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Article

Source Apportionment and Risk Assessment of Potentially Toxic Elements Based on PCA and PMF Model in Black Soil Area of Hailun City, Northeast China

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Abstract: The presence of potentially toxic elements (PTEs) in black soil represents a major concern in China. Despite its importance, scant research has been conducted on the prevailing status, ecological implications, and risks to human well-being associated with PTEs in China's northeastern black soil belt. In our study, 304 soil samples (0-20 cm) were collected in Gonghe Town, Hailun City. The pollution degree and spatial distribution patterns of soil PTEs were analyzed by using the single-factor pollution index (*PI*) and the Nemerow pollution index (*NPI*). The source apportionment of PTEs was carried out by combining correlation analysis, principal component analysis (PCA), and positive matrix factorization (PMF) methods. Meanwhile, the indices of ecological risk (*RI*) and human health risk (*HI*) were employed to gauge the latent ecological and health hazards due to a range of soil contamination origins. The results demonstrated that the mean concentrations of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn) were 11.16 ± 1.32 mg/kg, 0.11 ± 0.04 mg/kg, 65.29 ± 3.46 mg/kg, 22.56 ± 1.32 mg/kg, 0.03 ± 0.01 mg/kg, 27.07 ± 1.46 mg/kg, 26.09 ± 2.84 mg/kg, and 66.01 ± 4.52 mg/kg, respectively. The overall PTEs in the study region exhibited slight pollution levels. The PCA and PMF model source apportionment was validated against each other to yield four sources, which were natural source (33.2%), irrigation source (29.5%), traffic source (23.4%), and fertilizer source (13.2%). The overall *RI* in the study region was determined to be at the level of slight ecological risk. The potential non-carcinogenic risk of PTEs to both children and adults was overlooked, while the carcinogenic risk was deemed to be within acceptable limits. The comprehensive analysis of PTEs, pollutant sources, *RI*, and *HI* concluded that the fertilizer source should be the primary control source, with Cd identified as the first control PTE. The irrigation source and the traffic source were identified as the secondary control sources, with As, Pb, and Hg identified as the secondary control PTEs. This study revealed the status, risks, and sources of PTEs in black soils and provided a scientific basis of PTEs control for policymakers.

Keywords: potentially toxic elements; PCA; PMF; source apportionment; risk assessment; black soil; Hailun City; Northeast China

1. Introduction

Soil, as a vital component of the Earth's ecosystem, plays a crucial role in supporting life and maintaining ecological balance [1–3]. However, the increasing anthropogenic activities have led to the accumulation of potentially toxic elements (PTEs) in the soil, posing significant threats to both the environment and human health [4,5]. The black soil region of northeast China is renowned for its fertile land, which is essential for agricultural productivity [6,7]. Yet, this region has not been spared from the infiltration of PTEs [8–10], which necessitates a comprehensive evaluation of their distribution, potential risks, and sources.

The presence of PTEs in soil can be attributed to various natural and anthropogenic sources [11–13], including industrial emissions, agricultural practices, and atmospheric deposition. These elements, even at low concentrations, can have detrimental effects on soil fertility, crop growth [14], and the food chain, eventually impacting human health [15]. Therefore, understanding the distribution patterns, assessing the ecological and health risks, and identifying the sources of PTEs are of paramount importance for the development of effective management strategies.

In this study, we employ the principal component analysis (PCA) and the Positive Matrix Factorization (PMF) model, two robust statistical techniques widely recognized in environmental research [16], to apportion the sources of PTEs in the black soil area of Hailun City. PCA is a dimensionality reduction method that simplifies the complexity of large datasets by identifying the underlying patterns, while PMF is a receptor model that quantitatively apportions the contributions of different sources to the observed pollutant concentrations.

Our objectives are to (1) investigate the spatial distribution pattern of PTEs, (2) evaluate their potential ecological and health risks, and (3) identify the predominant sources contributing to their presence in the soil. By integrating the findings from PCA and PMF model, we aim to provide a clearer understanding of the pollution characteristics and prioritize management strategies to mitigate the risks associated with PTEs in the black soil of Hailun City. The findings anticipate bolstering the formulation of policies and steering sustainable land stewardship, thereby ensuring the enduring health of the black soil and the prosperity of the communities that depend on it.

2. Materials and Methods

2.1. Study Region

The study region is located in Gonghe Town, Hailun City, which is situated in the core area of black soil in northeast China, with a total area of about 174.16 km², spanning the latitude 126°31'25" to 126°45'30" East and longitude 47°15'51" to 47°25'16" North, with an elevation ranging from 165 to 238 meters above sea level (Figure 1). The region under investigation is defined by a continental monsoon climate, which is marked by a mean annual temperature of 2.7 °C, alongside with an annual precipitation of 580.5 mm and an annual rate of evaporation that goes beyond 837 mm. The stratigraphy of the study region is predominantly consisting of middle Pleistocene lacustrine deposits, upper Pleistocene alluvial deposits and Holocene floodplain deposits. The average value of black soil layer is 65 cm thick and its bulk density is recorded at 1.37 g/cm³. Gonghe Town is primarily an agricultural community, with a focus on soybean, corn, potato et al. In recent years, the town has witnessed the emergence of transportation, commerce, and other tertiary industries, leading to its transformation into a nascent business center [17].

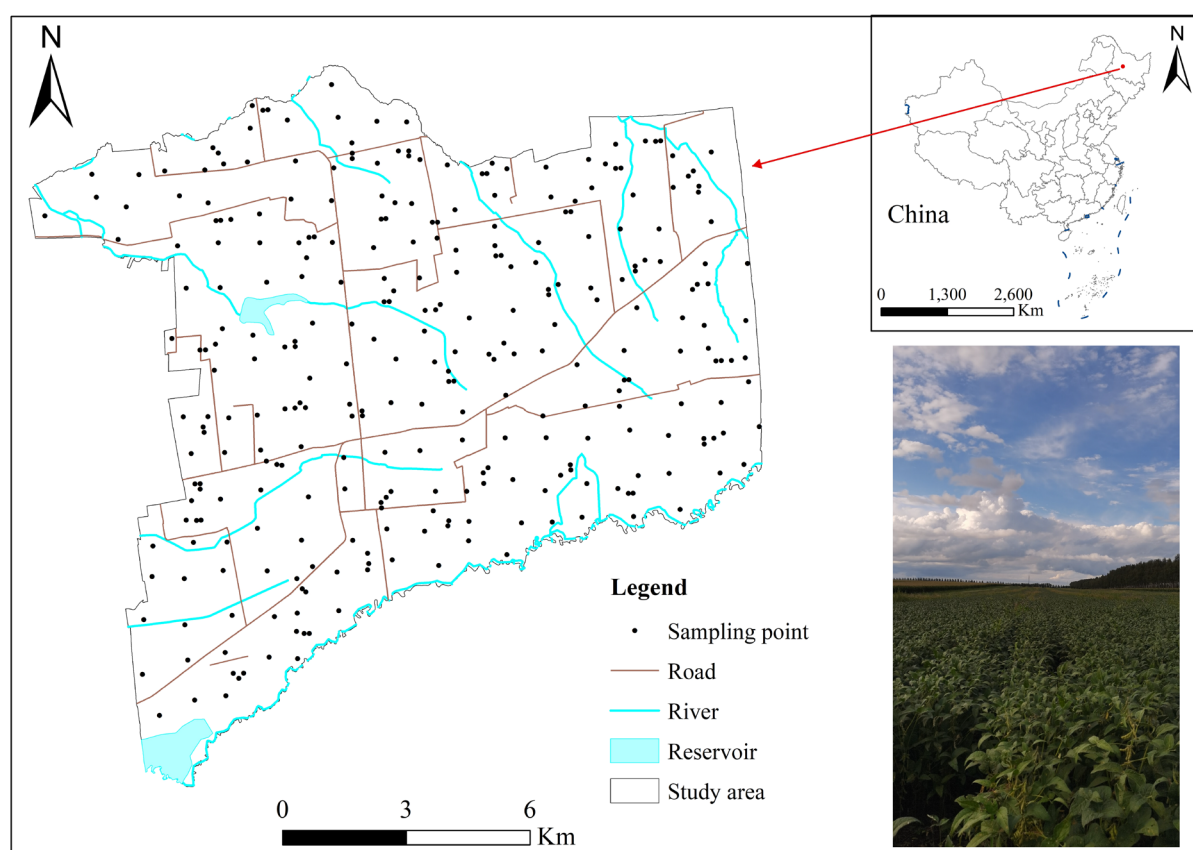


Figure 1. Map of study region location and sampling sites.

2.2. Sampling and Analysis

A total of 304 surface soil samples were collected from May to August 2021, and all sampling points were located using GPS. Combined with the land use, soil type, and geological construction of the research region, the grid layout was implemented with ArcGIS 10.8 software, with a sampling density of 8 points per km² and a sampling depth of 0-20 cm. Sampling was carried out using the Plum Blossom Point method, which consists of an equal mix of five subsamples to form one sample, retaining about 1 kg of soil sample. Once collected, the samples were meticulously placed in cloth bags, assigned unique identifiers, sealed, and then subjected to a precise weighing process. Subsequently, the samples were air-dried in a well-ventilated and clean environment, ensuring optimal conditions for preservation. Post-drying, the samples underwent sieving with a 10-mesh nylon sieve to meticulously exclude plant roots, stones, and other impurities. The purified samples were subsequently divided into sample sizes and sent to the laboratory for subsequent analysis.

The analytical testing of soil samples for PTEs and pH was done by the laboratory of the Harbin Center for Integrated Natural Resources Survey, China Geological Survey. The methodologies employed for analysis, alongside their respective detection thresholds, are shown within Table 1.

Adhering to the precision and accuracy criteria of the national soil standards (GBW series), a random 5% subset of the samples was chosen for concurrent analysis throughout the testing process. The results demonstrated that 100% of the duplicate samples passed the test, and the quality of the data analysis was found to meet the relevant requirements.

Table 1. Laboratory analytical methods and detection limits.

Element	Analytical Methods	Detection Limit	Digestion Method
Arsenic	AFS	0.6	aqua regia
Cadmium	ICP-OES	0.01	HF+HCl+HNO ₃ +HClO ₄
Chromium	XFS	2.79	Pressed powder pellets
Copper	XFS	0.85	Pressed powder pellets
Mercury	AFS	0.0005	aqua regia
Nickel	XFS	1	Pressed powder pellets
Lead	XRF	1.88	Pressed powder pellets
Zinc	XRF	1.5	Pressed powder pellets
pH	ISE	0.1	HF+HCl+HNO ₃ +HClO ₄

The unit of PTEs is mg/kg; pH is dimensionless. See literature[9] for analytical methods.

2.3. Study Methods

For the purpose of this investigation, four metrics were engaged to determine the degree of soil contamination in the study region: the single-factor pollution index (*PI*), the Nemerow pollution index (*NPI*), the potential ecological risk coefficient for individual PTEs (*Er*), and the overall ecological risk index (*RI*). The grading criteria of each index are presented in Table 2 [9,18]. A quantitative description of the potential risk of soil PTEs to human health was achieved through the application of the human health risk index (*HI*). PCA and PMF were utilized to identify the origins of soil PTEs within the study region and to measure the proportional contribution of each source, to establish a theoretical foundation for subsequent management strategies.

Table 2. Class of indices: *PI*, *NPI*, *Er*, *RI*.

Class	<i>PI</i>	<i>NPI</i>	<i>Er</i>	<i>RI</i>
1	<1 uncontaminated	≤0.7 clean	<40 slight ecological risk	<150 slight ecological risk
2	1-2 lightly contaminated	0.7-1 warning limit	40-80 moderate ecological risk	150-300 moderate ecological risk
3	2-3 moderately contaminated	1-2 slight pollution	80-160 considerable ecological risk	300-600 high potential ecological risk
4	>3 strongly contaminated	2-3 moderate pollution	160-320 high ecological risk	≥320 significantly high ecological risk
5		>3 heavy pollution	≥320 serious ecological risk	

2.3.1. Single-Factor Index (PI)

PI serves as a metric for evaluating the contamination level of an individual PTE within the study region [19,20]. The index can be calculated as Equation (1):

$$PI = \frac{C_i}{S_i} \tag{1}$$

here *PI* refers to the single-factor pollution index of PTE *i* in the soil; *C_i* refers to the determined concentration of PTE *i* in the sample measured in mg/kg; *S_i* refers to the background value in Songnen Plain [21]. The classification levels are presented in Table 2.

2.3.2. Nemerow Pollution Index (NPI)

The *NPI* can be employed to evaluate the contamination status of PTEs in the soil of the study region [22]. This index can be calculated as Equation (2):

$$NPI = \sqrt{\frac{PI_{ave}^2 + PI_{max}^2}{2}} \quad (2)$$

here, *NPI* represents the aggregate pollution index for the sampling site; PI_{ave} and PI_{max} correspond to the mean and the highest value of *PI* in PTEs. The classification levels are presented in Table 2.

2.3.3. Index of Potential Ecological Risk (RI)

Håkanson [20] proposed the index of potential ecological risk, which can be utilized for evaluating soil contamination by PTEs and the associated ecological risks, with the calculation detailed in Equation (3):

$$RI = \sum_{i=1}^n E_r^i = \sum_{i=1}^n (T_r^i \times C_f^i) = \sum_{i=1}^n (T_r^i \times \frac{C_i}{C_n^i}) \quad (3)$$

here, *RI* refers to the potential ecological risk index; E_r^i represents the potential ecological risk index for an individual PTE; T_r^i represents the corresponding toxicity coefficient for an individual PTE, with As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn having coefficients of 10, 30, 2, 5, 40, 5, 5, and 1, respectively [20]. C_f^i is the contamination index for an individual PTE; C_i and C_n^i refer to the background concentrations of PTEs in the soil. The classification levels are presented in Table 2.

2.3.4. Human Health Risk Index (HI)

HI can quantitatively describe the human health hazards of soil PTEs. According to the EPA standard [23], PTEs may enter the human body via three primary routes—ingestion from hand-to-mouth activity, inhalation, and skin absorption—posing both carcinogenic and non-carcinogenic threats to human health. [24]. In calculating the risk to humans from different pathways, it is necessary to distinguish between adults and children, given that the likelihood of children's exposure to carcinogenic PTEs is higher than that of adults. The formula for adults is as Equation (4)-(6):

$$ADD_{ing} = \frac{C_i \times IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (4)$$

$$ADD_{inh} = \frac{C_i \times InhR \times EF \times ED}{PEF \times BW \times AT} \quad (5)$$

$$ADD_{iderm} = \frac{C_i \times SA \times SL \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (6)$$

here, ADD_{ing} , ADD_{inh} and ADD_{iderm} represent the mean daily intake of a PTE through ingestion from hand-to-mouth activity, inhalation, and skin absorption; C_i indicates the concentration of the PTE in milligrams per kilogram; Additional parameters are listed in Yu's study [9].

The formula for children is as Equation (7)-(9):

$$LADD_{ing} = \frac{C_i \times EF}{AT} \times \left(\frac{IngR_{child} \times ED_{child}}{BW_{child}} + \frac{IngR_{adult} \times ED_{adult}}{BW_{adult}} \right) \times 10^{-6} \quad (7)$$

$$LADD_{inh} = \frac{C_i \times EF}{PEF \times AT} \times \left(\frac{InhR_{child} \times ED_{child}}{BW_{child}} + \frac{InhR_{adult} \times ED_{adult}}{BW_{adult}} \right) \quad (8)$$

$$LADD_{iderm} = \frac{C_i \times EF \times SL \times ABS}{AT} \times \left(\frac{SA_{child} \times ED_{child}}{BW_{child}} + \frac{SA_{adult} \times ED_{adult}}{BW_{adult}} \right) \times 10^{-6} \tag{9}$$

The risks that are non-carcinogenic and carcinogenic are evaluated through the subsequent Equation (10)-(11):

$$HI = \sum_{i=1}^n HQ_i = \sum_{i=1}^n \frac{ADD_{iing} + ADD_{iinh} + ADD_{iderm}}{RfD_i} \tag{10}$$

here, *HI* represents the cumulative non-carcinogenic risk posed by all soil PTEs; *HQ_i* signifies the non-carcinogenic risk index for an individual PTE; *RfD_i* denotes the reference dose of toxicity; A value of *HI* < 1 suggests an absence of notable non-carcinogenic risk, while *HI* > 1 suggests the presence of potential non-carcinogenic risk, the probability of which increases with increasing value [25].

$$TCR = \sum_{i=1}^n CR_i = \sum_{i=1}^n \left(ADD_{iing} + ADD_{iinh} + ADD_{iderm} \right) \times SF_i \tag{11}$$

here, *TCR* denotes the composite carcinogenic risk index for all PTEs; *CR_i* is the carcinogenic risk associated with a specific PTE; and *SF* is the corresponding reference slope factor, which are detailed in Table 3 [9]. If *TCR* < 1 × 10⁻⁶, suggests an insignificant carcinogenic risk; 1 × 10⁻⁶ < *TCR* < 1 × 10⁻⁴, the risk is deemed acceptable; if *TCR* > 1 × 10⁻⁴, it indicates a significant carcinogenic risk [25,26].

Table 3. Threshold dose and slope factors of PTEs through different pathways.

PTEs	RfD [mg/(kg·d)]				SF [mg/(kg·d)]		
	ADD _{iing}	ADD _{iderm}	ADD _{iinh}	LADD _{iinh}	Through Mouth	Skin	Breathing
Arsenic	3.0 × 10 ⁻⁴	3.0 × 10 ⁻⁴	3.52 × 10 ⁻⁶	5.86 × 10 ⁻⁶	1.5	1.5	4.3 × 10 ⁻³
Cadmium	1.0 × 10 ⁻³	2.5 × 10 ⁻⁵	2.35 × 10 ⁻⁶	3.91 × 10 ⁻⁶	6.1	6.1	6.3
Chromium	3.0 × 10 ⁻³	7.5 × 10 ⁻⁵	2.35 × 10 ⁻⁵	3.91 × 10 ⁻⁵			
Copper	4.0 × 10 ⁻²	4.0 × 10 ⁻²					
Mercury	3.0 × 10 ⁻⁴	2.1 × 10 ⁻⁵	7.04 × 10 ⁻⁵	1.17 × 10 ⁻⁵			
Nickle	2.0 × 10 ⁻²	8.0 × 10 ⁻⁴	2.11 × 10 ⁻⁵	3.52 × 10 ⁻⁵			
Lead	3.5 × 10 ⁻³	5.3 × 10 ⁻⁴	8.21 × 10 ⁻⁵	1.37 × 10 ⁻⁴			
Zinc	3.0 × 10 ⁻¹	3.0 × 10 ⁻¹					

2.3.5. Positive Matrix Factorization (PMF)

PMF is a multivariate factor analytical technique that operates on the principle of minimal iterative refinement [27]. The basic equations are as Equations (12)-(15):

$$X_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \tag{12}$$

here, *X_{ij}* denotes the concentration of element *j* in sample *i*; *g_{ik}* signifies the contribution to sample *i* by factor *k*; *f_{kj}* refers to the specific contribution from factor *k* to element *j*; *e_{ij}* represents the residual error for PTE *j* in sample *i*.

The calculation of the objective function *Q* is performed according to the subsequent Equation (13):

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{u_{ij}} \right)^2 \quad (13)$$

here, u_{ij} is the uncertainty of PTE j in the sample i .

For cases where the concentration of an element is less than or equal to the method detection limit (MDL), the calculation of uncertainty proceeds as indicated:

$$u_{ij} = \frac{5}{6} \times MDL \quad (14)$$

For cases where the concentration of an element is more than its MDL, the calculation of uncertainty proceeds as indicated:

$$u_{ij} = \sqrt{(Errorfraction + c)^2 + (0.5 \times MDL)^2} \quad (15)$$

here, c refers to the concentration of a single element; *Errorfraction* refers to the error fraction of the analytical method; and *MDL* represents the method detection limit value.

2.3.6. Source-oriented Potential Ecological Risk and Human Health Risk

By employing the PMF model to identify the contributions of each PTE to disparate pollution sources and amalgamating this data with ecological risk assessment results, the degree to which different sources contribute to ecological risk was established [28]. The methodology for this calculation is outlined in Equations (16) and (17):

$$RI_j = \sum F_{ij} \times RI_i \quad (16)$$

$$D_{j,RI} = \frac{RI_j}{RI} \quad (17)$$

here, RI_j represents the potential ecological risk of the source category j ; F_{ij} represents the contribution of the PTE i in the source category j ; c refers to the potential ecological risk of the PTE i ; RI_i represents the contribution of the potential ecological risk of the source category j ; and RI refers to the total PTEs ecological risk index.

Utilizing the contributions of individual PTEs to various pollution sources as determined by the PMF model, in conjunction with outcomes from health risk assessments, different sources' contribution to human health risk was derived [28]. This was calculated by the following Equations (18)-(21):

$$HQ_j = \sum F_{ij} \times HQ_i \quad (18)$$

$$CR_j = \sum F_{ij} \times CR_i \quad (19)$$

$$D_{j,HQ} = \frac{HQ_j}{HI} \quad (20)$$

$$D_{j,CR} = \frac{CR_j}{CR} \quad (21)$$

here, HQ_j represents the non-carcinogenic hazard quotient of the source j , while CR_j denotes the carcinogenic risk for the same source; F_{ij} refers to the concentration of PTE i in the source j ; $D_{j,HQ}$

indicates the percentage contribution of the non-carcinogenic hazard quotient to source j ; $D_{j,CR}$ signifies the percentage contribution of the carcinogenic risk to source j .

2.4. Statistical Analysis

Descriptive statistics, correlation assessments, and PCA were conducted utilizing SPSS v22.0 (IBM, USA) and Originpro 2024 (OriginLab, USA); soil PTEs contamination source analysis work was performed using EPA PMF v5.0 (USEPA, USA) with SPSS v22.0 (IBM, USA); ArcGIS 10.8 (ESRI, Redlands, CA, USA) and OriginPro 2024 (OriginLab, USA) were employed for mapping correlations; and Excel 2019 (Microsoft Inc., Seattle, WA, USA) for calculating values of PI , NPI , RI , and HI .

3. Results

3.1. Statistical Characteristics and Spacial Distribution of PTEs

Table 4 illustrates the statistical synthesis of PTE and pH values and shows that the mean concentrations for As, Cd, Cr, Cu, Hg, Ni, Pb and Zn were 11.16, 0.11, 65.29, 22.56, 0.03, 27.07, 26.09 and 66.01 mg/kg respectively. In comparison, the mean concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn were found to exceed the background concentrations of the Songnen Plain by factors of 1.22, 1.49, 1.54, 1.27, 1.14, 1.29 and 1.27, respectively [21]. While Hg was 0.97 of the background value.

The soil samples from the study region exhibited a weakly acidic (pH mean 6.39). With the exception of a single sample that displayed a Cd concentration surpassing the risk control standard's screening value for environmental quality in soils [29], all PTEs of the other samples did not exceed the screening value. The variability indices (CV) of the eight PTEs analyzed within the soil samples are ranked as follows: Cd (0.36) > Hg (0.30) > As (0.12) > Pb (0.11) > Zn (0.07) > Cu (0.06) > Cr (0.05) = Ni (0.05).

Table 4. Statistics of PTEs and pH in the soil samples.

Elements	Min	Mean	Max	Median	SD	CV	Background value	Screening value
Arsenic	5.56	11.16	16.88	11.13	1.32	0.12	9.14	40.00
Cadmium	0.06	0.11	0.47	0.10	0.04	0.36	0.073	0.30
Chromium	51.15	65.29	75.84	65.45	3.46	0.05	42.46	150.00
Copper	17.72	22.56	28.71	22.48	1.32	0.06	17.78	50.00
Mercury	0.02	0.03	0.08	0.03	0.01	0.30	0.031	1.30
Nickel	22.51	27.07	30.94	27.03	1.46	0.05	23.65	60.00
Lead	21.18	26.09	57.30	25.74	2.84	0.11	20.23	70.00
Zinc	51.66	66.01	106.81	65.93	4.52	0.07	52.05	200.00
pH	5.45	6.39	8.51	6.24	0.52	0.08	8.30	

The coefficient of variation (CV); Standard Deviation(SD); The unit of the content of each element is mg/kg; pH is dimensionless.

The spatial pattern of PTEs in the study region was obtained by the inverse distance weighting method (Figure 2). The spatial distribution of Cr, Ni, Cu, and Zn in the surface soil exhibited a similar pattern, with elevated concentrations observed in the northern and western regions, declining towards the southeast, and no notable peaks in the central area of the town. However, there were sporadic instances of elevated concentrations in the southeast, particularly in the vicinity of the river. The elements Cd and Hg exhibit a comparable spatial distribution, characterized by elevated concentrations near agricultural lands in rural settlements. Similarly, As and Pb show a related distribution, with high concentrations localized to areas adjacent to rivers.

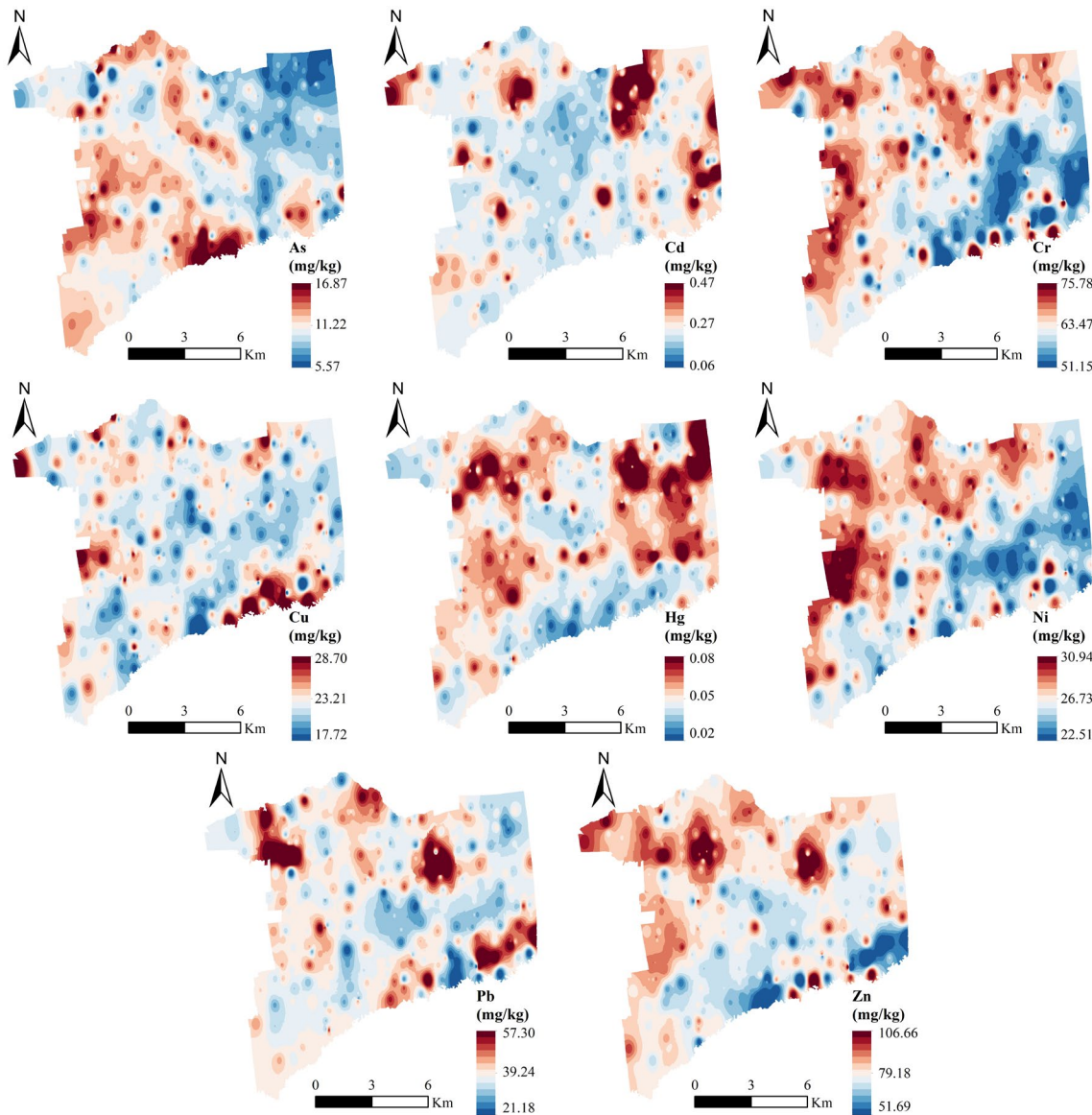


Figure 2. Spatial distribution of PTEs in the study region.

3.2. Status of PTEs Pollution

Grading based on the calculated PI values (Figure 3) shows that 3.95%, 2.63%, 0.33%, 67.76%, 1.32%, and 0.33% of the samples were As, Cd, Cu, Hg, Ni, Pb, and Zn non-polluted ($PI < 1$); meanwhile, 96.05%, 89.80%, 100.00%, 99.67%, 30.59%, 98.68%, 99.34%, and 99.01% were As, Cd, Hg, Pb, and Zn lightly polluted ($1 < PI < 2$); in addition, Cd, Hg, Pb and Zn moderately contaminated samples accounted for 5.59%, 1.64%, 0.66% and 0.66% ($2 < PI < 3$); lastly, there are individual samples of Cd in the state of strong contamination, which accounted for only 1.97% ($PI > 3$).

NPI outcomes showed that the majority of soil samples (95.07%) mainly exhibited ecological risks of slight pollution ($1 < NPI < 2$). Meanwhile, 4.28% and 0.66% were classified at the thresholds of moderate pollution ($2 < NPI < 3$) and heavy pollution ($NPI > 3$).

The results of the *PI* and *NPI* showed that there is overall slight pollution of PTEs in the study region. Moderate and heavy PTE pollution existed in individual sampling sites and their main polluting elements were Cd, Hg, Pb and Zn.

Table 5 presents the outcomes of the potential ecological risk index for PTEs, with the average *Er* values arranged from lowest to highest as follows: Zn, Cr, Ni, Cu, Pb, As, Hg, and Cd.

[illegible]

The E_r levels associated with As, Cr, Cu, Ni, Pb, and Zn were all determined to be beneath 40, a figure that denotes a low level of ecological hazard. The E_r values of Cd exhibited a range of ecological risks, with 39.47%, 56.58%, 3.29% and 0.66% of soil samples displaying slight, moderate, considerable and high ecological risks, respectively. The E_r values attributed to Hg revealed that 67.76% of soil samples faced a slight ecological risk, 30.59% a moderate ecological risk, and 1.64% a substantial ecological risk. In terms of the RI, the soil samples' values extended from 81.82 to 259.02, averaging at 118.42, which corresponds to slight ecological risk in 93.09% and moderate ecological risk in 6.91% of the cases. In sum, the ecological risk level of the study region is classified as slight.

3.4. Human Health Risk of PTEs

Table 6 displays the HQ for adults and children across three exposure pathways, listed from highest to lowest as follows: HQ for ingestion, dermal, and inhalation exposures. The HQ values for various PTEs in soil, ranked from greatest to least, are: As, Cr, Pb, Ni, Cu, Hg, Zn, and Cd. The combined HQ for multiple PTEs via the three exposure routes were calculated to be 1.17×10^{-1} for adults and 3.24×10^{-1} for children. The findings indicate that while children experienced a higher HI than adults, neither group surpassed the threshold of 1, which is the non-carcinogenic risk alert value, signifying no human health risk.

Table 6. Results of non-carcinogenic risk evaluation by different exposure routes.

Element	HQ_{iing}		HQ_{iinh}		HQ_{iderm}		HI	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Arsenic	5.54×10^{-2}	1.45×10^{-1}	5.03×10^{-4}	4.28×10^{-4}	6.25×10^{-3}	2.55×10^{-2}	6.21×10^{-2}	1.70×10^{-1}
Cadmium	1.62×10^{-4}	4.22×10^{-4}	7.33×10^{-6}	6.24×10^{-6}	2.43×10^{-5}	9.91×10^{-5}	1.93×10^{-4}	5.27×10^{-4}
Chromium	3.24×10^{-2}	8.46×10^{-2}	4.41×10^{-4}	3.76×10^{-4}	4.88×10^{-3}	1.99×10^{-2}	3.77×10^{-2}	1.05×10^{-1}
Copper	8.40×10^{-4}	2.19×10^{-3}			1.90×10^{-4}	7.73×10^{-4}	1.03×10^{-3}	2.96×10^{-3}
Mercury	1.49×10^{-4}	3.89×10^{-4}	6.78×10^{-8}	5.78×10^{-7}	4.01×10^{-4}	1.63×10^{-3}	5.50×10^{-4}	2.02×10^{-3}
Nickel	2.02×10^{-3}	5.26×10^{-3}	2.04×10^{-4}	1.73×10^{-4}	1.90×10^{-4}	7.73×10^{-4}	2.41×10^{-3}	6.21×10^{-3}
Lead	1.11×10^{-2}	2.90×10^{-2}	5.05×10^{-5}	4.28×10^{-5}	1.66×10^{-3}	6.75×10^{-3}	1.28×10^{-2}	3.58×10^{-2}
Zinc	3.28×10^{-4}	8.55×10^{-4}			1.76×10^{-5}	1.01×10^{-4}	3.45×10^{-4}	9.56×10^{-4}
Total risk	1.02×10^{-1}	2.67×10^{-1}	1.21×10^{-3}	1.03×10^{-3}	1.36×10^{-2}	5.55×10^{-2}	1.17×10^{-1}	3.24×10^{-1}

Given that slope factors are only accessible for As and Cd, a carcinogenic risk assessment was conducted solely for these two elements across three exposure routes. Table 7 illustrates that the carcinogenic risks (CR) for both adults and children, ranked from highest to lowest, are dominated by ingestion, followed by dermal and inhalation exposures. The order of carcinogenic risk for PTEs in the population is As being more significant than Cd. The RI for exposure to PTEs through the three pathways was calculated as 1.03×10^{-5} for adults and 2.60×10^{-5} for children. For all age groups, the carcinogenic risk fell within the acceptable range of $1 \times 10^{-6} < CR < 1 \times 10^{-4}$.

Table 7. Results of carcinogenic risk evaluation by different exposure routes.

Element	CR_{iing}		CR_{iinh}		CR_{iderm}		TCR	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children

Arsenic	8.20×10^{-6}	2.14×10^{-5}	2.51×10^{-12}	3.55×10^{-12}	9.25×10^{-7}	3.77×10^{-6}	9.12×10^{-6}	2.52×10^{-5}
Cadmium	3.24×10^{-7}	8.46×10^{-7}	8.74×10^{-7}	5.06×10^{-11}	1.22×10^{-9}	4.97×10^{-9}	1.20×10^{-6}	8.51×10^{-7}
Total risk	8.52×10^{-6}	2.22×10^{-5}	8.74×10^{-7}	5.41×10^{-11}	9.27×10^{-7}	3.78×10^{-6}	1.03×10^{-5}	2.60×10^{-5}

3.5. Source Analysis of PTEs

3.5.1. Pearson Correlation Analysis

Figure 4 presents the outcomes of Pearson's correlation analysis for the eight PTEs, revealing statistically significant positive associations between Cr, Cu, Ni, and Zn ($p < 0.01$), as well as between Pb and As, Cd, Ni, and Zn ($p < 0.01$), and between Hg and Zn ($p < 0.01$).

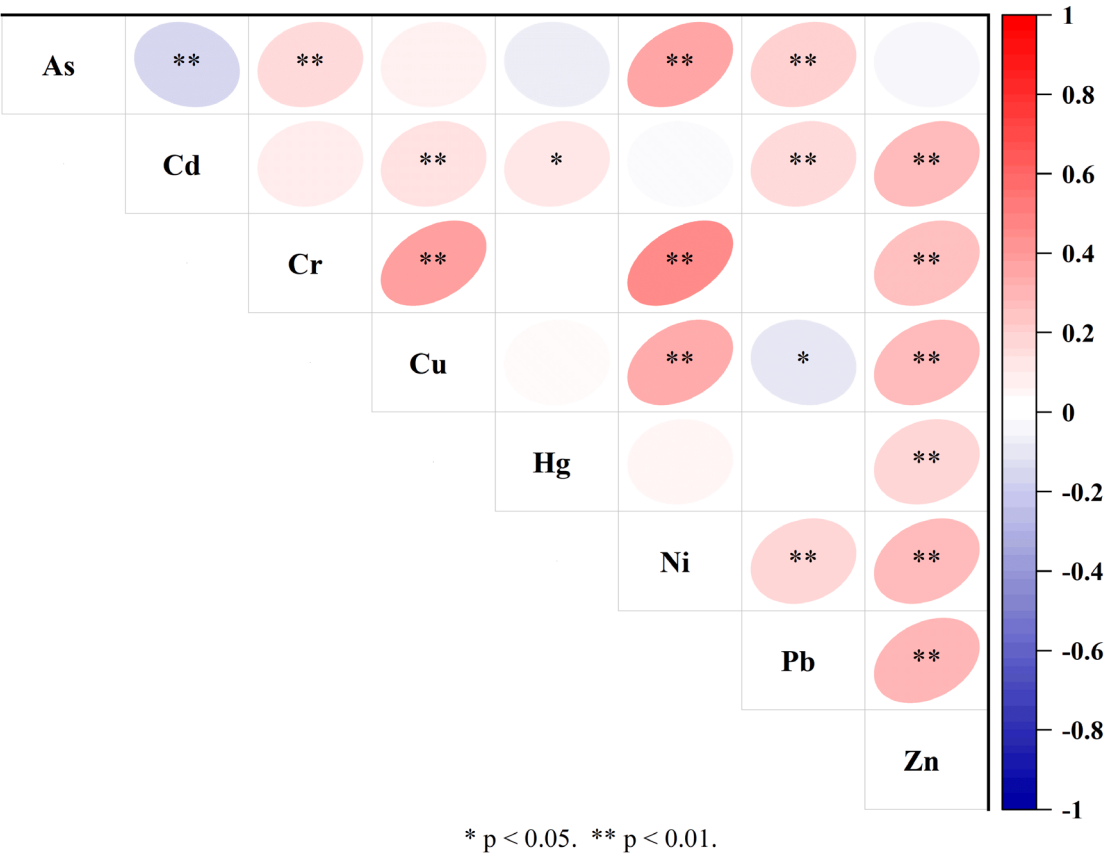


Figure 4. Pearson correlation analysis results.

3.5.2. PCA

Prior to PCA execution, the concentration data of PTEs successfully met the criteria of the KMO and Bartlett's test ($KMO = 0.61$, Bartlett's significance = 0.00). Table 8 displays the retention of three principal components, each with an eigenvalue exceeding 1.0, which together accounted for a cumulative variance of 61.80%. The first principal component (PC1) accounted for 27.97% of the variance, characterized by substantial positive loadings for Cr, Cu, Ni, and Zn with values of 0.708, 0.633, 0.752, and 0.653, respectively. The second principal component (PC2) represented 18.34% of the variance, with Cd and Hg showing significant positive loadings of 0.670 and 0.457, respectively. Lastly, the third principal component (PC3) elucidated 15.49% of the variance, with As and Pb exhibiting notable positive loadings of 0.358 and 0.848, respectively.

Table 8. Factor load matrix of principal component analysis.

Element	Principal component		
	PC1	PC2	PC3
Arsenic	0.331	-0.669	0.358
Cadmium	0.289	0.670	0.056
Chromium	0.708	-0.155	-0.314
Copper	0.633	-0.010	-0.512
Mercury	0.204	0.457	0.001
Nickel	0.752	-0.362	0.035
Lead	0.329	0.105	0.848
Zinc	0.653	0.442	0.164
Eigenvalues	2.238	1.467	1.239
Variance contribution rate/%	27.97	18.34	15.49
Cumulative variance contribution rate/%	27.97	46.31	61.80

3.5.3. PMF Model

The soil PTEs data were subjected to source apportionment analysis using the EPA PMF 5.0 software, ensuring a signal-to-noise ratio (S/N) of at least 8.0 for each element, fulfilling the modeling prerequisites. Simultaneously, the factor count was configured to range from two to seven, with the model iterated 20 times. The determination of the most optimal factor count was achieved by evaluating the ratio of $Q_{robust}/Q_{expected}$ across various factor counts. The findings indicate that the model achieves optimal stability with a factor count of four, as illustrated in Figure 5.

Factor 1 constituted 33.2% of the overall pollution source variance, with Cr, Cu, Ni, and zinc Zn exhibiting the most substantial loadings, contributing 35.7%, 36.2%, 33%, and 36.3% respectively; Factor 2 represented 29.5% of the total pollution source variance, with As and Pb having the most significant contributions at 54.6% and 35.3% respectively; Factor 3 made up 23.4% of the total pollution sources, with Hg being the predominant contributor at a rate of 66%.

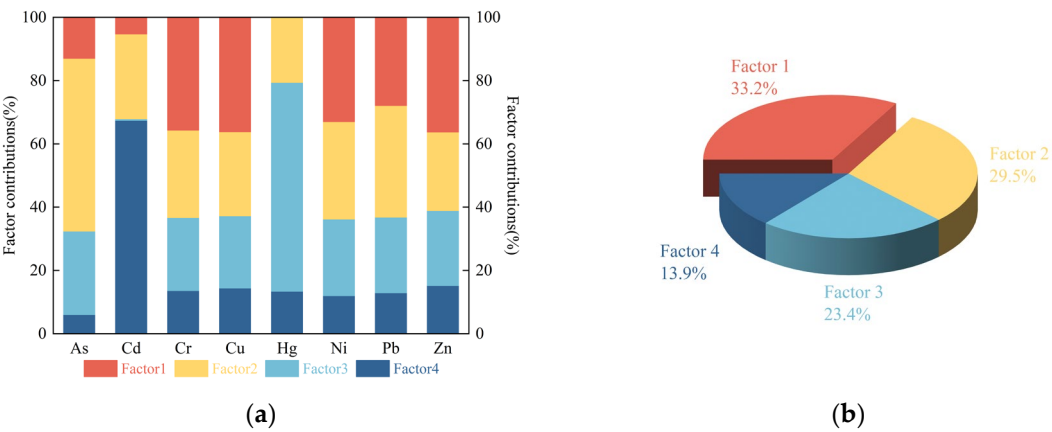


Figure 5. (a) Factor profiles of PTEs derived from the PMF model; (b) The percentage of contribution by an individual factor using the PMF model.

4. Discussion

4.1. Source Apportionment

4.1.1. PCA

PC1 primarily represents Cr, Cu, Ni and Zn. Combined with the results of Pearson correlation analysis (Figure 4), there is a significant positive correlation between Cr, Cu, Ni and Zn ($p<0.01$),

indicating that the four elements are most likely of the same source, which is consistent with the results of PCA. In terms of spatial distribution (Figure 2), the four elements of Cr, Cu, Ni and Zn have similar spatial distribution patterns, are more evenly distributed spatially, are less affected by human activities, and their genesis is generally related to the soil-forming parent material [30]. The geologic construction of the study region is all Quaternary stratigraphy, which is relatively homogeneous. Therefore, PC1 was described as a natural source.

PC2 primarily represents Cd and Hg. The coefficient of variation is large (>0.3), which indicates that the spatial distribution is uneven, most likely due to anthropogenic interference [31]. According to the results of *PI*, there are sporadic high values of Cd and Hg, indicating that the soil has been polluted by external factors. Combined with the spatial distribution (Figure 2), the areas of high values of Cd and Hg are located around the center of towns and villages with farmland. The study region is under the influence of various external pollution sources such as automobile exhaust, domestic sewage, and pesticides and fertilizers [32]. Therefore, PC2 was described as an anthropogenic pollution sources.

PC3 primarily represents As and Pb. Combined with the results of Pearson correlation analysis (Figure 4), there is a significant positive correlation between As and Pb ($p < 0.01$), indicating that the four elements are most likely from the same source [33]. Combined with the spatial distribution (Figure 2), the distribution areas of high As and Pb values are mainly concentrated in farmland near water facilities such as water systems, reservoirs and irrigation canals. According to the fieldwork, river water is used for the irrigation of farmland in the high-value area. Meanwhile, the river water polluted by industrial effluents may contain PTEs such as As and Pb, which in turn may contaminate the farmland soil [34]. Therefore, PC3 was described as an irrigation source.

4.1.2. PMF Model

Factor 1 was dominated by Cr, Cu, Ni and Zn. The coefficients of variation for all four PTEs are less than 0.1, indicating that they are less influenced by external factors and are most likely controlled by the geologic background and soil parent material [35]. In China, Cr, Cu and Ni are often used as indicators of natural sources [36,37]. Hu [38] found that Cu and Zn in soils are mainly derived from rock weathering and soil parent material. Liao [39] found that Cr, Cu, and Zn are mainly controlled by geochemistry, and are derived from natural backgrounds, such as soil parent material. In addition, the spatial distribution and contamination of the four elements are similar, and there is no serious contamination. Therefore, we defined factor 1 as a natural source.

Factor 2 was dominated by As and Pb, and this factor was primarily distributed near rivers, reservoirs and main irrigation canals in the area (Figure 6). The field survey revealed that there is a long-standing practice of using river water to irrigate the cultivated land in the study region. It has been shown that As and Pb elements in the soil are partly derived from industrial “three wastes” [40–42]. There are factories such as brick-making factories upstream of the rivers in the study region, and there are instances of industrial wastewater discharges into the rivers. Ultimately, this leads to the accumulation of As and Pb in the soil after irrigation [43]. Therefore, we defined factor 2 as an irrigation source.

Factor 3 was dominated by Hg. By comparing the spatial distribution (Figure 2) of Hg with the distribution of Factor 3 contribution values (Figure 6), it was found that the high-value overlap area is located near the main rural roads. The study region is dominated by agriculture and has a high level of annual agricultural transportation activity. It has been shown that Hg enrichment is closely related to transportation activities [44]. Guo [45] found that automobile fuels are enriched with Hg, which leads to the emission of tailpipe fumes that can cause Hg contamination of soil on both sides of the road [46]. Therefore, we defined factor 3 as a traffic source.

Factor 4 was dominated by Cd. By comparing the spatial distribution (Figure 2) of Cd with the distribution of Factor 4 contribution values (Figure 6), it was found that the areas of high concentration and contribution values overlap. The high-value area is point-like in the farmland area, indicating that they are subject to the greatest anthropogenic influences [5]. The study region is in China's grain production base, with a high level of agricultural mechanization and efficient

fertilization techniques. It has been shown that Cd contents of farmland are strengthened by applying fertilizers [38]. Meanwhile, due to the presence of cadmium in poultry feed, the manure produced after poultry feeding is applied to farmland as fertilizer, which can lead to farmland pollution [47]. Therefore, we defined factor 4 as a fertilizer source.

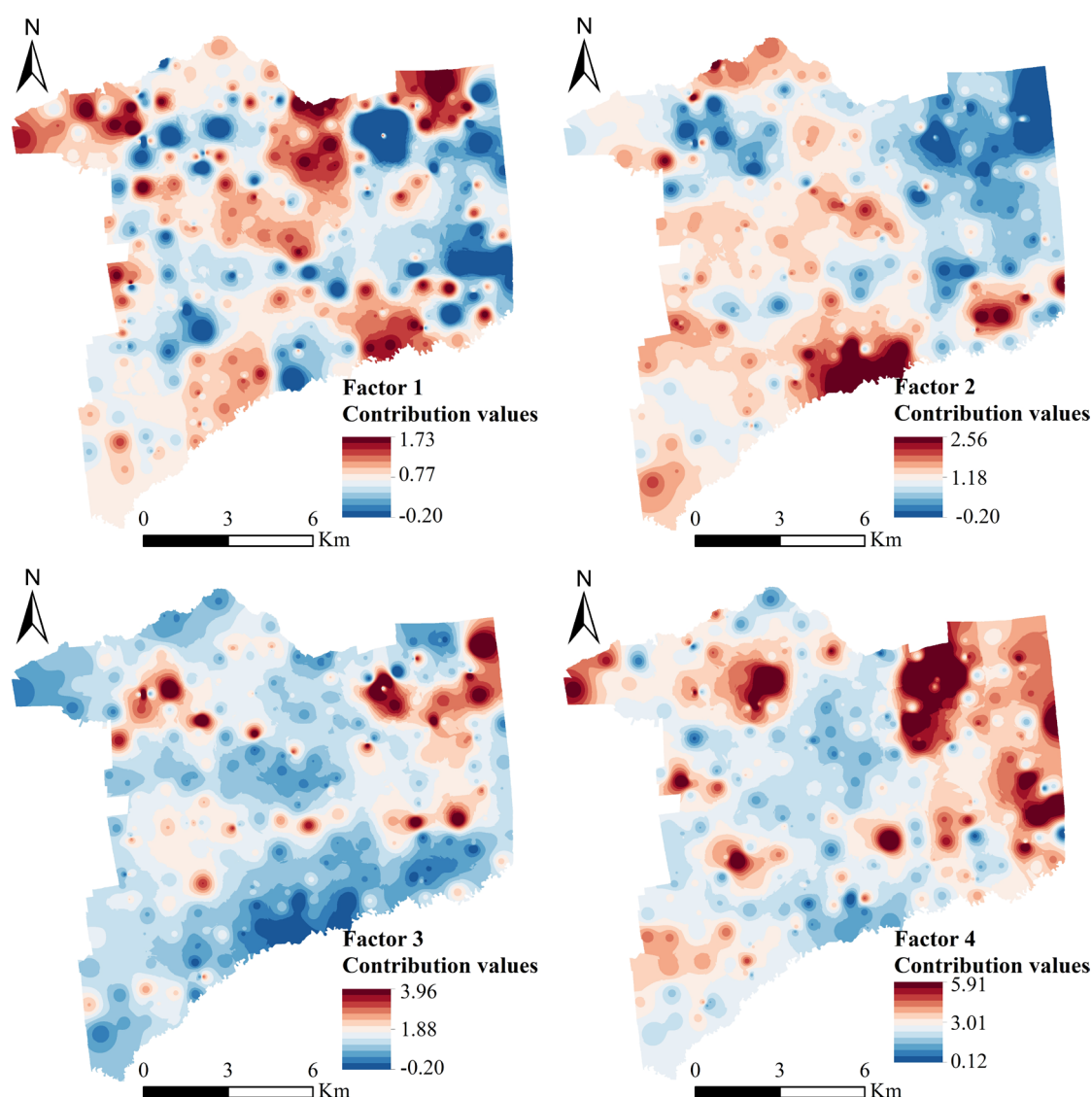


Figure 6. Spatial distribution of source contribution value of factor based on PMF model.

4.1.3. Comparison of PCA and PMF Model Source Identification

A comparison of the source apportionment results obtained from PCA and PMF revealed that they are inherently consistent. In terms of principal component positive loadings and factor contributions, factors 3 and 4 can be regarded as further resolutions of PC2. PC1 corresponds to factor 1. PC3 corresponds to factor 2. It can be found that PMF classifies the source identification results of PCA in more detail, which further validates the reliability of source apportionment. The conclusion is consistent with the findings of Zhou [48].

In summary, comparing the results of the two methods has improved the reliability and accuracy of source apportionment. However, the source identification of the PMF is better [16], so the results of the PMF are used in the following discussions.

4.2. Source-Oriented Analysis of Priority Control Factors for PTEs

A source-oriented risk assessment can assist in the identification of discrepancies in the nature of hazards emanating from disparate sources. [48]. To prioritize pollution sources for control, this study combines four sources of pollution with ecological and health risks.

Pollution sources affecting the potential ecological risk of soil are, in descending order: fertilizer source > traffic source > irrigation sources > natural source (Figure 7).

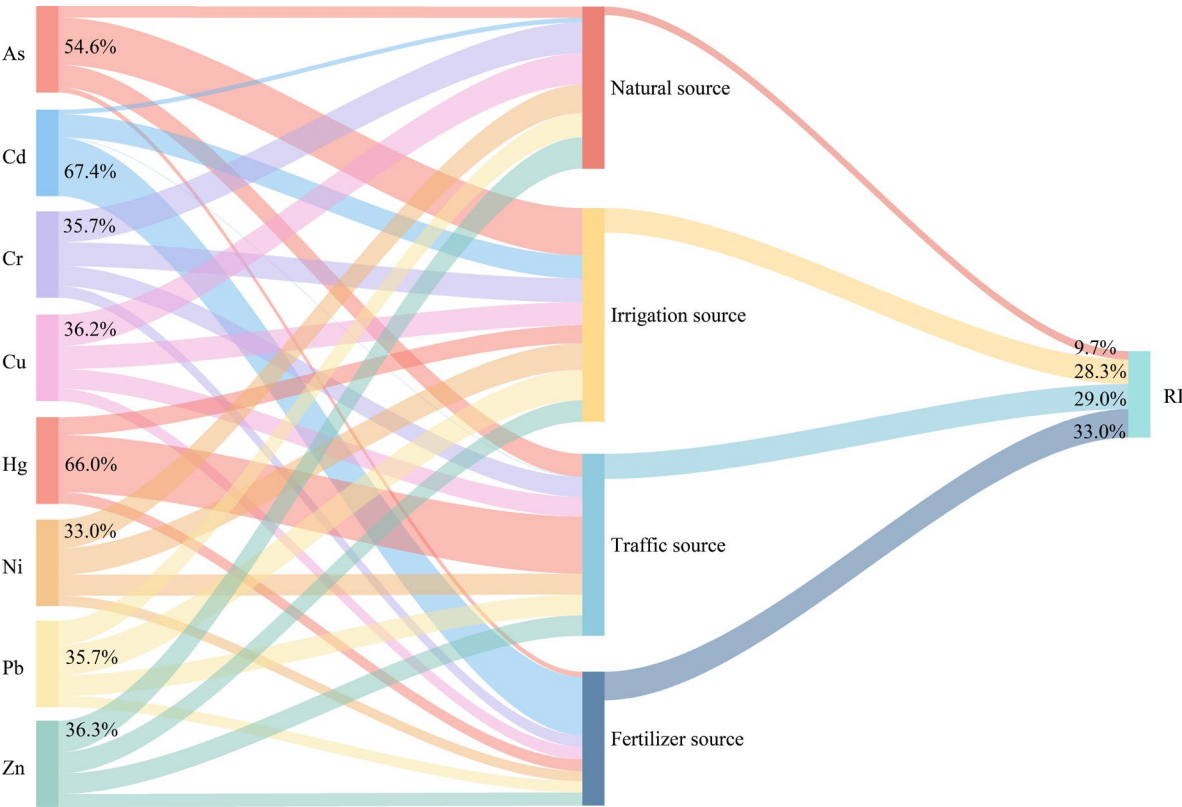


Figure 7. Relationship among PTEs, pollution sources and potential ecological risk.

Fertilizer source is the primary source of pollution affecting the *RI* of soil, with a contribution rate of 33.0%, and the PTEs are dominated by Cd. Cd in soil is easily absorbed by plant roots and transferred to various organs of plants, and is toxic to plants after accumulating to a certain concentration [49]. Some studies have shown that consumption of Cd-containing agricultural products is more readily absorbed by the human body, far exceeding the effects on human health of direct ingestion via the three exposure routes of hand-to-mouth activity, inhalation, and skin absorption [50]. Therefore, the control of fertilizer sources should be strengthened, such as the application of organic fertilizer with lower toxicity instead of chemical fertilizer [51]. In addition, irrigation sources and traffic sources have similar contribution rates of 28.3% and 29.0%, respectively. They should be considered as secondary sources of potential ecological risks of soil, with PTEs dominated by As, Pb and Hg. Low concentrations of As, Pb and Hg may also be toxic to plants and microorganisms [52,53]. Therefore, government departments should strengthen the control of irrigation and transportation sources. For example, reducing the discharge of factory wastewater and raising the standards of vehicle exhaust emissions [54,55].

The HI findings indicate that children experience elevated health risks in contrast to adults. Consequently, the study concentrated its analysis on children as a definitive group [28]. From Figure 8, the irrigation source is the primary source of health risk, contributing 42.7% and 53.7% to *HI* and carcinogenic risk *TCR*, respectively, with PTEs dominated by As and Pb. As and Pb are highly toxic. Above certain concentrations, they can damage the brain and nervous system [56,57]. Therefore, control of irrigation source needs to be strengthened. The traffic source is the secondary source of health risk, contributing 25.1% and 25.5% to *HI* and *TCR*, respectively, with PTEs dominated by Hg.

Hg deposition can be enriched in the body through bioaccumulation, presenting a significant risk to human health; for instance, chronic exposure at low levels during pregnancy may lead to a decrease in the intelligence quotient of offspring [58]. Therefore, control of traffic source needs to be strengthened, such as building more green belts with high adsorption capacity to gradually reduce air and soil pollution [59,60].

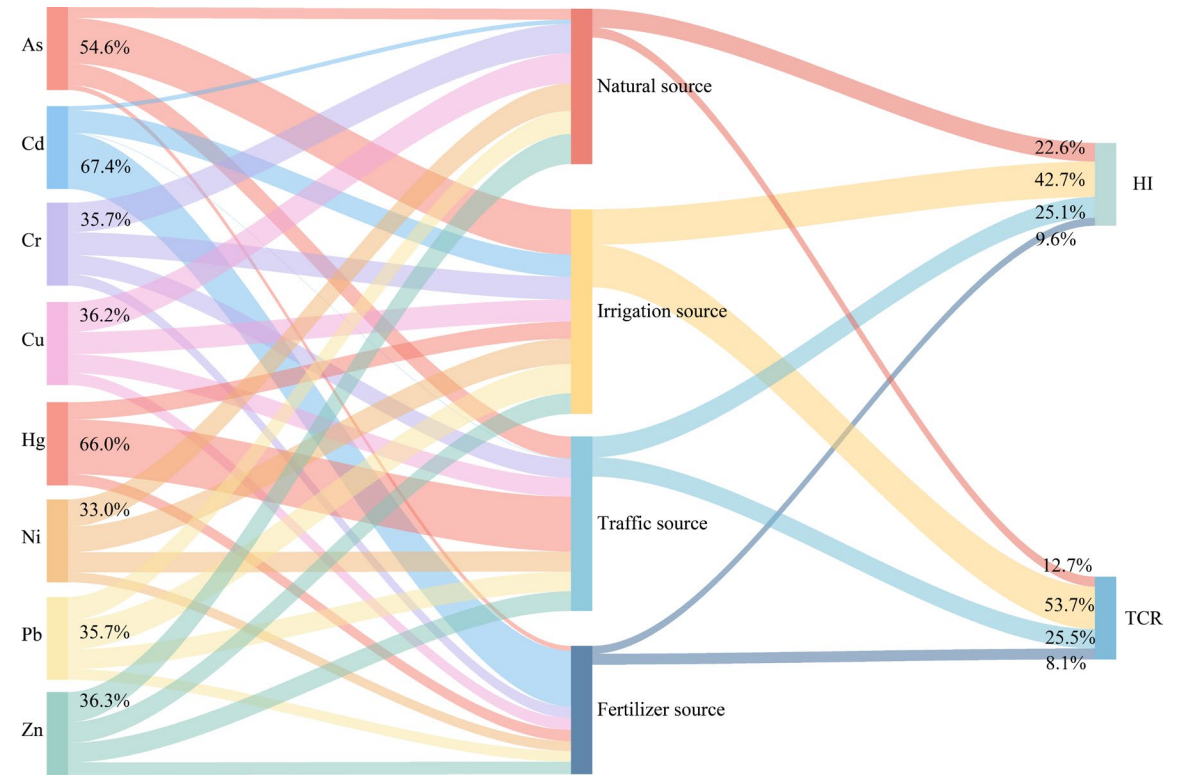


Figure 8. Relationship among PTEs, pollution sources and human health risk.

Findings from HI and RI, tailored to specific sources, exhibited discrepancies. The HI, as detailed in Tables 6 and 7, indicated that the non-carcinogenic risks attributable to As, Pb, and Hg from irrigation and traffic sources were negligible, and the carcinogenic risks fell within acceptable limits, posing no harm. In contrast, the RI instigated by Cd from fertilizer sources, was deemed moderate. Authorities should concentrate on mitigating the RI posed by PTEs, prioritizing fertilizer sources for control, with Cd as the key PTE to regulate, followed by irrigation and traffic sources, focusing on As, Pb, and Hg as secondary targets for control.

5. Conclusions

The study region is at a slight soil PTEs pollution level. There are only individual sampling sites with moderate and heavy pollution, which main PTEs are Cd, Hg and Pb.

Through PCA, the pollution sources within the study region were identified and divided into three main groups: a natural source rich in Cr, Cu, Ni, and Zn; an anthropogenic source with significant contributions from Cd and Hg; and an irrigation source primarily defined by As and Pb. The PMF model provided a more granular classification, differentiating the sources into four categories and calculating their respective contributions, which included a fertilizer source predominantly containing Cd (13.9%); an irrigation source with As and Cd as the main pollutants (29.5%); a traffic source characterized by high levels of Hg (23.4%); and a natural source with Cr, Cu, Ni, and Zn as the leading elements (33.2%).

A comparison of the source analysis results between the PCA and PMF models shows that they are generally consistent. PMF further classified the anthropogenic pollution source classified by PCA into fertilizer source and traffic source with the same identification PTEs, which further improved the reliability and accuracy of the source apportionment.

The RI within the study region is deemed slight. However, certain sampling locations exhibit moderate ecological risk, primarily due to the presence of Cd and Hg as the predominant PTEs. For the population, including children and adults, the non-carcinogenic risk is considered insignificant, and the carcinogenic risk remains within acceptable thresholds, with As being the leading PTE of concern.

The comprehensive analysis of PTEs, pollution sources, human health ecological risks and potential ecological risks concluded that fertilizer source should be the primary control source and Cd is the first control PTE; irrigation source and traffic source are the secondary control sources in the study region, and As, Pb and Hg are the secondary control PTEs.

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