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Characteristics and Potential Ecological Risks of Heavy Metal Content in the Soil of a Plateau Alpine Mining Area in the Qilian Mountains

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Abstract: In recent years, the ecological and environmental problems caused by mining in the Qilian Mountains have attracted considerable attention, and the government has carried out a number of comprehensive ecological environment remediation projects there, among which ecological restoration in the Qilian Mountain alpine mining area is an essential task. As a result, heavy metals have been studied in the soil of the Qilian Mountain alpine mining area. This can provide a scientific basis and data support for the establishment of a demonstration index for monitoring ecological environmental restoration in mining areas. In order to understand the content and contamination status of heavy metals in the soil surrounding the alpine mining area of Qilian Mountain, 56 soil samples were collected to determine the levels of eight heavy metals, including Cd, Hg, As, Pb, Cr, Cu, Zn, and Ni. The spatial distribution of heavy metals in the soil of the study area was analyzed based on a statistical approach. The single-factor pollution index (Pi), Nemerow comprehensive pollution index (PN), geoaccumulation index (Igeo), and potential ecological risk index (RI) were used to evaluate soil heavy metal pollution and potential ecological risk. Principal component analysis (PCA), positive matrix factorization (PMF) models, and geostatistical analysis were also used to investigate the source of heavy metals. The results show that the average Cd, As, Cr, Cu, Zn, and Ni content of the grassland soil around the mining area exceeds the soil background values in both Qinghai Lake Basin and Qinghai Province. The spatial distribution of the eight heavy metal elements in soil showed an island-like pattern, with high-value areas of each metal element appearing, indicating that human activities in the study area had negative effects on the soil environment. The value of the single pollution index showed that levels of Ni, Cd, Cu, Cr, Hg, and As pollution were low, while there was no Pb or Zn pollution. The Nemerow integrated pollution index had an average value of 1.39, indicating a slight pollution trend. The average values of Cr and Zn in the geoaccumulation index ranged from 0 to 1, indicating mild to moderate contamination in the studied region. The average value of the integrated ecological risk index in the study area was 135.43, which is in the intermediate ecological risk range. In descending order of size, the average ecological risk index of each heavy metal element was Hg > Cd> As > Ni > Cu > Pb > Cr > Zn. From the perspective of the spatial distribution pattern of ecological risk, the two high-value discriminants were in the western part of the study area, close to the mining area. Zn, Cu, Pb, and Cd in soils were mainly affected by human activity, while Cr and Ni were mainly affected by soil geochemistry. Cd is the main contaminant in the study area, and soil Cd contamination of the grassland in the study area must be considered.

Keywords: plateau alpine; heavy metals; potential ecological risk; pollution assessment; soil; southern piedmont of Qilian Mountains

Citation: Zhang, F.; Cao, G.; Cao, S.; Zhang, Z.; Li, H.; Jiang, G. Characteristics and Potential Ecological Risks of Heavy Metal Content in the Soil of a Plateau Alpine Mining Area in the Qilian Mountains. *Land* **2023**, *12*, 1727. https://doi.org/10.3390/land12091727

Academic Editor: Evangelia Golia

Received: 13 July 2023
Revised: 23 August 2023
Accepted: 31 August 2023
Published: 5 September 2023

1. Introduction

Soil is the most complex and diverse ecosystem in the world [1]. Heavy metal elements are key composites in maintaining the environmental quality of soil. If their concentration is above a caustic limit, they can affect the physical and chemical properties of the soil, inhibit microbial activity, and cause soil quality and yield to decline. Moreover, it is difficult for heavy metals to migrate and degrade with the natural degradation of the soil [2–4], and so they have become one of the most significant soil pollutants. After the Industrial Revolution, under the influence of rapid and unwise industrialization and intensive agricultural practices [5], heavy metal content in the soil environment gradually increased, and heavy metal pollution of the soil ecosystem has become a great challenge to the human environment [6]. Heavy metal pollution is characterized by a lengthy residual period, irreversibility, a modest amount of transfer, severe toxicity, concealment, complex chemical properties, and strong ecological response. It has acute and chronic toxic effects through its transfer into the human and animal food chain. In addition, the accumulation risk of potential antibiotic resistance genes caused by soil heavy metal pollution can also interact with other environmental pollutants (such as microplastic particles), increasing their potential adverse effects [7,8]. As such, it poses a major potential risk to the ecosystem. It has become a major problem that endangers human health and environmental safety [9], which has become an issue of great concern to numerous governments and societies [5–9]. In order to solve food safety problems caused by soil pollution and devote themselves to the restoration of metal-polluted soil ecosystems, they have begun to monitor, control, or restrict the use of heavy metals [10–12].

In China, soil is an essential carrier for the construction of ecological civilization, and soil pollution prevention has always been an essential task for the protection of national ecological security [13]. However, heavy metal pollution is the most prominent soil environmental pollution problem in China at present [14]. The causes of soil contamination in China clearly show the signature of multiple sources, multiple paths, multiple interwoven factors, and are complex and variable. Compared with those from natural sources, the heavy metals discharged due to human disturbance have a larger content and a wider range [15]. There are a large number of heavy metals in the rocks and mineral layers of mining areas, so the metal-mining-related industries make a considerable contribution to the environmental input of heavy metals [5]. This cannot be ignored because solid waste, waste gas, wastewater, and other pollutants directly or indirectly generated in the process of exploration, mining, and beneficiation will cause heavy metal pollution to the surrounding environment [16–18]. Numerous studies have shown that the concentration of heavy metals in soil in the surrounding industrial and mining areas is significantly higher than that in other areas [19–24], and the treatment of soil heavy metal pollution in mining areas is an essential work in the restoration of territorial spatial ecology in mining areas [25–27]. At present, there are few studies on soil heavy metals in alpine mining areas. It is essential to study and assess the amount of heavy metal elements and their ecological risks in the surrounding environment of mining areas for pollution prevention and ecological environment protection and restoration.

The Qilian Mountains are an “essential area for water conservation” in China’s key ecological functional areas [28–30] and play the dual role of “ecological security barrier of the Qinghai–Tibet Plateau” and “sand prevention belt in the north” [31,32]. At present, social and economic activities such as urban construction, factories, mining enterprises, and transportation have become increasingly frequent, aggravating the prominent problem of local ecological environment destruction in the Qilian Mountains, which has critically affected the overall and long-term ecological barrier function and ecological service function of the region [33–35]. Meanwhile, the issue of illegal mining has come to light, and ecological and environmental problems in the region have attracted public attention. Relevant monitoring results show that the increase in industrial and mining land in key areas of the Qilian Mountains is the most significant problem [36–39], and the soil environmental problems caused by mineral exploration, mining, and smelting activities cannot be ignored [40–44].

Therefore, it is highly essential to assess the contamination properties and risks of heavy metals in the soil surrounding mining areas. We aim to provide data to establish a scientific basis for comprehensive ecological environmental remediation and control of heavy metal pollution in the Qilian Mountains. We also strive to provide a reference for the prevention and control of heavy metal pollution similar to the study of plateau mining areas.

2. Methods

2.1. Description of the Study Area

The study area is located on the northern eastern margin of the Qinghai–Tibet Plateau, in the core area of the Qilian Mountain National Park, the southern foot of the western Qinghai Mountains, and the northwestern part of Qinghai Lake. It is an essential part of the ecological barrier of the Qilian Mountains, and its ecological function and status are extremely significant. It has a continental plateau climate with distinct verdant zones (Figure 1). The regional altitude is 3329.4–3553.18 m, the annual average temperature is −0.39 °C, the annual average precipitation is 450 mm, the annual average evaporation is 1544.84 mm, the four seasons are not distinct, the climate is cold, and the temperature difference between day and night is large. It has a typical highland continental climate. Vegetation in the study area is relatively well developed and is dominated by warm grassland and alpine meadows, with soil types dominated by boggy meadow soil, alpine meadow soil, and extensive frozen soil. It belongs to the typical ecologically fragile area of the Qinghai–Tibet Plateau. Mining activities began in the study site in the 1970s and 1980s, during which there were very small-scale mining activities. Since the establishment of the Qilian Mountain Nature Reserve and Qilian Mountain National Park, all mining and mining activities have been stopped, and the ecological restoration and management measures of "one mine and one policy" have been adopted.

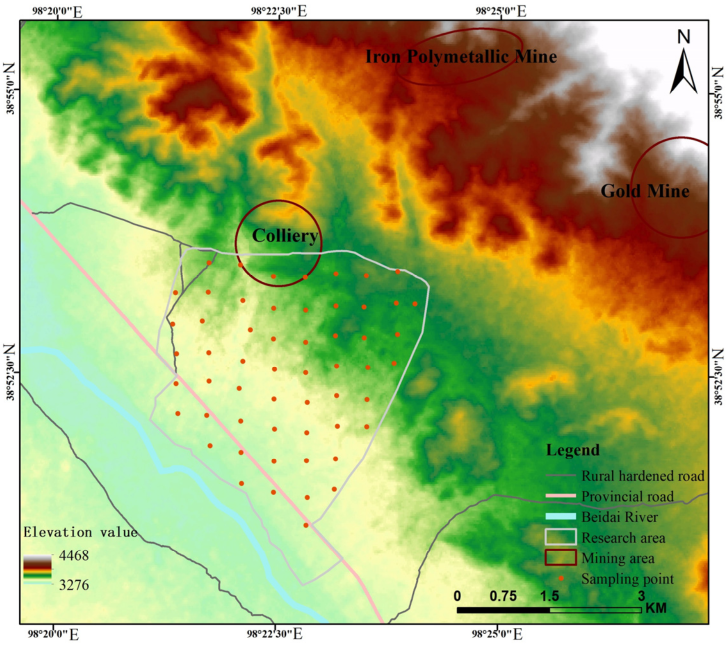

Figure 1. Digital elevation model (DEM) image map of the study area.

2.2. Sampling Process and Preparation

A total of 56 surface soil samples were mapped and collected in the area during the month of August 2019. To obtain representative samples, a series of standard soil sampling procedures were adopted (Technical Specification for Monitoring of Farmland Soil Environmental Quality (NY/T 395-2012)) [45], and sampling sites (Figure 1) were identified using a global positioning system (GPS). The two-diagonal 5-point mixed sampling method was used to reduce the influence of random error. We cut 10 cm deep and 5 cm wide with a sampling shovel (0–20 cm in depth), and scraped the sampling shovel with a bamboo knife. Samples were then mixed and divided into four divisions, retaining less than 2.5 kg of the air-dried soil samples, which were then placed in labeled cloth bags and taken back to the laboratory. They were dried with the dryer set within the temperature range of 35 ± 5 °C, and were knocked and rolled with a wooden rod and hammer to remove impurities. Tiny plant roots were removed using an electrostatic adsorption separation device. A nylon sieve with a pore size of 2 mm was used to remove sand with a particle size greater than 2 mm. The soil samples were then ground with an agate ball grinder, and passed through a nylon sieve with a pore diameter of 1 mm. Based on the four-part method, the remaining soil samples were weighed and bottled.

2.3. Soil Sample and Laboratory Analysis

The sample pH value test method refers to the solid–liquid 1:2.5 glass electrode method from Soil Testing—Part 2: Method for Determination of Soil PH. The digestion process of Cd, Cr, Cu, Ni, Pb, and Zn in soil samples was based on the national standard (HJ 491-2009, GB/T 171381997, GB5085.3-2007) [46–48]. After digestion, the content of the samples was determined using an inductively coupled plasma mass spectrometer (ICP-MS); the content of As and Hg was digested using an HNO3-HCl mixture, and then the concentration of mercury and As were analyzed using an atom fluorescence spectrometer (AFS 8220). To ensure quality/control, four standard reference samples, one duplicate sample, and two reagent blanks were inserted into each digestion group (50 samples) to assess the accuracy and precision of the analysis. The used GBW07405 (GSS-1, GSS-16, GSS-28) were obtained from China National Standard Reference Material Center. The detailed recoveries of each heavy metal were as follows: Cd (84–95%), Hg (91–104%), As (93–96%), Pb (91–102%), Cu (92–101%), Zn (89–103%), Cr (89–93%), and Ni (90–101%). The relative standard deviation of duplicate samples across all batches was <5%. In addition, the method detection limits (MDL) for Cd, Hg, As, Pb, Cr, Cu, Zn, and Ni were 0.03, 0.002, 0.01, 0.02, 0.4, 0.05, 0.27, and 0.07 $mg \cdot kg^{-1}$, respectively.

2.4. Data Analysis

In this study, Excel 2016 and SPSS 23.0 were used for the statistical analysis of soil heavy metal content. Preliminary data analysis, correlation analysis, cluster analysis, and principal component analysis were carried out using SPSS 23.0 (SPSS Inc., Chicago, IL, USA). Excel 2016, Origin 2018, and ArcGISPro 2.5 were used to evaluate heavy metal contamination and clarify the spatial distribution of heavy metals.

2.5. Evaluation Method of Soil Heavy Metal Pollution

2.5.1. Evaluation of Contamination Status and Ecological Risks of Heavy Metals

The degree of soil pollution was evaluated using the single-factor pollution index method and the Nemerow comprehensive pollution index method [49]. The single-factor pollution index can be calculated using Equation (1):

$$P_i = C_{is}/C_{ib} \tag{1}$$

where P_i is the single-factor pollution index of heavy metal i, C_{is} is the measured content of soil heavy metal i (mg·kg) and C_{ib} is the background value of soil heavy metal i (mg·kg). The five classes of P_i represent the increasing soil contamination levels (Table 1).

The Nemerow comprehensive pollution index can be calculated using Equation (2):

$$P_N = \sqrt{\frac{\left(P_{j,max}\right)^2 + \left(\overline{P_{j,avg}}\right)^2}{2}} \tag{2}$$

where P_N is the integrated pollution index, $P_{j,max}$ is the maximum value of heavy metal single-factor pollution index at monitoring point j and $P_{j,avg}$ is the average of the single-factor pollution index of all heavy metals at monitoring point j. The five classes of P_N represent the increasing soil contamination levels (Table 1).

Table 1. The contamination grades of the single-factor index (P_i) and Nemerow comprehensive pollution index (P_N).

P_i	Pollution Classification	P_N	Pollution Classification
$P_i \leq 1$	Unpolluted	$P_N \leq 0.7$	Clean/Safe
$1 < P_i \leq 2$	Mildly pollution	$0.7 < P_N \leq 1.0$	Still clean/warning limit
$2 < P_i \leq 3$	Slightly polluted	$1.0 < P_N \leq 2.0$	Slightly polluted
$3 < P_i \leq 5$	Moderately polluted	$2.0 < P_N \leq 3.0$	Moderately polluted
$P_i > 5$	Heavily polluted	$P_N > 3.0$	Heavily polluted

2.5.2. Geoaccumulation Index (I_{geo})

The geoaccumulation index (I_{geo}) was originally defined by Muller and so is also known as the Muller index. This is a method proposed in the 1960s for quantitative assessment of heavy metal contamination levels in sediment. Later, it was widely used in the pollution evaluation of heavy metals, which is one of the most widely used methods globally [50–52]. This metric, which incorporates the action of diagenesis into the pollution assessment, not only reflects the naturally variable character of the heavy metal distribution but also distinguishes between the effects of human activities on the environment and is an essential parameter for distinguishing between the effects of human activities [53]. I_{geo} can be calculated using Equation (3):

$$I_{geo} = \log_2[C_{is}/(C_{ib} \times 1.5)] \tag{3}$$

where C_{is} is the concentration of the measured metal in the sample, C_{ib} is the pre-industrial (geochemical background) content of this metal. In this study, the regional soil background concentrations of Qinghai Province [54] were chosen as the criterion values. The constant 1.5 compensates for possible natural fluctuations in the content of a given substance in the environment, as well as detecting very small anthropogenic influences. Seven classes of I_{geo} represent the increasing soil contamination levels (Table 2).

Table 2. The classification and description of geoaccumulation index (I_{geo}).

Geoaccumulation Index (I_{geo})	Soil Quality
$I_{geo} \leq 0$	Unpolluted
$0 < I_{geo} \leq 1$	Unpolluted to moderately polluted
$1 < I_{geo} \leq 2$	Moderately polluted
$2 < I_{geo} \leq 3$	Moderately to heavily polluted
$3 < I_{geo} \leq 4$	Heavily polluted
$4 < I_{geo} \leq 5$	Heavily to extremely polluted
$5 < I_{geo}$	Extremely contaminated

2.6. Potential Ecological Risk Index (PERI)

The potential ecological hazard index (PERI) was proposed by Hakanson. It integrates the concentration of heavy metal elements with toxicology, environmental effects, and ecological effects and has been used to assess the contamination and ecological risk of heavy metal elements in sedimentology [55]. This method can directly reflect the hazard of single or multiple heavy metal elements. This approach has been widely used to study the heavy metal contamination of surrounding soil in different mining areas and to illustrate the potential ecological risks posed by overall contamination. The PERI can be calculated using Equation (4):

$$PERI = \sum E_i = \sum (T_i \times C_i) = \sum (T_i \times C_{is}/C_{ib}) \tag{4}$$

where E_i is the individual potential ecological risk of the *i* metal, T_i is the toxic response factor of the *i* metal. The toxicity coefficients of the heavy metals Cd, Hg, As, Pb, Cr, Cu, Zn, and Ni were 30, 40, 10, 5, 2, 5, 1, and 5, respectively [56]. C_i is the pollution index of the *i* metal, C_{is} is the concentration of the examined *i* metal in the soil sample, and C_{ib} is the evaluation reference value of the *i* metal, which is the soil metal background value of Qinghai Province in this study. Four grades of PERI are defined and listed in Table 3.

Table 3. Classification levels of potential ecological risk of soil heavy metals.

Individual Potential Ecological Risk Index (E_i)	Comprehensive Potential Ecological Risk Index (RI)	Soil Quality
$E_i \leq 40$	$RI \leq 110$	Low risk
$40 < E_i \leq 80$	$110 < RI \leq 220$	Moderate risk
$80 < E_i \leq 160$	$220 < RI \leq 440$	Considerable risk
$160 < E_i \leq 320$	$440 < RI \leq 880$	High risk
$E_i > 320$	$RI > 880$	Very high risk

3. Results and Discussions

3.1. Analysis of Heavy Metal Element Content in Soil

The descriptive statistical analysis results (Table 4) showed that the average pH of soil in the study area was 8.60, ranging from 7.99 to 9.02. The pH value of the sampling points was greater than or equal to 7.5, and the coefficient of variation was 2.41%, indicating that the physical and chemical properties of soil in the mining area were stable. This indicates that the soil in the sampling area is weakly alkaline, consistent with the overall alkaline background of soil in Qinghai.

The mean concentrations of Cd, Hg, As, Pb, Cr, Cu, Zn, and Ni in the study area were 0.20, 0.02, 14.36, 19.94, 94.76, 29.90, 77.02, and 52.67 mg·kg^{-1}, respectively. The contents exceed the soil background values in Qinghai Province by a factor of 5.9, 2.0, 1.7, 1.3, 2.7, 1.5, and 3.1, respectively. The proportion of eight heavy metal elements above the background value of Qinghai Province were 83.93%, 75.00%, 48.21%, 32.14%, 98.21%, 87.50%, 26.79%, and 100.00%, respectively. The elements can be listed in descending order of amount above background level of Qinghai Province as Ni > Cr > Cu > Cd > Hg > As > Pb > Zn. Compared with the soil background values of Qinghai Lake Basin, the proportion of points higher than background levels were 83.93%, 75.00%, 96.43%, 39.29%, 100.00%, 92.86%, 89.29%, and 100.00%, respectively, and the degree of above background values was Ni = Cr > As > Cu > Zn > Cd > Hg > Pb. Compared with the screening value of soil pollution risk of agricultural land in "Soil Pollution Risk Control Standard for Agricultural Land (Trial)" (GB 15618-2018) [57], there were no points exceeding the standard except for Cd, the exceeding rate of which was 1.79%.

The coefficient of variation can effectively reflect the average degree of variation in each sampled point in the overall sample. If the variation is greater than 0.5, it indicates that the spatial distribution of heavy metal content in the soil is uneven, there is local point source pollution, and exogenous substances are caused by the entry of [58]. The coefficients of variation in the concentration of different heavy metals in the soil in the study area were Cd (55.05%) > Cu (24.14%) > Ni (23.73%) > Hg (23.64%) > Cr (18.15%) > Zn (17.74%) > As (15.55%) > Pb (12.23%), of which Cd can be categorized as extremely variant, and Cu, Ni, and Hg were moderately variant. This shows that the sources of Cd, Cu, Ni, and Hg are relatively large by external interference, Cd is more clearly affected by some local pollution sources. This indicates that the soil in the sampling area is affected by human activity and has some degree of accumulation, as well as the possibility of local contamination.

The remaining four elements are below 20%, indicating that they have a relatively minor influence.

Table 4. Statistics of heavy metal concentrations in grassland of the study area (n = 56).

Elements	Cd	Hg	As	Pb	Cr	Cu	Zn	Ni	pH
Mean (mg·kg^{-1})	0.20	0.02	14.36	19.94	94.76	29.90	77.02	52.67	8.60
Median (mg·kg^{-1})	0.17	0.02	13.95	19.90	92.45	28.90	76.05	47.45	8.63
Kurt (mg·kg^{-1})	20.54	−0.11	5.46	1.26	2.35	4.35	1.78	1.60	0.61
Deviation (mg·kg^{-1})	4.03	0.31	1.71	0.78	1.30	1.46	0.79	1.55	−0.51
Min (mg·kg^{-1})	0.10	0.01	10.80	15.90	67.50	17.60	50.80	39.90	7.99
Max (mg·kg^{-1})	0.82	0.04	23.80	28.10	158.00	59.20	123.00	90.50	9.02
SD (mg·kg^{-1})	0.11	0.01	2.23	2.44	17.20	7.22	13.67	12.50	0.21
CV%	55.05	23.64	15.55	12.23	18.15	24.14	17.74	23.73	2.41
Qinghai Lake Basin BV (mg·kg^{-1})	0.14	0.06	11.66	20.47	54.17	19.72	64.28	24.96	-
Qinghai BV (mg·kg^{-1})	0.14	0.02	14.00	20.90	70.10	22.20	80.30	29.60	-
GB 15618-2018 [57] (mg·kg^{-1})	0.60	3.40	25.00	170.00	250.00	100.00	300.00	190.00	-

CV: coefficient of variation. SD: standard deviation. Qinghai Lake Basin BV: background concentrations of heavy metals in soils of Qinghai Lake Basin obtained from [59]. Qinghai BV: background concentrations of heavy metals in soils of Qinghai Province obtained from CNEMC (1990) [54].

Currently, there is no uniform standard for the selection and pollution assessment of heavy metals in soil. National soil environmental quality standards and local soil background values are used as evaluation criteria in the same study area, which can produce totally different levels of contamination. The national soil environmental quality standard integrates the average value of soil in different regions of the country and is influenced by terrain, climate, wind direction, natural environment, and other conditions, which inevitably leads to bias in the evaluation results. Although the selection of soil background values as the pollution evaluation standard is relatively strict, the evaluation result is likely to be considered as the most serious. However, in view of the restoration of the ecological environment and protection of the natural ecology in the alpine mining area, it is a top priority to maintain the maximum value of the quality of the soil environment in the natural context and ensure a high-quality soil environment. Multiple background values were selected for analysis in this study, which are strict but of some guiding significance. In the future, the evaluation results will be more reasonable and applicable, based on the soil background values of the Qilian Mountains as the evaluation criteria.

3.2. Spatial Distribution Characteristics of Soil Heavy Metal Elements

The interpolation technology of GIS statistical analysis can transform discrete data points into surfaces, realize the expression from dot data to surface data, and more intuitively reflect the spatial variation characteristics of soil heavy metals [60]. Due to the discontinuity and non-normal distribution, the reverse distance weight (inverse-distance-weighted, IDW) interpolation method and interpolation were used to obtain the spatial distribution of heavy metal content in the study area (Figure 2). The results show that the soil pH value is mainly distributed in the higher-altitude (3400 m) areas in the northeast of the study area, which may be related to the soil salinization and tiny groundwater depth caused by the greater salinity. The spatial distribution of the eight heavy metal elements, with the exception of Cr and Ni, shows essentially an island-like pattern of high-value regions, with high-Cd-value regions located in the northwest and west. The distribution characteristics of Hg, As, Pb, Zn, and Cu are similar, with Pb, Zn, and Cu mainly located in the regions of high values and Pb, Zn, and Cu in the middle, with similar distribution characteristics. The features of the Cr and Ni distributions are similar, and the high-value distributions are consistent. This suggests that different heavy metal elements in surface soils have different contamination properties and different abilities to be released into the surface environment from underground, and the content of heavy metals in the surface soil is different in spatial distribution.

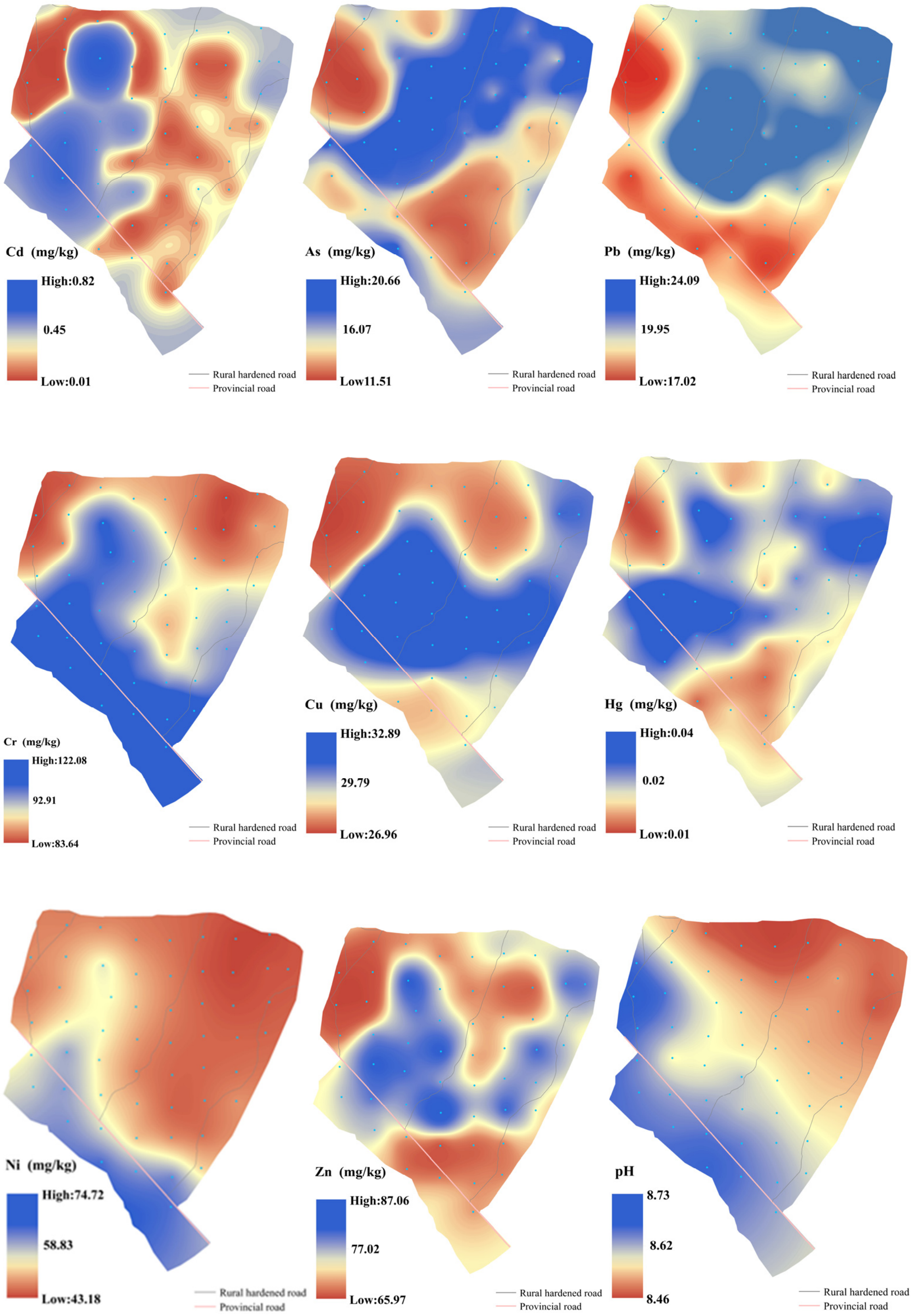

Figure 2. Spatial distribution of heavy metal concentrations and pH in surface soils.

3.3. Evaluation of Soil Pollution Degree

Taking the soil background value of Qinghai as the evaluation basis, the single pollution index and the Nemerow comprehensive pollution index of 56 soil samples from the study area were calculated (Table 5). The average value of the single pollution index of each heavy metal element in the soil, in descending order, was Ni (1.78), Cd (1.43), Cu (1.35), Cr (1.35), Hg (1.21), As (1.03), Pb (0.95), and Zn (0.96). Levels of Ni, Cd, Cu, Cr, Hg, and As were slightly polluting, while Pb and Zn levels were pollution-free. P_N was 1.06–2.02, with an average value of 1.39, indicating that the whole study area was mildly polluted.

Table 5. Grading of heavy metal pollution in the soil of the study area.

Elements	Cd	Hg	As	Pb	Cr	Cu	Zn	Ni
Single-factor index ($P_{i,ave}$)	1.43	1.21	1.03	0.95	1.35	1.35	0.96	1.78
Nemerow synthesis indices ($P_{N,ave}$)	1.51	1.30	1.16	1.10	1.51	1.46	1.06	2.02

3.4. Evaluation of the Geological Accumulation Index

As shown in Figure 3 in I_{geo} of this study, the geological cumulative index of Cd, Hg, As, Pb, Cr, Cr, Cu, Zn, and Ni in the soil of the study area ranged from −1.00 to 0.75 for Cd (average −0.27), −1.25 to 0.02 for Hg (average −0.67), −1.14 to 1.96 for As (average −0.22), −0.85 to −0.02 for Pb (average −0.53), −0.35 to 0.88 for Cr (average 0.12), −0.43 to 0.75 for Cu (average −0.06), 0.08 to 1.22 for Zn (average 0.47), and −2.01 to −0.42 for Zn (average −1.20).

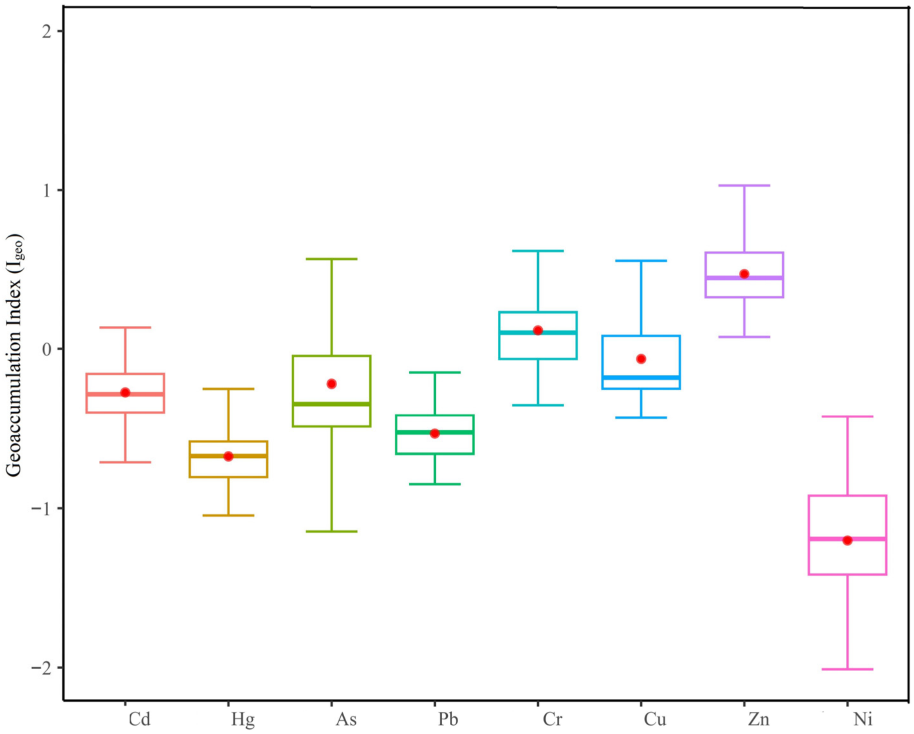

Figure 3. Comparative analysis of concentration box line graphs of the geological cumulative index of Cd, Hg, As, Pb, Cr, Cr, Cu, Zn, and Ni.

The I_{geo} contamination classification (Table 2) indicates that there is no Cd, Hg, As, Pb, Cu, or Ni contamination in the study region as a whole, whereas the mean Igeo values for Cr and Zn all range from 0 to 1, suggesting the existence of slight to moderate contamination of these metals.

The soil in the study area was either not contaminated with heavy metals or showed signs of minor local contamination according to the three evaluation results, which tended to be consistent overall. However, there are slight differences in the specific evaluation results, mainly due to the different emphases of the various evaluation methods. The Nemerow composite pollution index method is slightly more strict than the single-factor pollution index method in the assessment of the pollution grade at some sampling points, as the method over-reflects the role of the largest polluting elements on the environmental quality of the soil, resulting in larger evaluation results. However, in the evaluation process of this study, the two methods are complementary and have a strong degree of fit. The geological accumulation index method fully considers the effect of geological processes on the background values and emphasizes that the level of heavy metal contamination scales linearly with the heavy metal content. The obtained evaluation results are essentially consistent with the previous two indexing methods, with no clear differences.

3.5. Ecological Risk Assessment of Heavy Metal Pollution in Soil

The ecological risk level (Table 6) of each heavy metal element was ranked from high to low as Hg (48.32) > Cd (42.94) > As (10.26) > Ni (8.90) > Cu (6.73) > Pb (4.77) > Cr (2.70) > Zn (0.96), indicating that the potential ecological risk of Cd, As, Pb, Cu, Zn, and Ni was at a low level. In terms of the combined potential ecological risk index of multiple heavy metals, the average *RI* score for each site was 125.57, which is at a medium pollution risk. This suggests that there is significant contamination of heavy metals. The contribution values of each heavy metal to ecological risk were as follows: Hg (38.88%) > Cd (32.89%) > As (8.47%) > Ni (7.32%) > Cu (5.47%) > Pb (3.95%) > Cr (2.23%) > Zn (0.78%), which corresponded exactly to their ecological risk levels, with Hg and Cd being the primary contributors.

Table 6. Evaluation results of soil heavy metal potential ecological risk.

Item	Cd	Hg	As	Pb	Cr	Cu	Zn	Ni
E_i (min)	20.80	26.80	7.71	3.80	1.93	3.96	0.63	6.74
E_i (max)	179.34	80.60	17.00	6.72	4.51	13.33	1.53	15.29
E_i (avg)	42.94	48.32	10.26	4.77	2.70	6.73	0.96	8.90
RI (min)	75.03							
RI (max)	287.12							
RI (avg)	125.57							

The comprehensive potential ecological risk index of soil heavy metals around the mining area shows that the pollution was of medium risk. Hg and Cd were the main contributing factors, which is consistent with the results of numerous experts and scholars on the heavy metal pollution of soils in farmland and coal gangue dumps in abandoned coal mining land [43]. The results show that open-pit coal mining and slag in the process of discharge and long-term accumulation pose a threat to the surrounding soil, and there are certain potential ecological risks that should be given attention by relevant departments. Cd is one of the five most dangerous environmental pollutants. Although the alkaline soil in the mining area is conducive to the fixed deposition of heavy metals, the content of the effective state in the environment is relatively elevated. With the restoration and treatment of the ecological environment, the pH of the soil is bound to shift, and some potential carbonate states will be transformed. In particular, the content of Cd (water soluble and ion exchange) with a significant proportion of carbonate will increase, which will pose a potential threat to the ecological environment. The average values of Hg and Cd are higher than the background values, indicating that the long-term accumulated solid wastes such as slag are washed by rainfall and snow water, and part of the leaching solution flows into the nearby soil. At the same time, the potential ecological risk index reflects the situation of heavy metal pollution in the mining area environment, and the selected Hg and Cd are the two most significant ecological risk factors, which is particularly significant for the prevention and control of heavy metal pollution. In view of the elevated toxicity coefficients of Hg and Cd (40 and 30, respectively), attention should be paid to them in the later ecological restoration and management. Although the heavy metals in the soil around the mining area are in a safe/slightly polluted state, soil heavy metal pollution is an irreversible process, especially in the fragile grasslands in the extremely cold areas of the study site. When using solid wastes such as slag for soil reconstruction, passivating agents and amendments can be added to reduce the possibility of heavy metals entering the soil, thereby reducing the risk of heavy metal pollution. At the same time, the continuous monitoring of the soil environment should be strengthened to restore vegetation as soon as possible to prevent the deterioration of the soil environment.

3.6. Soil Heavy Metal Source Analysis

Related analysis and principal component analysis can be used to resolve the source of heavy metals in soil. Pearson correlation analysis of the soil heavy metal content in the study area found that the heavy metal pollutants were not completely independent, and there were significant associations between most heavy metal elements (Figure 4). Among them, we found a strong positive correlation between As and Cu, Hg, Pb, and Zn ($p < 0.01$), a strong positive correlation between Cr and Cd, Cu, Ni, and Zn ($p < 0.01$), a strong positive correlation between Cd and Cu, Hg, Ni, and Zn ($p < 0.01$). There was a strong positive correlation between Cu and Hg, Pb, and Zn ($p < 0.01$), a strong positive correlation between Hg and Pb and Zn ($p < 0.01$), a strong positive correlation between Pb and Zn (r = 0.723, $p < 0.01$), but the correlation coefficients were slightly different, the correlation coefficients were 0.52–0.93, indicating that these elements may have the same geochemical process in terms of pollution source, migration distribution and enrichment, etc. The correlations between Cu and Ni and Ni and Zn were strong and significant ($p < 0.05$). Therefore, it can be preliminarily inferred that the source pathway of these elements is similar, and the strong correlation between the elements indicates that principal component analysis is necessary.

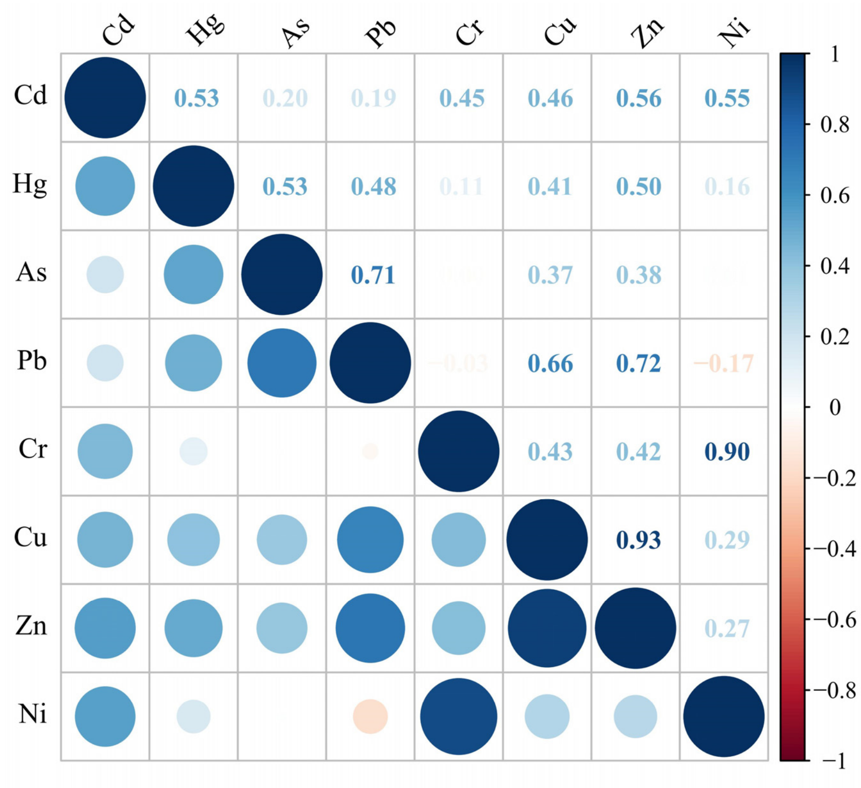

Figure 4. Results of correlation analysis of heavy metal contents. The correlation is significant ($p < 0.05$).

3.6.1. Principal Component Analysis (PCA)

The results of the principal component analysis (Table 7) show that the eigenvalues of the first two principal components were greater than 1, explaining 74.19% of the total variance, which met the requirements of the analysis and provided a sufficient summary for all indicators. The variance contribution of the first principal component (PC1) was 47.86%. Zn, Cu, Pb, and Cd had large loads on PC1, with 0.917, 0.874, 0.712, and 0.647, respectively. Compared with the descriptive statistical results, the average value of Zn, Cu, Pb, and Cd exceeded the background value of Qinghai soil. The correlation between elements was also strong (Figure 4), the pollution distribution pattern was similar (Figure 2), and they were distributed near roads in the high-value areas, causing the enrichment of Pb elements near traffic roads. This is likely caused by the incomplete combustion of vehicle fuel; the use of lubricants; vehicle tires, engines, and brake disc wear; etc. [61,62]. Studies show that levels of Pb, Cu, and Zn are high in the surface soil along the Tibetan Highway [63]; thus, PC1 is mainly influenced by traffic-related factors. The heavy metals Ni, Cr, and Pb on the second principal component (PC2) have high loads, and, according to the spatial distribution pattern of heavy metals, Ni, Cr, and Pb are 0.826, 0.757, and −0.618, respectively. The spatial distribution of these elements is similar (Figure 2), and the average content of Ni and Cr is higher than the background value of Qinghai's soil environment. The main source may be non-human factors related to soil background values associated with soil minerals [64]. The loads of Pb in both the first and second principal components indicate that it may have a dual source. The results of the principal component analysis show that the inputs of Zn, Cu, Pb, Ni, and Cr influenced the study area more than Hg, As, and Cd and were the main influencing factors of soil environmental quality in the study area.

Table 7. Principal component analysis matrix of heavy metals in soils of the study area.

Element	PC1	PC2
Zn	0.917	−0.072
Cu	0.874	−0.041
Pb	0.712	−0.618
Cd	0.677	0.352
Hg	0.647	−0.289
As	0.584	−0.505
Ni	0.457	0.826
Cr	0.538	0.757
Characteristic value	3.829	2.106
Variance contribution rate %	47.86	47.86
Total variance contribution rate/%	26.33	74.19

3.6.2. Positive Matrix Factorization (PMF) Model

The dataset was imported into the PMF model for analysis, with the number of factors set to 2 to 5 and with 20 runs each. The results show that the model is most stable when the number of factors is 3, and the run with the lowest value of Qtrue/Qexpect is chosen as the final result. Therefore, the run with the highest number of factors was chosen as the best result (Figure 5).

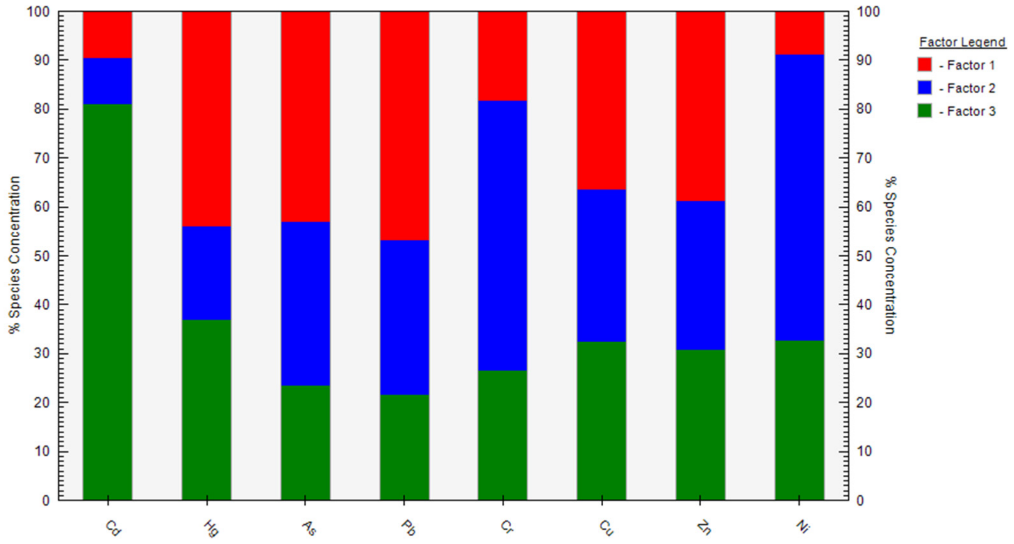

Figure 5. Contribution rate of each factor to heavy metals according to PMF model source analysis.

Factor 1 accounted for 27.01% of the total sources and included mainly Hg (44.07%), Pb (46.84%), As (43.03%), and Zn (38.73%). The four representative elements all have contents exceeding the soil background value of Qinghai Province, and their Cvs were moderately sized. The wastewater, waste gas, and waste residue produced by mining activities contain a large amount of Zn, Pb, As, and Hg and enter the soil in various ways after discharge, resulting in soil pollution. Therefore, it can be inferred that source 1 is the source of industrial activities such as mining. Factor 2 accounted for 44.09% of the total sources. It was the largest factor among the three factors and mainly included Cr (55.28%) and Ni (58.33%). The average content of Ni and Cr is higher than the background value for Qinghai. The main source may be non-human factors, mainly related to the soil background value related to soil minerals. Factor 3 accounted for 28.9% of the total sources and mainly included Cd (81.12%) and Hg (36.92%). Traffic arteries and additional hardened roads run through the study area, suggesting that the pollution may be caused by a combination of excessive traffic volume, high-emission vehicles, and high-altitude, high-emission, high-level accumulation.

By clarifying the source of heavy metals in the soil of the study area, we can provide useful scientific information for the prevention and control of heavy metal pollution in the soil of the study area and the ecosystem in the neighboring area. Correlation analysis is an extremely mature form of analysis that is widely used in the analysis of the sources of soil heavy metals. Through the correlation analysis of different heavy metal contents in the soil of the study area, it was found that the correlation between most heavy metal elements was significant, whether at the level of 0.01 or 0.05. In particular, Cu and Cr, Pb, Cd, Zn, and Cr and Zn, Cd, Pb, Ni, Zn, and Cd are closely related. Thus, Cu, Zn, Cd, Pb, Cr, and Ni can be classified into one category, with Hg and As forming another category. Based on the above results, it can be preliminarily concluded that heavy metals in soil are interdependent in spatial distribution and have similar geochemical properties. Under the same external environmental conditions, their trend is essentially the same, and they have a high degree of concomitancy. As the study area is located in an extremely cold area with an altitude of more than 4000 m in the Qilian Mountain National Natural Ecological Reserve, there has been almost no human disturbance or destruction other than mining activities. Therefore, the sources of heavy metals are relatively specific, and the sources of heavy metals can be determined as mining activities and transportation. In the comprehensive process of soil reconstruction in the study area, emphasis should be placed on the analysis of the correlations and internal relationship between different heavy metals, comprehensive prevention and control of heavy metal pollution, and reducing the loss of human and material resources.

4. Conclusions

(1) Descriptive statistical analysis shows that the contents of the heavy metal elements are accumulated to some extent. The average levels of all elements did not exceed the upper limit of the national soil environmental quality standard. The average contents of Cd, As, Cr, Cu, Zn, and Ni exceeded the soil background values in the Qinghai Lake Basin and Qinghai Province.

(2) Geostatistical analysis showed that the spatial distribution of eight heavy metal elements in the soil of the study area showed an obvious island-like distribution pattern, and the high-value points of each heavy metal element appeared in several areas, indicating that human activities (mining and transportation) had a negative impact on the soil environmental quality in the study area. The spatial distribution patterns are similar for Zn, Cu, and Pb; Cr and Ni; and Cu and Zn. The southern part of the study area is close to the provincial highway, and the grasslands surrounding the highway in the east and west have high levels of heavy metal elements.

(3) The single-factor pollution index values of Ni, Cd, Cu, Cr, Hg, and As are slightly polluted, while Pb and Zn are pollution-free. The comprehensive pollution index of Mero in the study area was 1.39, indicating that the whole study area was slightly polluted.

(4) The mean value of RI in the study area shows moderate ecological risk. The spatial distribution pattern of the RI shows a clear island pattern, with the soil in the western part of the study area having the largest potential ecological risk index.

(5) The correlation between the elements in the study area is strong, while the correlation between Hg, As, Ni, Pb, and Cr is not strong, indicating that the degree of accumulation of heavy metals is different and has heterogeneous characteristics. Pollution areas are mostly caused by the frequent activities of transport and mining industries, so the interference of human activities is the main factor responsible for the enrichment of the soil with heavy metals. Soil Ni and Cr are dominated by the geochemical origin of the soil in the studied region. Zn, Cu, and Cd are mainly affected by human activities. It is the main element responsible for soil contamination in the study area, and the contamination of the soil in the study area with Cd and Pb should be of concern.

(6) In order to improve the accuracy of source analysis and deepen the understanding of different source analysis methods, this study compares the results of different source analysis methods for source identification. The two principal components of heavy metals in the studied region were resolved by PCA and accounted for 74.19% of the total variance. The optimal number of factors for the analysis of the PMF receptor model was three, with F1, F2, and F3 contributing 27.01%, 44.09%, and 28.90%, respectively, to the eight heavy metals. By comparison, the elements contained in the first principal component of PCA correspond to factors 1 and 3 of the PMF model, and the elements in the second principal component of PCA correspond to factor 2 of the PMF model. Although the results for heavy metal clustering and grouping from the two methods do not exactly agree, they show the same trend in the classification of heavy metal elements, which validates the reliability of the results and provides accurate source factors for the source analysis.

Author Contributions: F.Z. and G.C.: Conceptualization, Writing—review and editing, Project administration, Supervision. G.C. and S.C.: Investigation, Statistical analyses. F.Z.: Writing—review and editing, Supervision. Z.Z. and H.L.: Investigation, Formal analysis. G.J.: Writing—review and editing, Project administration, Funding. All authors have read and agreed to the published version of the manuscript.

Funding: Qinghai Province Innovation Platform Construction Special Project—Qinghai Province Key.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no known conflict of interest.

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