199	33.2	15	-0.87	1.148
Cr	Spherical	0.001	2.824	0	0.687	5.13	37.1	-0.46	1.0178
Cu	Linear	17.3	21.509	0.804	0.067	2.95E+02	54.07	-1.66	1.0790
Cd	Linear	0.059	0.059	1	0	4.27E-03	54.07	-0.01	1.0201
Pb	Gaussian	0.03	4.474	0.002	0	23.7	3	-0.15	1.0081

3.3.2 Results of kriging spatial interpolation method for heavy metals

The results of the heavy variance function analysis were imported into ArcGIS geostatistics, as shown in Figure 4 for the kriging interpolation plot. [3].



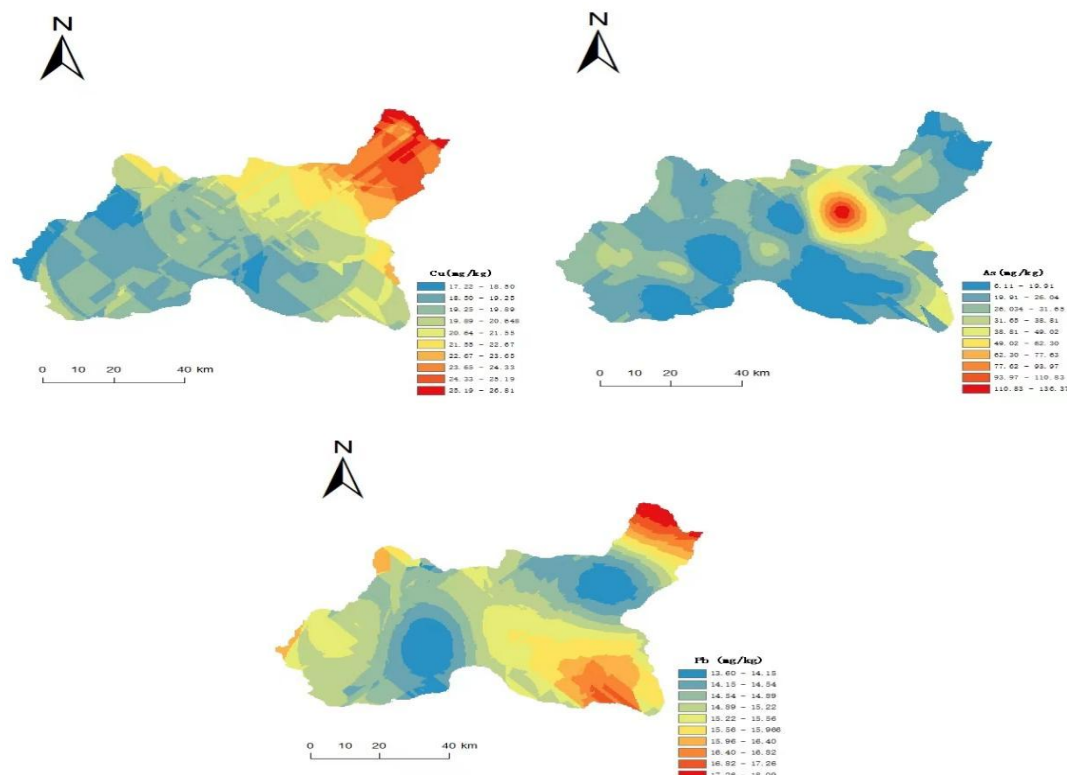


Figure 4. Spatial distribution of soil heavy metal concentrations in the Daxia River basin

3.4 FA- PCA-APCS-MLR heavy metal source analysis

3.4.1 Multivariate analysis of heavy metals.

The FA-PCA-APCS-MLR receptor model was transformed into absolute principal factor scores by factor analysis and principal component analysis, and then multiple linear regression analysis was performed on each absolute principal factor score. Pearson correlation matrix was calculated by principal component analysis to examine the relationship between heavy metals, and a significant positive correlation was found when the correlation between heavy metal elements was less than 0.01, as shown in Table 5 and Table 6. Bartlett's sphericity test ($0.00 < 0.05$) and KMO measurement test ($0.627 > 0.5$) were performed on the soil sample data, and the results showed that the correlation between the elements was strong and suitable for principal component analysis and factor analysis [4]. Finally, three principal components with eigenvalues > 1 were obtained, as shown in Table 7.

Table 5. Pearson correlation coefficients among heavy metals

HM.	As	Cd	Cr	Cu	Pb
As	1				
Cd	-0.063	1			
Cr	0.048	0.726	1		
Cu	-0.041	0.638	0.616	1	
Pb	0.063	0.196	0.005	0.332	1

Table 6. Results of principal component analysis for each element

HM.	PC1	PC2	PC3
As	-0.014	0.035	0.997
Cd	0.893	0.110	-0.067
Cu	0.805	0.348	-0.056
Cr	0.919	-0.136	0.088
Pb	0.089	0.978	0.040
Variance (%)	45.972	22.190	20.231
Accumulation(%)	47.783	68.162	88.393

Table 7. Source contribution data for heavy metals in soils

HM.	r ²	C	Apcs 1	Apcs 2	Apcs 3	PC1	PC2	PC3
As	1	7.578	-0.31	0.79	22.66	2.51	1.94	98.36
Cu	0.75	0.83	0.25	0.03	-0.02	39.69	42.28	22.98
Cd	0.79	42.22	32.82	-4.87	3.13	35.50	17.04	12.49
Cr	0.86	6.33	3.99	1.72	-0.28	52.87	18.95	56.14
Pb	0.96	6.51	0.20	2.22	0.09	2.83	89.80	7.90

The adjusted r^2 values range from 0.45 to 0.97 and >0.83 in most cases, indicating that the source assignment results based on the model are plausible[5]. As shown in the table, industrial pollution was the main source of Cd and Cu in the soil with the contribution of 35.50% and 39.69%, respectively. Automobile exhaust was the main source of Pb with a contribution of 89.80%, and agricultural emissions were the main source of As and Cr, accounting for 98.36% and 56.14% of the total emissions.

4. Conclusion

By analyzing and comparing the five heavy metals in the Daxia River basin, the mean values of As and Cr severely exceeded the background values in Gansu Province, indicating that the study area was polluted. the highest coefficient of variation of As indicated that it was more influenced by human activities. The distribution of heavy metal elements showed less in the southwest and more in the northeast. Among them, As and Cr are influenced by agricultural activities, transportation is the main source factor for Pb, and Cr, Cu and Cd are influenced by industrial activities.

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