Geochemical characteristics and sources of heavy metal elements in the southern and western surface soils of Fengdu County, Chongqing

Jinhua Luan[1], Fei Chen[2, *], Feng Hu[2], Ruigang Zhang[1], Mohuan Ning[3], Heming Tian[2], Jiahui Duan[3], Lingling Mao[2], Haitong Zhao[1], Yachuan Cui[2], Zhiwei Cui[2]

[1.] Chongqing Institute of Geology and Mineral Resources (Chongqing Key Laboratory of Major Geological Events and Resource and Environmental Effects), Chongqing 401120, China

[2.] Chongqing Institute of Geology and Mineral Resources (Field Scientific Observation and Research Station of Ecological Restoration in Chongqing Typical Mining Areas, Ministry of Natural Resources), Chongqing 401120, China

[3.] Chongqing Geological Survey Institute, Chongqing 401122, China

Corresponding author: Fei Chen Email: 365696439@qq.com

Abstract. In order to explore the current situation and sources of heavy metal element pollution in the surface soil of the southern and western parts of Fengdu County, Chongqing. In this paper, the test and analysis results of 2955 surface soil samples collected from the project of "Chongqing Jiaoshi Dam Width, Liziwan Width, etc. a total of five 1:50,000 Land Quality Geological Survey" project were carried out. The single pollution index method and the land accumulation index method were used to evaluate the current status of heavy metal pollution in crops and soil. At the same time, correlation analysis and principal component analysis were performed. The results show that: (1) Compared with the soil heavy metal background in the Three Gorges Reservoir area, the average values of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in the study area are enriched to different degrees, except that the average content of Cr is lower than the background value. Among them, As, Cd and Hg elements were obviously enriched. (2) The calculation results of the single index of heavy metals in the surface soil showed that Cd pollution was the main in the area. Cu was only slightly to slightly polluted, and the number of lightly polluted samples accounted for only 0.07%. (3) The average Igeo trend of heavy metals in surface soil in the region was Cd>Hg>As>Pb>Zn>Cu>Ni>Cr. As, Pb, Zn, Cu, Ni and Cr were mainly non-slightly polluted. Cd and Hg elements were heavily polluted, but the sample accounted for a small proportion. The overall display area is dominated by Cd element pollution. (4) The source analysis results show that As, Cu, Pb, Ni, Zn and Cr in the study area are mainly derived from the earth's crust. Its content is related to the geological setting. The pollution of Hg and Cd is likely to be affected by human activities, mainly from atmospheric deposition.

Keywords: The southern and western parts of Fengdu County; topsoil; heavy metal elements.

1. Introduction

Soil is the foundation of life on Earth. It is also the foundation of human development[1] Along with the modernization of industry and agriculture. In particular, human activities such as direct application of pesticides, chemical fertilizers, livestock and poultry manure, automobile exhaust emissions, and the inflow of three wastes from industrial and mining enterprises all affect the concentration of heavy metal elements in the surface soil to varying degrees. Soil heavy metals are persistent, highly mobile, highly toxic, refractory to degradation, and difficult to effectively remove[2,3]. Excessive heavy metals will cause the deterioration of soil, air, groundwater and other ecosystems. The health and safety of animals and plants are threatened. In turn, it will induce ecological and environmental disasters.

There are two main sources of heavy metals in soil: natural and human activity. The natural source is mainly the soil parent material. Anthropogenic sources can be divided into industrial sources (e.g., mining, smelting, coal burning, transportation, etc.), domestic sources (transportation, waste water, domestic waste, coal, etc.), and agricultural sources (fertilizers, pesticides, irrigation water, etc.) according to the type of human activity[4]. At present, the analysis of soil heavy metal pollution sources in China is still mainly based on qualitative source identification. The source analysis methods used mainly include PCA, correlation analysis, spatial analysis, etc.

This paper relies on the results of the project of "Chongqing Jiaoshi Dam Width, Liziwan Width, etc., a total of five 1:50,000 land quality geological surveys". The distribution characteristics of heavy metal elements in the study area were analyzed. Principal component analysis (PCA) was used to analyze the pollution sources, which provided a scientific basis for the prevention and control of soil heavy metal pollution, ecological environmental protection and healthy life of residents in the study area.

2. An overview of the study area

The study area is located in the western area south of the Yangtze River in Fengdu County. It mainly includes 8 townships and towns, including Zhanpu Town, Sanhe Street, Shuanglu Town, Xingyi Town, Baoluan Town, Sanjian Township, Nantianhu Town, and Fairy Lake Town (Figure.1), with an area of about 964km^2. The study area belongs to the central subtropical humid monsoon climate zone and the "eastern monsoon agroclimatic zone". The climate is mild all year round, with abundant rainfall, with an average annual precipitation of 823.8mm. The altitude difference in the study area is large, and the three-dimensional climate is obvious. The terrain is generally high in the south and low in the north. The northern Yangtze River is dominated by hilly landforms, and gradually transitions to the middle and low mountain landforms to the south. There are depressions between the mountains in the south. Late Paleozoic-Mesozoic strata are mainly exposed in the area. The structure is dominated by folds. The fracture is not well developed. The minerals are mainly non-metallic minerals such as sandstone, shale for bricks and tiles, limestone, etc., and their scale is mostly small-medium-sized. The main soil types in the study area were paddy soil, purple soil, yellow soil, yellow-brown soil and calcareous soil. In particular, purple soil and paddy soil are the majority. The land use types are mainly agricultural land such as dry land, paddy field, and forest land.

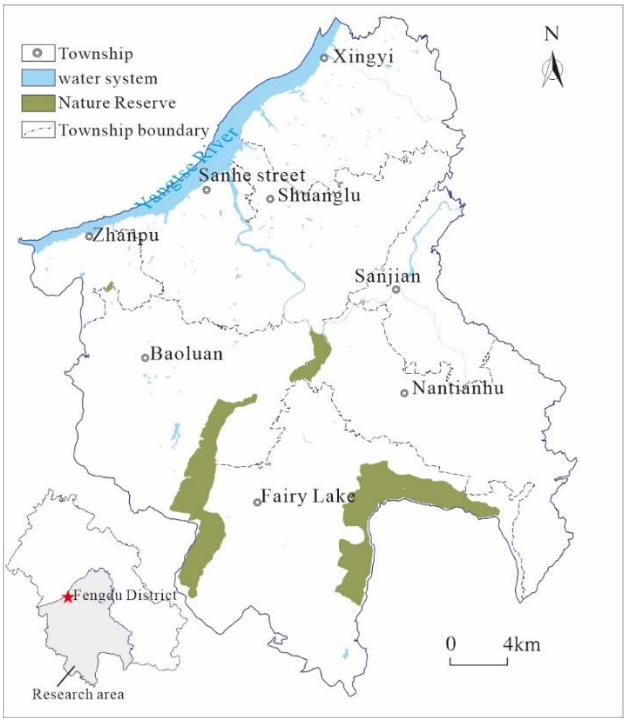

Figure. 1 Geographic location of the study area

3. Materials and methods

3.1 Sample collection and analysis

Samples were collected according to the sampling density of 1:50,000 land quality geochemical survey. Based on the principle of uniform distribution of sample points and effective control of patches, sampling points were arranged according to the grid (Figure. 2). The surface sample is collected from a central point and 4-6 sub-sampling points. The sampling depth is between 0-20cm. After mixing the collected samples in aliquots, 2 kg of samples were taken using the quarter method and stored tightly sealed in a polyethylene ziplock bag. A total of 3015 samples (including 60 replicates) were collected. Samples are naturally air-dried. Remove debris such as grit and plant roots from the sample. The sample was crushed and passed through a nylon sieve with a pore size of 10 mesh.

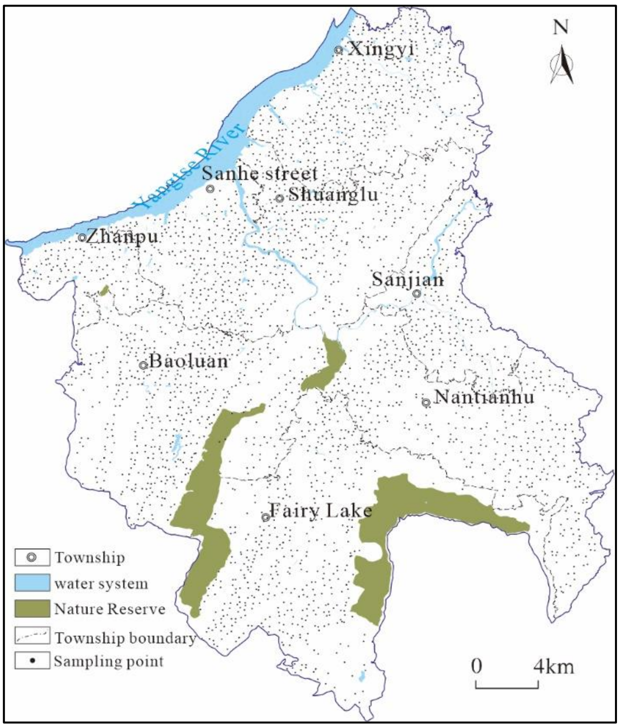

Figure. 2 Location map of surface soil sampling in the study area

The soil samples were analyzed and determined by the Chongqing Mineral Resources Testing Center of the Ministry of Natural Resources for As, Cd, Cu, Hg, Cr, Ni, Pb, Zn and pH. The test methods for Cd, Cu, Cr and Ni were inductively coupled plasma spectroscopy (ICP-AES). The Pb and Zn test methods are X-ray fluorescence spectroscopy (XRF). The test method for As and Hg is atomic fluorescence (AFS). The pH test method is the ion electrode method (ISE). The testing process implements the "Quality Management Practice for Geological and Mineral Laboratory Testing" (DZ/T0130-2006). The accuracy and precision of analysis and testing are strictly monitored by means of internal laboratory inspection, password spot check, external inspection and other means. The results showed that the pass rate of 60 duplicate samples was greater than 90%. The pass rate of 288 external standard control samples was greater than 90%, and the data reporting rate was 100%. The pass rate of repeatability inspection samples is higher than 90%, and all quality indicators meet the requirements of the specification. This indicates that the quality of the analyzed data is reliable.

3.2 Data processing and analysis methods

The authors used geostatistical methods to conduct descriptive statistical analysis of the basic parameters of heavy metal elements in surface soil. Including maximum, minimum, mean, median, standard deviation, coefficient of variation (Cv), etc. Correlation analysis and principal component analysis were used to analyze the sources of heavy metal elements in the surface soil of the study area.

The pollution status of heavy metal elements in the surface soil of the study area was comprehensively evaluated by the single pollution index method and the geoaccumulation index method. The formula used in the single pollution index method is as follows: $Pi = Ci/Si$ (Pi - single pollution index; CI - Measured value of pollutant index i in soil; Si - the secondary standard value of the pollutant index i in the soil given in the GB15618), where $Pi \leq 1$ is clean, $1<Pi \leq 2$ is slightly polluted, $2<Pi \leq 3$ is light pollution, $3<Pi \leq 5$ is moderate pollution, and $Pi > 5$ is heavily polluted. The geoaccumulation index method can be used to evaluate the degree of heavy metal accumulation in soil, which comprehensively considers the background value caused by natural geological processes and the impact of human activities on heavy metal pollution [5-8]. Calculation formula: $I_{\text{geo}} = \log_2[Cn/1.5Bn]$. Where Cn is the concentration of element n in the sample, Bn is the background value of element n, and the study area belongs to the Three Gorges Reservoir area, so the soil background value of the Three Gorges Reservoir area [9] and 1.5 are selected as the correction index, which may be used to correct the change of the background value caused by diagenesis [10]. The pollution level classification criteria are as follows: $I_{geo} \leq 0$ is no pollution, $0<I_{geo} \leq 1$ is light pollution, $1<I_{geo} \leq 2$ is moderate pollution, $2< I_{geo} \leq 3$ is moderate pollution, $3< I_{geo} \leq 4$ is severe pollution, $4< I_{geo} \leq 5$ is severe pollution, and $I_{geo}>5$ is severe pollution.

4. Results and Discussion

4.1 Characteristics of heavy metal element content in surface soil

According to the statistical results of heavy metals in the surface soil of the study area (Table 1). The average values of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in the study area were 9.64 mg/kg, 0.29 mg/kg, 76.59 mg/kg, 28.07 mg/kg, 0.08 mg/kg, 31.96 mg/kg, 29.67 mg/kg, 81.98 mg/kg and 5.90 mg/kg, respectively. Compared with the background of heavy metals in the soil of the Three Gorges Reservoir area, except for the average content of Cr element lower than the background value, the average content of heavy metal elements in the other seven areas exceeded the background value. They exceeded the background values by 65%, 116%, 12%, 74%, 8%, 24%, and 17%, respectively. The results showed that there were different degrees of enrichment of As, Cd, Cu, Hg, Ni, Pb and Zn elements in the study area. Among them, As, Cd and Hg elements were obviously enriched.

Table 1 Characteristics of heavy metal content in surface soil（n=2955）

Index	Maximum mg/kg	Minimum mg/kg	Average value mg/kg	Median mg/kg	Standard deviation (SD)	Coefficient (Cv)	Background values of heavy metals in soil in the Three Gorges Reservoir area
As	32.45	0.74	9.64	6.93	6.64	0.69	5.835
Cd	5.38	0.04	0.29	0.26	0.20	0.69	0.134
Cr	216.00	14.20	76.59	74.50	23.30	0.30	78.03
Cu	173.00	1.90	28.07	26.40	12.53	0.45	25.00
Hg	1.23	0.01	0.08	0.06	0.06	0.73	0.046
Ni	108.00	2.90	31.96	31.80	10.60	0.33	29.47
Pb	119.00	8.00	29.67	28.30	7.39	0.25	23.88
Zn	272.00	14.30	81.98	82.70	21.61	0.26	69.88
pH	8.82	3.72	5.90	5.56	1.13	0.19	——

The coefficient of variation (Cv) is a mathematical indicator that measures the degree of variability in one or more groups of soil sample data. The smaller the value, the higher the spatial uniformity of the heavy metal elements, and the lower the dispersion tendency. Conversely, the discrete trend is higher[11]. Previous studies have suggested that the size of the coefficient of variation can be divided into low ($Cv<0.2$), moderate ($0.2 \leqslant Cv<0.5$), and high ($0.5 \leqslant Cv<1$)[2,12]. The coefficient of variation of heavy metal elements in the study area was as follows: Hg>As>Cd>Cu>Ni>Cr>Zn>Pb. Among them, Hg, As, and Cd are highly variable. Cu, Ni, Cr, Zn, and Pb are moderate variants. In conclusion, the spatial distribution of the eight heavy metal elements in the surface soil of the study area had certain spatial distribution differences. It is more affected by the geographical context and human activities.

4.2 Calculation results of individual indices of soil heavy metals

The calculation of the single index of heavy metals in the surface soil of the study area was completed by the Jinwei geochemical evaluation software GeoIPASV4.2. The selection of Si was based on land use type and pH. The results of the evaluation are shown in Table 2. The results show that except for Cd and Cu, the samples of the remaining six heavy metal elements Pi≤1 account for more than 99% of the eight heavy metal elements in the study area. The sample size of 1<Pi≤2 was less than 0.5%. There were different degrees of Cd and Cu pollution in the area. Among them, Cd element has moderate-severe pollution, but the proportion is very small. Cu was only slightly to slightly polluted, and the number of lightly polluted samples accounted for only 0.07%. In summary, the heavy metal elements in the study area were mainly Cd pollution.

Table 2 Evaluation of individual pollution index of heavy metal elements in surface soil (n=2955%) (%)

Pi	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
≤1	99.52	76.39	99.81	96.57	99.96	99.70	99.89	99.93
1-2	0.45	21.56	0.15	3.32	—	0.26	0.07	0.04
2-3	—	1.23	—	0.07	—	—	—	—
3-5	—	0.45	—	—	—	—	—	—
≥5	—	0.34	—	—	—	—	—	—

4.3 Calculation results of soil heavy metal accumulation index

The calculation results and statistical data of heavy metal accumulation index of surface soil in the study area are shown in Table 3 and Figure 3. The trend of soil heavy metal mean Igeo was Cd>Hg>As>Pb>Zn>Cu>Ni>Cr. Cd element was severe-heavily polluted in 0.37%. Moderate to moderate contamination accounted for 14.01%. The rest are non-polluted - lightly polluted. The proportion of Hg was severe-severely polluted was 0.1%. Moderate to moderate contamination accounted for 15.6% of the samples. The rest are non-polluted - lightly polluted. 17.77% of the samples were moderately polluted by As elements. The rest are non-polluted - lightly polluted. 0.07% of the samples were moderately polluted with Pb. The rest are non-polluted - lightly polluted. 0.1% of the samples were moderately polluted with Zn. The rest are non-polluted - lightly polluted. 0.57% of the samples were moderately to moderately polluted with Cu. The rest are non-polluted - lightly polluted. 0.07% of the samples were moderately polluted with Ni. The rest are non-polluted - lightly polluted. The proportion of non-polluting samples of Cr element reached 96.24. Mild contamination accounted for 3.76%. The evaluation results of the land accumulation index are similar to those calculated by the individual indexes. The surface soil in the study area showed obvious Cd pollution, but its proportion was relatively low.

Table 3 Proportion of heavy metal accumulation index in surface soil (n=2955%) (%)

Igeo	As	Hg	Cu	Pb	Ni	Zn	Cd	Cr
≤0	56.82	53.81	85.38	80.17	90.29	89.92	26.87	96.24
0~1	25.41	30.49	14.04	19.76	9.64	9.98	58.75	3.76
1~2	17.77	15.03	0.54	0.07	0.07	0.10	13.10	—
2~3	—	0.58	0.03	—	—	—	0.91	—
3~4	—	0.07	—	—	—	—	0.30	—
4~5	—	0.03	—	—	—	—	0.07	—
＞5	—	—	—	—	—	—	—	—

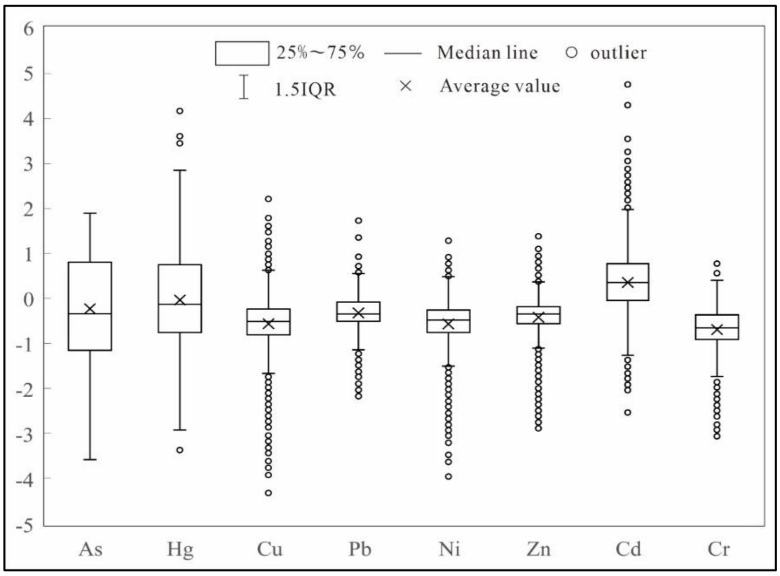

Figure. 3 The accumulation index of heavy metal elements in the surface soil of the study area

4.4 Analysis of the sources of heavy metals in surface soil

4.4.1 Correlation analysis

The authors used Spearman correlation analysis to preliminarily analyze the sources of eight heavy metal elements in soil. The results of correlation analysis are shown in Table 4. It can be seen from the table that As-Hg, As-Cr, Hg-Pb, Cu-Zn, Cu-Cr, Pb-Cr, Ni-Zn and Ni-Cr showed significant correlations. The higher the correlation coefficient, the stronger the relationship between these elements. There may be common or similar origins[13]. It can be preliminarily inferred that As, Cu, Pb, Ni, Zn, and Cr may have similar origins.

Table 4 Correlation coefficient of heavy metal elements in surface soil

Element	As	Hg	Cu	Pb	Ni	Zn	Cd	Cr
As	1							
Hg	.559**	1						
Cu	.460**	.369**	1					
Pb	.489**	.529**	.442**	1				
Ni	.461**	.239**	.439**	.377**	1			
Zn	.350**	.243**	.526**	.363**	.503**	1		
Cd	.475**	.436**	.471**	.414**	.321**	.356**	1	
Cr	.671**	.450**	.513**	.534**	.669**	.497**	.419**	1

Note: At the 0.01 level (two-tailed), the correlation is significant.

4.4.2 Principal component analysis

SPSS25.0 software was used to analyze the factors of each heavy metal in the soil samples in the study area after standardized treatment. To verify whether the data are suitable for principal component analysis. In this paper, the KMO test and Barlett spherical test were performed on the principal component analysis data. The results are shown in Table 5. The KMO is 0.841, which is greater than 0.7, and the Sig is less than 0.05. This result suggests that the data support principal component analysis. At the same time, according to the principle that the eigenvalue is greater than 1, two common factors are extracted. The cumulative variance contribution rate was 76.020%, so two common factors were extracted. This makes it possible to reflect the variance of 76.020% of the original variable, as shown in Table 6.

Table 5 KMO test and Barlett test

KMO The number of sampling suitability		0.841
Bartlett sphericity test	Approximate chi-square	18621.315
	df	28
	Sig	0.000

Table 6 Total variance explained

Ingredients	Initial eigenvalues			Extract the sum of squares of the load		
	Total	Variance percentage	Cumulative %	Total	Variance percentage	Cumulation %
1	4.892	61.151	61.151	4.892	61.151	61.151
2	1.189	14.869	76.020	1.189	14.869	76.020
3	0.694	8.679	84.699			
4	0.385	4.816	89.515			
5	0.330	4.119	93.634			
6	0.258	3.228	96.862			
7	0.171	2.135	98.997			
8	0.080	1.003	100.000			

The principal component load matrix of eight heavy metal elements in the soil in the study area is shown in Table 7. The variance contribution rate of the first principal component (F1) (61.151%) was much higher than that of the other principal components. The heavy metals with higher loads were As, Cu, Pb, Ni, Zn, and Cr. This indicates that the sources of these heavy metals may be the same. As can be seen from the foregoing, these heavy metal elements are mainly manifested as clean-light pollution. Only the Cu element has a small amount of mild contamination. A large number of studies have shown that As, Cu, Pb, Ni, Zn, Cr, etc. are mainly derived from the earth's crust in soil. In areas with less weathering activity, the content is similar to that in the parent material. This is related to the diagenetic composition. It is mainly affected by nature and less by humans[13,14]. Therefore, F1 is mainly affected by natural factors such as rock weathering and mapping parent material. F2 variance contributed (14.869%). The large loads of Hg and Cd elements indicate that the two elements are likely to be affected by human activities. External sources of CD include industrial sources and factors such as fossil fuel combustion, traffic dust and exhaust emissions, and pesticide and fertilizer applications. In the absence of industrial and mining enterprises, Cd is usually a marker element of agricultural production[15].

Table 7 Principal component load matrix

Element	Ingredients	
	F1	F2
As	0.787	0.349
Hg	0.644	0.567
Cu	0.801	-0.410
Pb	0.803	0.307
Ni	0.837	-0.469
Zn	0.828	-0.351
Cd	0.574	0.364
Cr	0.925	-0.090

5. Conclusion

(1) Compared with the soil heavy metal background in the Three Gorges Reservoir area, the average values of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in the study area were lower than those of the background value. As, Cd, Cu, Hg, Ni, Pb, and Zn were enriched to varying degrees. Among them, As, Cd and Hg elements were obviously enriched. The coefficient of variation of heavy metal elements in the study area showed that Hg, As and Cd belonged to high variability. Cu, Ni, Cr, Zn, and Pb are moderate variants. The results showed that the spatial distribution of the eight heavy metal elements in the surface soil of the study area had certain spatial differences. It is more affected by the geographical context and human activities.

(2) The calculation results of the single index of heavy metals in the surface soil showed that Cd pollution was the main in the area, and the Cu element was only slightly to slightly slightly polluted, and the number of samples with light pollution accounted for only 0.07%.

(3) The average Igeo trend of heavy metals in surface soil was Cd>Hg>As>Pb>Zn>Cu>Ni>Cr, As, Pb, Zn, Cu, Ni and Cr were mainly non-slightly polluted, and Cd and Hg were heavily polluted but the samples accounted for a relatively small proportion.

(4) The source analysis results show that As, Cu, Pb, Ni, Zn and Cr elements in the study area are mainly derived from the crust, and their contents are related to the geological background. The pollution of Hg and Cd is likely to be affected by human activities, mainly from atmospheric deposition.

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"Chongqing Jiaoshi Dam Width, Liziwan Width, etc. 5 1:50,000 Land Quality Geological Survey" (No.: Yu Gui Zi [2022] No. 61)

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