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Spatial Distribution, Leaching Characteristics, and Ecological and Health Risk Assessment of Potential Toxic Elements in a Typical Open-Pit Iron Mine Along the Yangzi River

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Abstract: Potential toxic elements (PTEs) pollution in the soil of abandoned open-pit mines can lead to great ecological risk to the areas around the mining districts. This study selected a typical abandoned open-pit iron mine along the Yangzi River in southeast China to investigate the spatial distribution, leaching characteristics, and ecological and health risk of the soil PTEs (As, Pb, Cd, Ni, Cr, Cu, and Zn). Leaching tests and sequential extraction were applied to study the migration of PTEs under the condition of rainfall. Different risk assessment methods were used to analyze the pollution and ecological risk of PTEs. The contents of As and Cu exceeded the background value of the Chinese soil guideline, with average contents of 50.71 ± 1.59 and 197.47 ± 16.09 , respectively. The leaching test and sequential extraction indicated that sites 8 and 9 posed the greatest risk of PTE migration. According to the map of the Nemerow integrated pollution index (NIP_I), the pollution level of the middle bare area of the study area was the highest, and Cu possessed the highest pollution index (PI) of 3.92. The average geo-accumulation index (I_{geo}) of As and Cu was between 1 and 2, reaching the pollution level of moderately contaminated. The average potential ecological risk coefficient (E_i) of As was the highest, and the contributions of As, Cu, and Cd to the potential ecological risk of the whole study area were 46.7%, 29.7%, and 14.3%, respectively. The range of the hazard index (HI) and the range of the As carcinogenic risk (CR_{As}) of all the sampling sites for children were 1.30–3.94 and 2.19×10^{-4} – 7.20×10^{-4} , and As accounted for more than 85% of the total noncarcinogenic risk, indicating that the comprehensive pollution of PTEs in the study area posed great carcinogenic and noncarcinogenic risks to children. This study can be a proper reference for the subsequent recovery methods and environmental management of the whole mining area.

Keywords: open-pit iron mine; potential toxic elements pollution; leaching potential; pollution risk assessment



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1. Introduction

During the process of exploitation and abandonment of metal mines, large amounts of potential toxic elements (PTEs) will enter and accumulate in the soil around the mines [1–3], and the mobile part of PTEs can migrate with rainwater, leading to environmental risk to the nearby rivers and lakes [2,4]. Moreover, PTEs will accumulate through the food chain and cause great risk to humans and ecosystems [5]. With the fast development of mining in China in the past few decades, the PTE pollution of soil caused by abandoned bare mines is getting more and more serious [6]. Taking the banks of the Yangtze River as an example, according to the remote sensing data in 2019 from the Chinese Ministry of Natural Resources, the area of abandoned bare mines within 10 km along the river mainstream and primary tributaries is 17,431.82 hectares, and under rough estimation, the amount of PTEs (Cd, Zn, Pb, Cr, Cd, As, and Hg) discharged into the environment could reach 5300 tons, which will cause great damage to the soil and water [7,8].

Among different kinds of metal mines, sulfur-bearing metal mines cause extreme pollution because of acid mine drainage (AMD) [9–11]. The pyrite mine is a typical sulfur-bearing mine, which continuously generates Fe^{2+} , SO_4^{2-} , and H^+ with the existence of oxygen, water (especially rainfall), and sulfur-oxidizing bacteria, then forming the acid mine drainage [12,13]. PTEs are inclined to leach from the soil and migrate to further regions under the washing of AMD [14]. The combination of low pH and high concentrations of PTEs can pose severe toxicological effects on edaphic and aquatic systems [15]. Previous studies have shown that AMD could bring massive PTEs to nearby regions, and the acid-soluble fraction of PTEs is easy to leach from the soil affected by AMD [16,17].

Assessing the extent of PTE pollution and the potential environmental risk of open-pit mines can offer a guideline for the subsequent pollution remediation and environmental management of mining areas [18]. Spatial distribution analysis of PTEs is conducive to seeking the seriously polluted areas and the priority control PTEs. In mine pollution studies, the leaching tests of PTEs are often ignored [19]. Also, there are few methods to assess the leaching risk based on a leaching test [20]. However, the leaching tests can offer valuable reference on the migration risk of PTEs [21]. It is reported that acid rainfall can greatly increase the average annual leach of PTEs (Zn, Cu, Pb, and Cd, etc.) from mine soils [22,23], and the leaching behavior and mechanism varied with elements and pH conditions [24]. Therefore, before the remediation of abandoned bare mines, it is necessary to analyze the distribution, mobility, and ecological risk of PTEs.

In view of that, a typical and abandoned bare pyrite mine along the Yangzi River was chosen for assessment. Before the application of remediation methods, this study investigated and assessed the PTE pollution for the first time, and the objectives of this study are to (1) quantify the contents and fractionation of PTEs: arsenic(As), lead(Pb), cadmium(Cd), nickel(Ni), chromium(Cr), copper(Cu), and zinc(Zn); (2) investigate the spatial distributions of PTEs in the study area; (3) investigate the leaching characteristics of PTEs; (4) assess the pollution level, ecological risk, and human health risk of PTEs.

2. Materials and Methods

2.1. Study Area

The city of Maanshan (longitude $31^\circ 24' \sim 32^\circ 02'$ N, latitude $117^\circ 53' \sim 118^\circ 52'$ E) is located 10 km east of Anhui province, and the Yangtze River runs across the city. Maanshan is famous for its iron mines, and the city is one of the seven biggest iron mine producing regions [25]. As time goes by, many bare iron mines are left without being restored, and the Xiaonanshan pyrite mine is a typical bare mine that has not been remediated. The Xiaonanshan pyrite mine (longitude $31^\circ 40' 12''$ N, latitude $118^\circ 36' 51''$ E) is located 10 km east of Maanshan city (Figure 1). The mining history of the Xiaonanshan mine can be traced back to 1916, and the mine is abandoned now, leaving bare regions and a water pit to be restored. It can be seen from the satellite map that nearly half of the mountain soil was bare, and the middle part of the bare area is red because of the iron mine corrosion. Moreover, there are ponds, farmlands, and villages on the north side of the iron mine.

2.2. Sampling and Analysis

To better investigate the distributions of PTE pollution in the bare area, 10 sampling sites were chosen according to the terrain of the mountain, and the sample locations were evenly spread at a distance of 150–200 m. Moreover, two sampling sites at the Northwest foot of the mountain were chosen to investigate the migration of PTEs (Figure 1). The sampling sites were located via a GPS app on a mobile phone. To make the samples more representative, 5 topsoil samples (a total of 60 samples) within 5 m from each site were collected according to the 5-point sampling method in July 2023 [26]. A stainless-steel shovel was used to collect all soil samples at a depth of 0–20 cm. All the samples were sealed in plastic bags for later analyses.

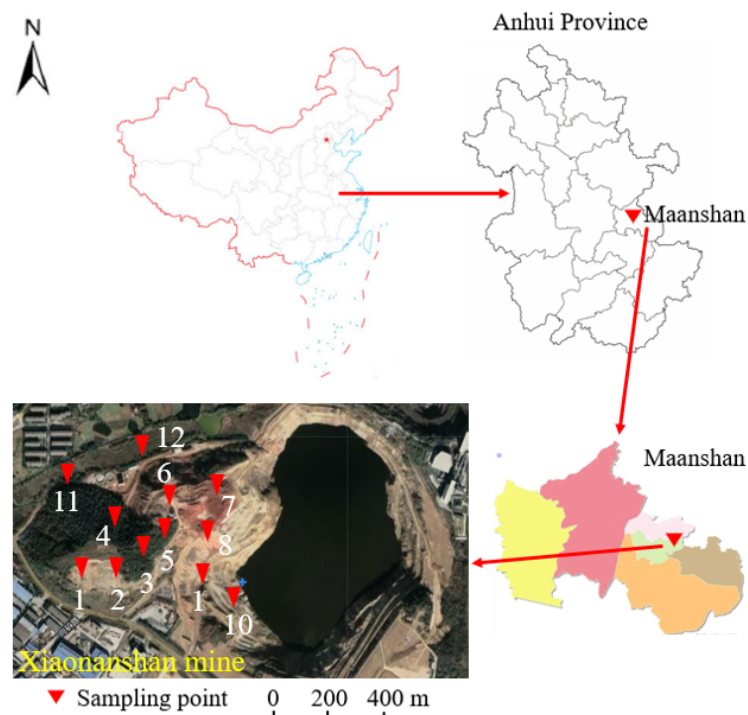


Figure 1. Location of the study area and sampling locations.

The soil samples were air-dried and passed through a 2 mm Nylon sieve. The pH values of the soil samples were determined at a 1:5 mass ratio using a Leici PHS-3F digital ion meter [27]. To measure the concentration of As, Pb, Cd, Ni, Cr, Cu, and Zn in the soil samples, 1.0 g of soil sample was digested with a mixture of acids (9 mL of HNO_3 + 3 mL of HCl + 5 mL of HF). After digestion, the PTEs' concentration was measured with an inductively coupled plasma spectrometer (ICP-OES, Agilent 720ES) [28]. The detection limits of As, Pb, Cd, Ni, Cr, Cu, and Zn are $1 \mu\text{g/L}$, $0.8 \mu\text{g/L}$, $0.05 \mu\text{g/L}$, $0.3 \mu\text{g/L}$, $0.15 \mu\text{g/L}$, $0.3 \mu\text{g/L}$, and $0.2 \mu\text{g/L}$, respectively. During the testing process of PTE concentration, various quality assurance and quality control (QA/QC) steps were conducted to make the results accurate and reliable, including instrument calibration, blank analysis, replicate analysis, and a quality control sample set, etc. The relative standard deviation (RSD) was less than 5%, and the recovery rate of the standard sample was between 92% to 110% in this study.

To determine the PTEs' fractionation in the soil samples, the BCR sequential extraction procedure was applied. The details of this method are available elsewhere, and the detailed procedure is summarized in Table 1 [29,30].

Table 1. Modified BCR three-step sequential extraction procedure.

Extraction Steps	Reagent/Concentration/pH	Soil Phase
1	0.5 g sample + 20 mL of 0.11 M Acetic acid CH_3COOH , pH 2.85	Exchangeable; water and acid-soluble
2	20 mL 0.5 M $\text{NH}_2\text{OH}\cdot\text{HCl}$, pH 1.5	Reducible
3	5 mL H_2O_2 (30% w/v) + 20 mL 1 M $\text{CH}_3\text{COONH}_4$, pH 2	Oxidizable
4	4 mL aqua regia ($\text{HCl}:\text{HNO}_3$, 3:1)	Residual

2.3. Leaching Test

2.3.1. Leaching Potential Test

To determine the leaching potential of PTEs in the soil samples, a modified toxicity characteristic leaching procedure (TCLP) test was conducted, according to the Chinese

standard (GB 5085.3-2007) [31]. In brief, 4.0 g of a soil sample was added to 50 mL sulphuric acid solution (pH = 3), and the mixture was agitated on a shaker at 120 rpm for 2, 4, 8, and 24 h at 50 °C. Then, the mixture was centrifuged, and the supernatant was filtered with a 0.45 µm membrane filter. The PTEs' concentration in the supernatant were measured via ICP-OES in an Agilent 720ES spectrometer.

2.3.2. Dynamic Leaching Test

The dynamic leaching test of PTEs from two typical sites was investigated in two down-flow columns (Figure 2), according to Method 1314 of the USEPA [32]. The inner diameter and height of the column are 8 and 15 cm. A 1000 g air-dried soil sample (maximum particle size is 3 mm) was filled into the column. To prevent potential migration of the particles out of the column, both ends of the columns were filled with washed fine-grained quartz sand and filter papers before being sealed. The filling materials in both columns were saturated with rainwater for 24 h before the test. According to Chinese Standard Weather Data, the flow rate for columns was 0.69 mL/min to simulate the local annual precipitation, and the process was conducted for 12 h every day, leaving the other 12 h to collect the leachate. Every day after 12 h of leaching, 20 mL of leachate samples were taken for measurement of PTE contents via ICP-OES. The dynamic leaching test was conducted for 7 days.

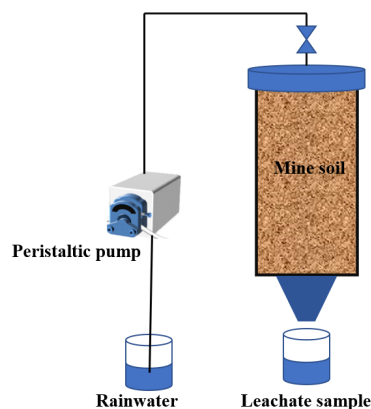


Figure 2. Schematic illustration of the dynamic column experiment.

2.4. Contamination Assessment

2.4.1. Nemerow Integrated Pollution Index

The Nemerow integrated pollution index (*NIPI*) was applied to assess the pollution level of PTEs in the soil [33,34], and the calculation formula is as follows:

$$P_i = \frac{C_i}{C_0} \quad (1)$$

$$NIPI = \sqrt{\frac{P_{ave}^2 + P_{max}^2}{2}} \quad (2)$$

where C_i is the content of heavy metal i in soil, C_0 is the background value of soil heavy metal i , P_i is the single pollution index of soil heavy metal i , P_{ave} is the average index of single pollution of heavy metal i , P_{max} is the maximum PI of each heavy metal, and $NIPI$ refers to the comprehensive index of each heavy metal. The $NIPI$ values can be divided as safe ($NIPI \leq 0.7$), precaution ($0.7 < NIPI \leq 1.0$), slight pollution ($1.0 < NIPI \leq 2.0$), moderate pollution ($2.0 < NIPI \leq 3.0$), and heavy pollution ($NIPI > 3$).

2.4.2. Geo-Accumulation Index

As one of the evaluation methods widely used for soil PTEs, the geo-accumulation index (I_{geo}) method was used to analyze and evaluate the PTE pollution of the Xiaonanshan pyrite mine [35,36]. The calculation formula is as follows:

$$I_{geo} = \log_2 \left[\frac{C_i}{(K \times C_0)} \right] \quad (3)$$

where C_i is the content of heavy metal i in the soil (mg kg^{-1}), C_0 is the background value of soil heavy metal i (mg kg^{-1}), and K is a coefficient taken to consider the variation of the background value caused by the difference of rocks in different places (this study, $K = 1.5$). The I_{geo} value can be classified into seven grades, which represent different contaminated levels (Table S1).

2.4.3. Potential Ecological Risk Assessment

The Hakanson potential ecological risk index method was used to evaluate the potential ecological risk of PTEs in the samples [37]. The calculation formula is as follows:

$$E_r^i = T_r^i \times PI \quad (4)$$

$$RI = \sum_{i=1}^n E_r^i \quad (5)$$

where PI refers to the single pollution factors of each heavy metal, E_r^i refers to the potential ecological risk factors of each heavy metal, T_r^i refers to the toxic response factors of each heavy metal (the toxic response factors of As, Pb, Cd, Ni, Cr, Cu, and Zn are 10, 30, 5, 5, 2, 5, and 1), and RI is the potential ecological risk index. The E_r^i and RI values can be classified into five grades, which are shown in Table S2.

2.5. Health Risk Assessment

Besides the soil environment, PTEs also threaten human health [38]. Half of the Xiaonanshan pyrite mine is totally bare, causing large amounts of polluted dust to be brought to nearby places. Considering the nearest village is within 350 m of the pyrite mine, the adults and children are likely to be affected by the PTEs through all three routes. In order to evaluate the risk extent of human health led by PTEs, the health risk assessment model from the USEPA was applied in this study [39]. Considering the differences in vulnerability of different age groups, residents are divided into children and adults [38,40]. The calculation formula is as follows:

$$ADI_{ing} = \frac{C_i \times IngR \times EF \times ED \times CF}{BW \times AT} \quad (6)$$

$$ADI_{inh} = \frac{C_i \times InhR \times EF \times ED}{PEF \times BW \times AT} \quad (7)$$

$$ADI_{der} = \frac{C_i \times CF \times EF \times ED \times AF \times SA \times ABS}{BW \times AT} \quad (8)$$

where ADI_{ing} , ADI_{inh} , and ADI_{der} are the average daily dose of metals by ingestion, respiration, and dermal absorption, respectively ($\text{mg kg}^{-1} \text{ d}^{-1}$); C_i refers to the content of heavy metal i in the soil (mg kg^{-1}), $IngR$ refers to the ingestion soil rate (mg d^{-1}), $InhR$ refers to the inhalation rate of soil ($\text{m}^3 \text{ d}^{-1}$), EF refers to the exposure frequency (d a^{-1}), ED refers to the exposure duration (a), CF refers to the conversion factor (mg kg^{-1}), BW refers to the body weight (kg), AT refers to the average time (days), PEF refers to the particle emission index ($\text{m}^3 \text{ kg}^{-1}$), SA refers to the exposed skin surface (cm^2), AF refers to the adhered skin index ($\text{mg cm}^{-2} \text{ d}$), and ABS refers to the dermal adsorption index. Values of the above parameters are shown in Table S3.

The noncarcinogenic and carcinogenic health risks of soil PTEs are calculated with the following formula:

$$HQ_i = \sum \frac{ADI_{ij}}{RfD_{ij}} \quad (9)$$

$$HI = \sum HQ_i \quad (10)$$

where HQ_i refers to the hazard quotient of each heavy metal on the noncarcinogenic risk, ADI_{ij} refers to the average daily intake through of the j th exposure route of each heavy metal ($\text{mg kg}^{-1} \text{d}^{-1}$), RfD_{ij} refers to the reference amount of the average daily intake of the j th exposure route of each heavy metal ($\text{mg kg}^{-1} \text{d}^{-1}$), and HI refers to the hazard factor. When HQ_i or $HI < 1$, the noncarcinogenic risk is low; when HQ_i or $HI \geq 1$, the noncarcinogenic risk is evident.

$$CR_i = ADI_{ij} \times SF_{ij} \quad (11)$$

$$TCR = \sum CR_i \quad (12)$$

where CR_i refers to the carcinogenic risk of each heavy metal, SF_{ij} refers to the carcinogenic slope factor of the j th exposure route of each heavy metal ($\text{mg kg}^{-1} \text{d}^{-1}$), and TCR refers to the total carcinogenic risk. When $1.00 \times 10^{-6} \leq CR_i$ (or $TCR < 1.00 \times 10^{-4}$), the carcinogenic risk is low; when CR_i (or $TCR \geq 1.00 \times 10^{-4}$), the cancer risk is evident. In this study, the carcinogenic risk of As was calculated. The toxicity index reference values of PTEs are presented in Table S4.

3. Results and Discussion

3.1. Contents and Fractionation of PTEs in Mine Soils

The average PTEs contents of As, Pb, Cd, Ni, Cr, Cu, and Zn in the study area were 50.71 ± 1.59 , 0.13 ± 0.01 , 29.30 ± 0.75 , 14.51 ± 0.44 , 36.30 ± 1.06 , 197.47 ± 16.09 , and $74.40 \pm 2.63 \text{ mg/kg}$, respectively (Table 2). The average concentration of each metal at different sites is shown in Table S5. The average value of As and Cu exceeded the background value of Maanshan soil and the value of Chinese soil guideline ($\text{pH} \leq 5.5$). The coefficient of variation (CV) showed the average degree of variation of each sampling site in the study area. The CV value of Cu is 97.79%, while the other six PTEs showed slight spatial changes with CV values ranging from 30.82 to 48.49%. The high CV value of Cu indicated that the concentration of Cu in the soil fluctuated greatly, leading to strong spatial changes. Considering that copper ore is often associated with iron ore, the spatial change for Cu was possibly due to the original distribution of copper ore [41]. The content Kurtosis values of each PTE is less than 3, indicating that the contents' distribution is a flatter-than-normal distribution [42]. The content skewness values of As, Pb, Cr, Cu, and Zn are more than 0, indicating the contents of the mentioned metals present an evident right deviation from the normal distribution, while the contents of Cd and Ni present a small deviation. The average value of the soil pH is 4.23 ± 0.06 , which may contribute to the process of acid leaching [43].

Table 2. Summary statistics of PTEs' concentrations (mg kg^{-1}) and pH in the soils around the iron mine.

	As	Cd	Pb	Ni	Cr	Cu	Zn	pH
Min	29.94	0.03	14.85	4.73	19.72	23.31	38.74	2.97
Mean $\pm$ SE ^a	50.71 ± 1.59	0.13 ± 0.01	29.30 ± 0.75	14.51 ± 0.44	36.30 ± 1.06	197.47 ± 16.09	74.40 ± 2.63	4.23 ± 0.06
Max	98.32	0.21	49.28	23.15	65.52	621.81	155.46	5.66
SD ^b	19.14	0.06	9.03	5.28	12.73	193.09	31.57	0.81
CV ^c (%)	37.74	48.49	30.82	36.40	35.06	97.79	42.44	19.23
Kurtosis	1.62	−1.59	0.51	−0.44	0.68	1.10	2.58	−0.88
Skewness	1.32	−0.06	0.78	−0.22	1.01	1.50	1.56	0.14
Background ^d	10.55	0.26	24.43	38.90	86.40	32.37	84.73	−
Chinese soil guideline ($\text{pH} \leq 5.5$) ^e	40	0.3	70	60	150	50	200	−

Notes: ^a Standard error; ^b Standard deviation; ^c Coefficient of variation; ^d Soil background values for soils in Maanshan; ^e Soil environment quality risk control standard for soil contamination of agricultural land.

3.2. Spatial Distribution of PTEs

The spatial distribution of As, Cd, Pb, Ni, Cr, Cu, and Zn concentrations and pH values in the study area are presented in Figure 3. According to the maps, the distribution

trends of Cu and Zn were similar. The areas with higher concentrations of Cu and Zn were confined to sites 8 and 9, and site 10 presented the highest concentration, indicating the possible migration of Cu from sites 8 and 9 to site 10. The distribution trends of As, Pb, Ni, and Cr are different from Cu, Cd, and Zn. The maximum concentration of As, Pb, Ni, and Cr came from the bare area (middle and southwest part) of the mine, where human activities like transportation were frequent, indicating the contaminants may be released from human activities [44]. The highest concentration of Cd came from sites 6, 8, and 9, and the Cd concentration of site 10 was less than the above sites, indicating that the migration speed of Cd was slower than Cu. The lowest pH values came from the bare area of the north and south part, and the pH value of sites 8 and 9 was higher, which was probably caused by the wash of large amounts of rainwater [45].

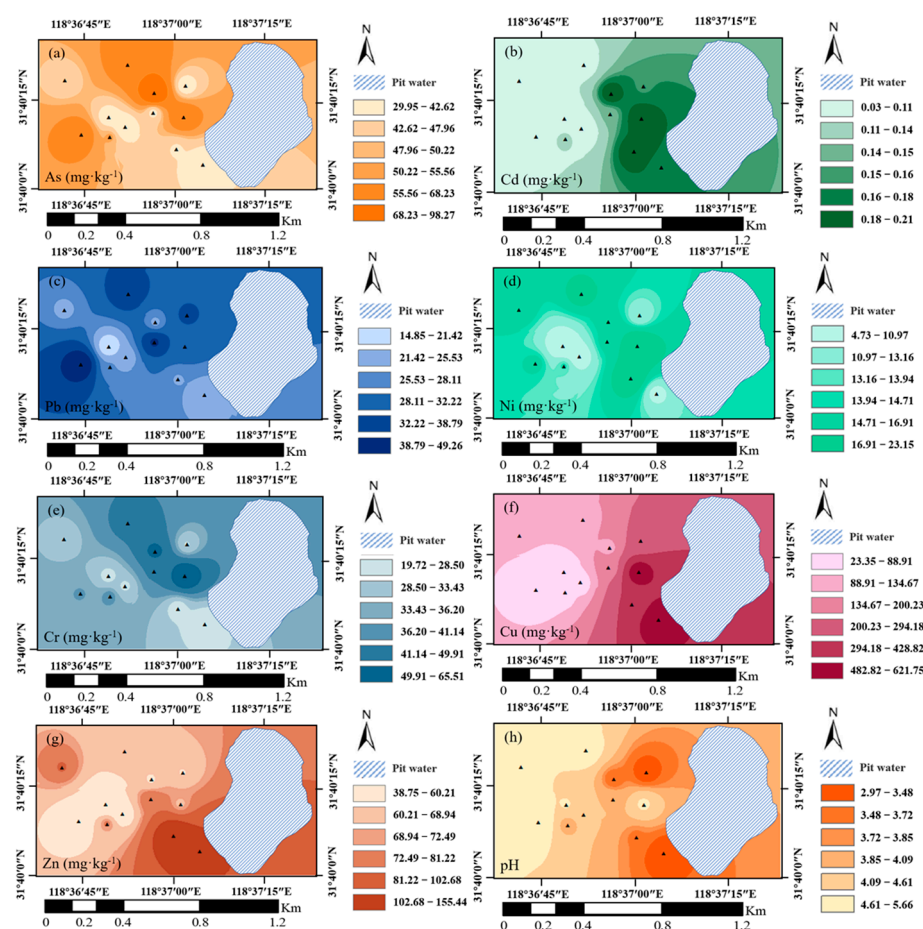


Figure 3. Maps of As (a), Cd (b), Pb (c), Ni (d), Cr (e), Cu (f), and Zn (g) concentrations and pH value (h) in the study area.

3.3. Sequential Extraction

The mobility and availability decrease in the order of acid-soluble fraction > reducible fraction > oxidizable fraction [46]. The PTE fractionations of Pb, Ni, Cd, As, Cr, Zn, and Cu in the soil samples are shown in Figure 4, and the results are described in terms of the percentage distribution. Acid-soluble fraction PTEs are mobile and bioavailable, leading environmental threats to nearby soil and water. Therefore, the percentage of acid-soluble fraction indicates the migration risk of PTEs. According to Figure 4, the largest percentage of all the PTEs (except for sample 8 from Cu fractionation) is the residual fraction. The acid-soluble and reducible fraction of Pb are less than 1%, and several samples possess a certain percentage of reducible Pb. For As and Cr, the fractionation difference among different samples is small. The acid-soluble fractions of Cr samples are less than 1%, and for As they are between 2 and 7%. For Ni, Cd, Zn, and Cu, there are obvious differences

between samples 8, 9, and other samples. The acid-soluble fractions of sample 8 and 9 of Ni, Cd, Zn, and Cu are 15.8% and 23.6%, 13.9% and 27.5%, 17.6% and 16.2%, and 56.0% and 6.7%, indicating great migration risk of PTEs. Considering the great proportion of the acid-soluble fraction of Cu in sample 8 (56.0%), site 8 might possess a higher amount of copper ore than other sites, and site 8 was the primary Cu pollution source of the study area. Moreover, the soil at site 8 was more porous than other sites, which accelerated the corrosion of copper ore. Though the contents of Cd, Ni, and Zn in soil are not high, given the large area of the mine, the leaching amount of acid-soluble PTEs could accumulate and cause damage to the environment [47]. It can be seen from Figure 1 that there are ponds and farmlands on the north side of the bare mine, which are only several hundred meters away from the mountain. PTE ions would transport with rainfall to the nearby ponds and farmlands. With the progress of agricultural activities, PTEs might accumulate through the food chain and threaten human health [48].

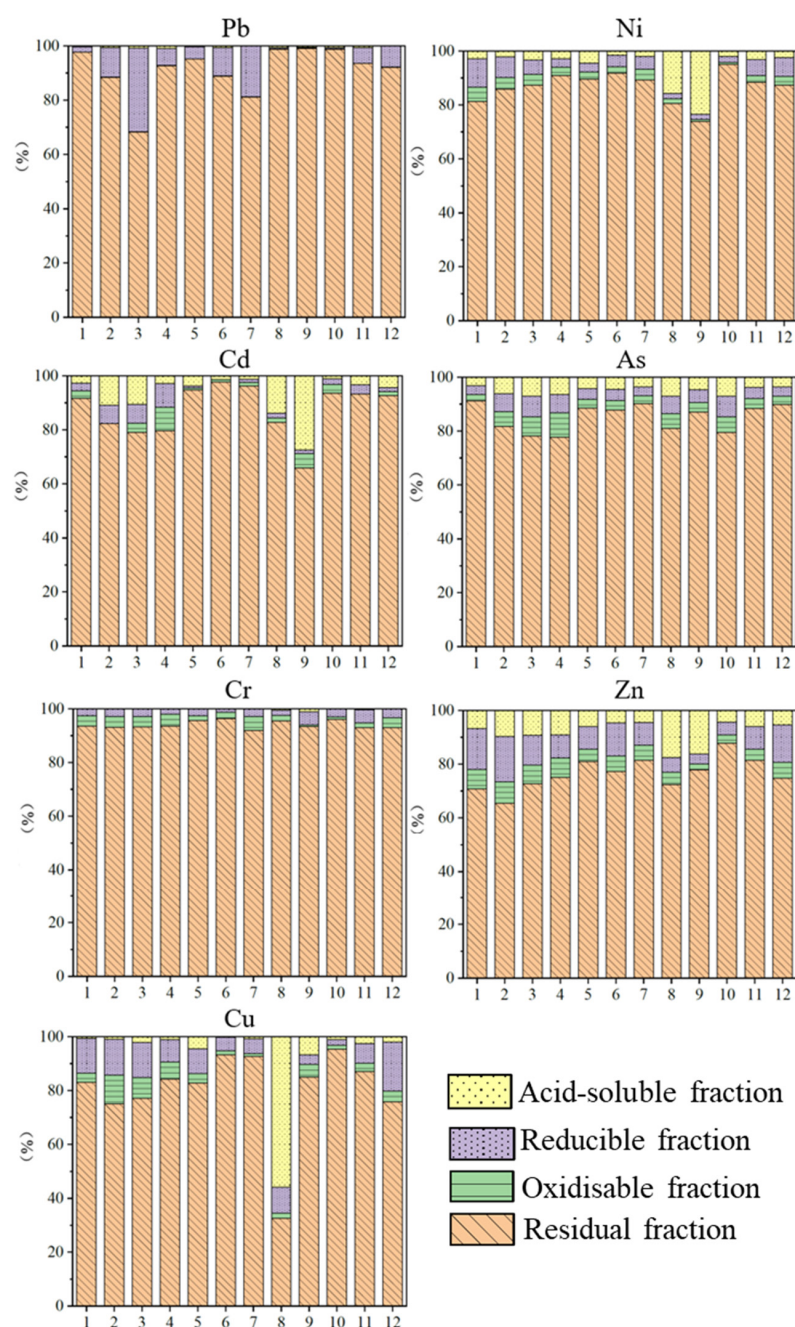


Figure 4. BCR extractable fractionations (%) of PTEs in soil samples of the study area.

3.4. Leaching Potential and Dynamic Leaching Tests

3.4.1. Leaching Potential of PTEs

Figure S1 presents the PTEs' leaching amount to the unit mass of the soil samples (mg/kg) in batch leaching tests. The test was designed to simulate severe leaching conditions to determine the largest leaching potential of different PTEs. According to Figure 5, the PTE leaching amount of soil sample 8 (brown) and 9 (deep green) were much higher than other samples, which was in accordance with the sequential extraction results that the percentage of acid-soluble fractions of PTEs of sample 8 and 9 are higher than other samples. The leaching amounts of Cd, Cr, Cu, and Pb from sample 8 were 0.07, 0.33, 172.8, and 0.54 mg/kg, and the leaching amounts of Ni, Zn, and As from sample 9 were 3.13, 19.28, and 0.082 mg/kg, which were the maximum leaching amount of all the samples. Meanwhile, based on the trend of curves in Figure S1, the leaching amount reached the maximum at 4 h, and the leaching amount began to decrease after 4 h, which was probably caused by the readsorption of heavy metal ions by soil samples [49,50]. Therefore, the leaching amount at 4 h can represent the highest PTE leaching potential of the soil samples.

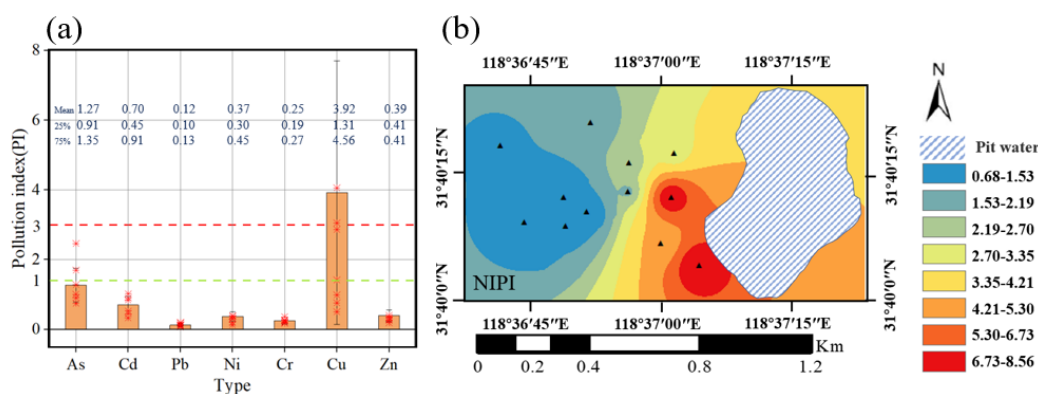


Figure 5. PI values (a) and map of NIPI values (b) of PTEs in the study area.

3.4.2. Dynamic Leaching of PTEs

According to the results of the leaching potential test, soil samples 8 and 9 were selected to conduct the dynamic leaching test because of their high leaching potential. Figure S2 presents the leaching contents of PTEs from soil sample 8 (a) and soil sample 9 (b). The amounts of Cd, Cr, Cu, Ni, Pb, Zn, and As released from soil samples 8 and 9 on the first day were the highest, which were 2.70×10^{-2} , 6.40×10^{-2} , 2.67×10^1 , 1.19×10^0 , 3.33×10^{-1} , 1.08×10^1 , and 6.00×10^{-4} mg/g for soil sample 8 and 1.77×10^{-2} , 3.40×10^{-2} , 3.12×10^0 , 2.13×10^0 , 2.80×10^{-1} , 2.71×10^1 , and 1.20×10^{-2} mg/g, respectively. The contents of PTEs released from the two samples decreased with time, and the leaching amounts of Cd, Cr, Cu, and Zn on the second day were less than 50% of the amounts on the first day, while the decreasing ranges of Pb and Ni were small.

The ratios of the PTE contents released on the first day/the total PTE contents released for 7 days and the total PTE contents released for 7 days/the highest leaching potential were calculated, and the results are shown in Figure S3. The ratios calculated from sample 8 and 9 are nearly the same. Based on the yellow bars, the ratios of contents released on the first day/the total PTEs contents released for 7 days of Cd, Cr, Cu, and Zn were more than 40%, and the highest ratio was 58.60% for Zn of sample 9, indicating that Cd, Cr, Cu, and Zn showed higher leaching efficiency than other PTEs on the first day. Based on the green bars, the ratios of the total PTE contents released for 7 days/the highest leaching potential of Ni, Pb, and Zn were more than 90%, and the highest ratio was 98.06% for Ni of sample 9, indicating that Ni, Pb, and Zn were more inclined to migrate with rainwater than other PTEs. The average difference among the ratios of the total PTE contents released for 7 days/the highest leaching potential between samples 8 and 9 was 4.13%, indicating that the highest leaching potential determined via the leaching potential test was an effective reference for mine soil leaching pollution assessment.

Notably, results of the leaching potential test and dynamic leaching test indicated that samples 8 and 9 possessed the highest leaching amount of PTEs. As the proportions of the acid-soluble fraction of Cu and Cd in samples 8 and 9 were much higher than other samples, the results of the leaching experiment were in accordance with the results of sequential extraction. Moreover, Cd, Cu, Zn, and Cr presented higher leaching efficiency. The wash of rainfall brought a large amount of PTEs to sites 8 and 9 [22], and a part of the PTEs settled in the two sites in an acid-soluble fraction which would leach out with the subsequent rainfall. Therefore, sites 8 and 9 became the confluence and origin of PTEs. Urgent actions should be taken to prevent the migration of PTEs in sites 8 and 9, and Cd, Cu, Zn, and Cr are the primary targets.

3.5. Contamination Assessment of PTEs

3.5.1. Pollution Index of PTEs

Figure 5 presents the PI and $NIPI$ values of PTE pollution in the study area. The average PI values of As, Cd, Pb, Ni, Cr, and Zn were less than 1, indicating that the six PTEs are in the safe class and pose little threat to the nearby environment. The average PI value of Cu was more than 3, and the pollution of Cu was serious and posed a great threat to the quality and safety of the soil. From the map of $NIPI$ values, the $NIPI$ values increased from the west part of the mine to the east, and the $NIPI$ value of sampling site 10 was the highest. From the middle part to the east of the mine, the $NIPI$ values were more than 3, indicating that the pollution level was severe. The sites with green plants (the western part of the mine) were still clean with an $NIPI$ value of less than 1.5, and the level of the middle part of the mine was between slight and moderate pollution. As the mine terrain was high in the west and low in the east, most rainfall flowed by sites 8 and 9 to the mine pit, making it difficult for the PTEs to migrate toward the west. Therefore, mountain terrain could be an important factor that influences the risk distribution [51,52].

3.5.2. Geo-Accumulation Index of PTEs

Figure 6 presents the I_{geo} values of PTEs in the study area. According to the results, the average I_{geo} values of Cd, Pb, Ni, Cr, and Zn were below 0, indicating that the overall pollution level of these PTEs was practically uncontaminated. The average I_{geo} values of As and Cu were between 1 and 2, reaching the pollution level of moderately contaminated, and certain sites showed higher environmental risk of $2 < I_{geo} < 4$, reaching the pollution level of moderately to heavily contaminated and heavily contaminated. As I_{geo} is calculated to assess the PTEs' accumulation degree in soil, the accumulation level of As and Cu in the study area is high.

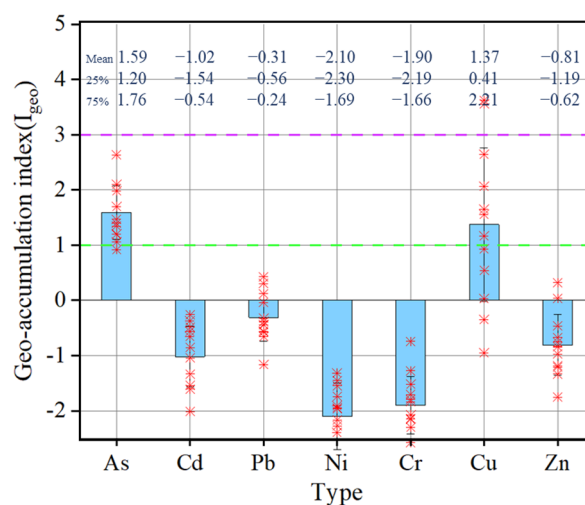


Figure 6. I_{geo} values of PTEs in the study area.

3.5.3. Potential Ecological Risk Index of PTEs

Figure 7 presents the E_i values(a) and the map of $PERI$ values of PTEs in the study area. According to the E_i values, the average E_i value of As was the highest, reaching the level of intermediate pollution, and other PTEs' pollution was at the level of slight pollution. The E_i values of an As sample and two Cu samples were more than 80, reaching the level of strong pollution, which indicated that the pollution level of the study area was uneven. From the map of $PERI$ values, the highest $PERI$ value was at sampling site 8, reaching the level of intermediate pollution. Pollution of the bare part in the middle of the mine was more serious than that of surrounding areas, leading to a great threat to the nearby plants and soils if no appropriate remediation method was applied in time. According to Figure 8, the contributions of As, Cu, and Cd to the $PERI$ value of the whole study area were 46.7%, 29.7%, and 14.3%, respectively, which accounted for a 90% pollution risk for the study area. Therefore, most of the remediation attention should be paid to the three kinds of PTEs in the future.

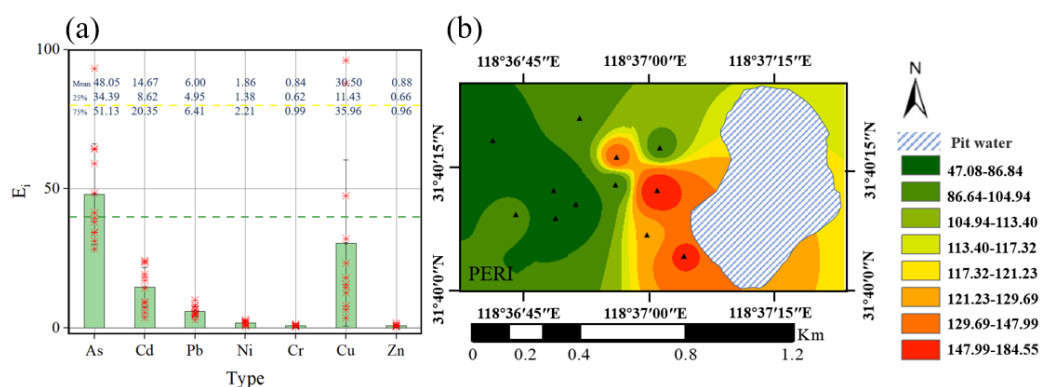


Figure 7. E_i values (a) and map of $PERI$ values (b) of PTEs in the study area.

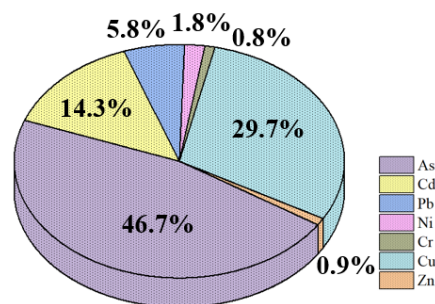


Figure 8. Contributions of PTEs to $PERI$ value of the whole study area.

3.6. Health Risk Assessment of PTEs

Table 3 presents the noncarcinogenic and carcinogenic risks (As) to adults and children. Because of the low contents of Cd, Ni, and Cr, this study only calculated the carcinogenic risks of As. The range of HI of all the sampling sites for adults and children were 0.16–0.50 and 1.30–3.94, and the range of CR_{As} of all the sampling sites for adults and children were 2.76×10^{-5} – 9.06×10^{-5} and 2.19×10^{-4} – 7.20×10^{-4} , respectively. All the HI and CR_{As} values were less than the risk value, indicating that the comprehensive pollution of PTEs in the study area had no carcinogenic and noncarcinogenic risk to adults. As for children, all the HI and CR_{As} values were more than the risk value, which posed great carcinogenic and noncarcinogenic risks to children. As content of sampling site 6 and Cu content of sampling site 8 were the highest of all the sampling sites; the HI and CR_{As} values of the two sampling sites were higher than other sites, indicating great health risk in the bare areas. Figure 9 presents the Contributions of PTEs to HI values of the whole study area. The percentages of different PTEs' contributions to HI_{adults} and $HI_{children}$ were almost the same, with As

accounting for more than 85% of the total noncarcinogenic risk. The results revealed that As was the main PTE in this mine that would pose potential risk on children's health.

Table 3. Noncarcinogenic and carcinogenic risks posed to adults and children.

Sampling Sites	Adults		Children	
	Noncarcinogenic Risks (<i>HI</i>)	Carcinogenic Risks of As (<i>CR</i>)	Noncarcinogenic Risks (<i>HI</i>)	Carcinogenic Risks of As (<i>CR</i>)
1	0.35	6.26×10^{-5}	2.80	4.97×10^{-4}
2	0.27	4.72×10^{-5}	2.12	3.74×10^{-4}
3	0.16	2.76×10^{-5}	1.30	2.19×10^{-4}
4	0.19	3.34×10^{-5}	1.49	2.65×10^{-4}
5	0.23	3.71×10^{-5}	1.82	2.94×10^{-4}
6	0.50	9.06×10^{-5}	3.94	7.20×10^{-4}
7	0.20	3.35×10^{-5}	1.62	2.66×10^{-4}
8	0.38	6.25×10^{-5}	3.04	4.96×10^{-4}
9	0.23	3.84×10^{-5}	1.79	3.05×10^{-4}
10	0.19	3.04×10^{-5}	1.54	2.41×10^{-4}
11	0.23	4.03×10^{-5}	1.84	3.20×10^{-4}
12	0.33	5.74×10^{-5}	2.62	4.56×10^{-4}
Average	0.27	4.68×10^{-5}	2.16	3.71×10^{-4}

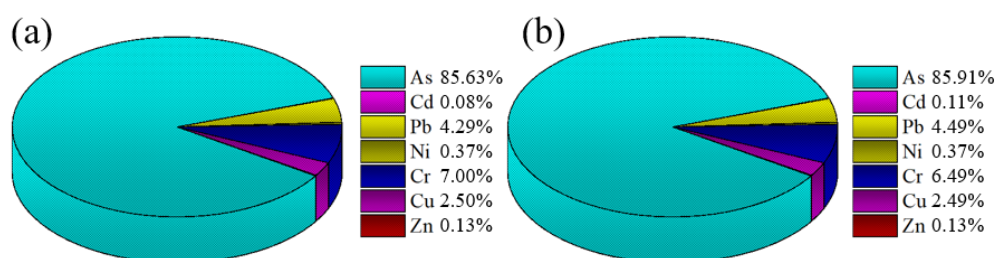


Figure 9. Contributions of PTEs to HI_{adults} (a) and $HI_{children}$ (b) values of the whole study area.

3.7. Limitations and Perspectives

This paper presented an in-depth study of PTEs' pollution assessment for the Xiaonanshan pyrite mine, but there are some limitations worth discussing. Firstly, this study only analyzed the contents of PTEs in summer, while the content variations during a long period have not been studied. Secondly, the PTEs' distributions and variations in the nearby ponds and farmlands are vacant, which are also important to the environmental risk assessment. Thirdly, we have not raised new or modified evaluation methods to properly assess the migration risk of PTEs in soils after rainfall. Therefore, in future studies, the perspectives should include the following: (1) study the variations in PTEs (contents and fractions) in the soils with time; (2) expand the study area to the nearby ponds and farmlands; (3) study the influence of rainfall on the transport of PTEs ions to nearby areas; (4) create new assessment methods to better evaluate the potential ecological risk of PTEs.

4. Conclusions

In this study, the spatial distribution, leaching potential, and ecological and health risk assessment of PTEs in soils around the Xiaonanshan pyrite mine in Maanshan were investigated for the first time. The average concentrations of As and Cu were 50.71 ± 1.59 and 197.47 ± 16.09 , which were 4.8 and 6.1 times the background value of Maanshan soil. The results of sequential extraction indicated that the acid-soluble fraction of the PTEs in sites 8 and 9 was much higher than that in other areas, which posed great risk of PTEs leaching. In addition, the leaching test proved that the leaching amount of PTEs on sites 8 and 9 was much higher than that of other areas. The highest leaching potential was an effective reference in assessing the leaching risk of PTEs. According to the results of the

PTE contamination assessment, site 10 showed the highest $NIPI$ value with the risk level of severe pollution, and the pollution of Cu is the most serious. The I_{geo} values indicated that the accumulation level of As and Cu in the study area is high. According to the results of $PERI$, pollution at site 8 was the worst, reaching the level of intermediate pollution, and As, Cu, and Cd accounted for 90% of the ecological risk for the study area. The health risk assessment results presented that noncarcinogenic and carcinogenic risks were likely to occur in children, and As accounted for more than 85% of the total noncarcinogenic risk.

According to this study, soil remediation methods are urgently needed to restore the soil of abandoned bare mines along the Yangzi River. More attention should be paid to the areas where PTEs are easier to leach out from the soil. PTE fixation technologies should be developed and applied to impede the migration of PTEs. Local residents, especially children, should avoid activities near the iron mine.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w16213017/s1>, Figure S1: PTEs contents in the leachate of the soil samples; Figure S2: Leaching contents of PTEs from soil sample 8(a) and soil sample 9(b); Figure S3: The ratios of the PTEs contents released on the first day/the total PTEs contents released for 7 days (yellow bar) and the total PTEs contents released for 7 days/the highest leaching potential(green bar); Table S1: Seven grades comprising the geo-accumulation index; Table S2: Five grades comprising the E_r^i and RI valu; Table S3: Values of relevant parameters.

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References

1. Davila, R.B.; Fontes MP, F.; Pacheco, A.A.; da Silva Ferreira, M. Heavy metals in iron ore tailings and flood plain soils affected by the Samarcodam collapse in Brazil. *Sci. Total Environ.* **2020**, *709*, 11. [CrossRef] [PubMed]
2. Qiao, P.; Wang, S.; Li, J.; Zhao, Q.; Wei, Y.; Lei, M.; Yang, J.; Zhang, Z. Process, influencing factors, and simulation of the lateral transport of heavy metals in surface runoff in a mining area driven by rainfall: A review. *Sci. Total Environ.* **2023**, *857*, 159119. [CrossRef]
3. Qin, H.; Takeichi, Y.; Nitani, H.; Terada, Y.; Takahashi, Y. Tellurium Distribution and Speciation in Contaminated Soils from Abandoned Mine Tailings: Comparison with Selenium. *Environ. Sci. Technol.* **2017**, *51*, 6027–6035. [CrossRef]
4. Kefeni, K.K.; Msagati, T.A.M.; Mamba, B.B. Acid mine drainage: Prevention, treatment options, and resource recovery: A review. *J. Clean. Prod.* **2017**, *151*, 475–493.
5. Du, B.; Zhou, J.; Lu, B.; Zhang, C.; Li, D.; Zhou, J.; Jiao, S.; Zhao, K.; Zhang, H. Environmental and human health risks from cadmium exposure near an active lead-zinc mine and a copper smelter, China. *Sci. Total Environ.* **2020**, *720*, 137585. [CrossRef] [PubMed]
6. Zhao, F.; Ma, Y.; Zhu, Y.-G.; Tang, Z.; McGrath, S.P. Soil Contamination in China: Current Status and Mitigation Strategies. *Environ. Sci. Technol.* **2015**, *49*, 750–759. [PubMed]
7. Yu, J.; Liu, X.; Yang, B.; Li, X.; Wang, P.; Yuan, B.; Wang, M.; Liang, T.; Shi, P.; Li, R.; et al. Major influencing factors identification and probabilistic health risk assessment of soil potentially toxic elements pollution in coal and metal mines across China: A systematic review. *Ecotoxicol. Environ. Saf.* **2024**, *274*, 116231.
8. Jiang, Y.; Guo, Q.; Deng, Y. Research progress in the distribution of heavy metals in sediments and soils in the Yangtze River Basin. *Chin. J. Ecol.* **2022**, *41*, 804–812.

9. Rodríguez-Sierra, C.J.; Adelman, D.; Vojta, Š.; Mansilla-Rivera, I.; Lohmann, R. Passive Sampling of Persistent Organic Pollutants in Four Coastal Aquatic Systems of Puerto Rico: A Pilot Study. *Bull. Environ. Contam. Toxicol.* **2019**, *103*, 770–775. [\[CrossRef\]](#)
10. Alegbe, M.J.; Ayanda, O.; Ndungu, P.; Nechaev, A.; Fatoba, O.; Petrik, L. Physicochemical characteristics of acid mine drainage, simultaneous remediation and use as feedstock for value added products. *J. Environ. Chem. Eng.* **2019**, *7*, 103097. [\[CrossRef\]](#)
11. Luo, Y.; Zheng, Z.; Wu, P.; Wu, Y. Effect of different direct revegetation strategies on the mobility of heavy metals in artificial zinc smelting waste slag: Implications for phytoremediation. *Chemosphere* **2022**, *286*, 131678. [\[PubMed\]](#)
12. Mohan, D.; Chander, S. Removal and recovery of metal ions from acid mine drainage using lignite—A low cost sorbent. *J. Hazard. Mater.* **2006**, *137*, 1545–1553. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Tu, Z.H.; Wu, Q.; He, H.; Zhou, S.; Liu, J.; He, H.; Liu, C.; Dang, Z.; Reinfelder, J.R. Reduction of acid mine drainage by passivation of pyrite surfaces: A review. *Sci. Total Environ.* **2022**, *832*, 155116. [\[CrossRef\]](#)
14. Tabelin, C.B.; Uyama, A.; Tomiyama, S.; Villacorte-Tabelin, M.; Phengsaart, T.; Silwamba, M.; Jeon, S.; Park, I.; Arima, T.; Igarashi, T. Geochemical audit of a historical tailings storage facility in Japan: Acid mine drainage formation, zinc migration and mitigation strategies. *J. Hazard. Mater.* **2022**, *438*, 129453.
15. He, M.; Wang, Z.; Tang, H. Spatial and temporal patterns of acidity and heavy metals in predicting the potential for ecological impact on the Le An river polluted by acid mine drainage. *Sci. Total Environ.* **1997**, *206*, 67–77. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Akcil, A.; Koldas, S. Acid Mine Drainage (AMD): Causes, treatment and case studies. *J. Clean. Prod.* **2006**, *14*, 1139–1145. [\[CrossRef\]](#)
17. Skousen, J.G.; Ziemkiewicz, P.F.; McDonald, L.M. Acid mine drainage formation, control and treatment: Approaches and strategies. *Extr. Ind. Soc.* **2019**, *6*, 241–249. [\[CrossRef\]](#)
18. Chen, R.; Han, L.; Liu, Z.; Zhao, Y.; Li, R.; Xia, L.; Fan, Y. Assessment of Soil-Heavy Metal Pollution and the Health Risks in a Mining Area from Southern Shaanxi Province, China. *Toxics* **2022**, *10*, 385. [\[CrossRef\]](#)
19. Lim, M.; Han, G.-C.; Ahn, J.-W.; You, K.-S.; Kim, H.-S. Leachability of Arsenic and Heavy Metals from Mine Tailings of Abandoned Metal Mines. *Int. J. Environ. Res. Public Health* **2009**, *6*, 2865–2879. [\[CrossRef\]](#)
20. Nguyen, X.P.; Islam, M.N.; Jo, Y.-T.; Park, J.-H. Variation of Cu and Zn Fractionation and Mobility in Mine Tailing Soil Due to Experimental Leaching. *Soil Sediment Contam. Int. J.* **2017**, *26*, 210–219. [\[CrossRef\]](#)
21. Zha, F.; Zhu, F.; Xu, L.; Kang, B.; Yang, C.; Zhang, W.; Zhang, J.; Liu, Z. Laboratory study of strength, leaching, and electrical resistivity characteristics of heavy-metal contaminated soil. *Environ. Earth Sci.* **2021**, *80*, 184. [\[CrossRef\]](#)
22. Wang, F.; Li, W.; Wang, H.; Hu, Y.; Cheng, H. The leaching behavior of heavy metal from contaminated mining soil: The effect of rainfall conditions and the impact on surrounding agricultural lands. *Sci. Total Environ.* **2024**, *914*, 169877. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Tian, S.; Liu, Z.; Mao, Q.; Ye, H.; Tian, C.; Zhu, Y.; Zhang, L. Leaching characteristics and environmental impact of heavy metals in tailings under rainfall conditions: A case study of an ion-adsorption rare earth mining area. *Ecotoxicol. Environ. Saf.* **2024**, *281*, 116642. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Li, W.; Deng, Y.; Wang, H.; Hu, Y.; Cheng, H. Potential risk, leaching behavior and mechanism of heavy metals from mine tailings under acid rain. *Chemosphere* **2024**, *350*, 140995. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Xu, S.; Wang, W. The significance of different scale copper geochemical anomalies and large ore deposit prediction in the middle-lower Yangtze River. *Earth Sci. Front.* **2012**, *19*, 84–92.
26. Yang, H.; Wang, F.; Yu, J.; Huang, K.; Zhang, H.; Fu, Z. An improved weighted index for the assessment of heavy metal pollution in soils in Zhejiang, China. *Environ. Res.* **2021**, *192*, 110246. [\[CrossRef\]](#)
27. Liu, B.; Xu, M.; Wang, J.; Wang, Z.; Zhao, L. Ecological risk assessment and heavy metal contamination in the surface sediments of Haizhou Bay, China. *Mar. Pollut. Bull.* **2021**, *163*, 111954. [\[CrossRef\]](#)
28. Ouyang, X.; Wang, Z.; Liu, X. Distribution patterns, risk assessment and potential sources of heavy metals in sediment in the Qiongzhou Strait, China. *Mar. Pollut. Bull.* **2024**, *203*, 116481. [\[CrossRef\]](#) [\[PubMed\]](#)
29. Ure, A.M.; Quevauviller, P.; Griepink, B. Speciation of heavy metals in soils and sediments an account of the improvement and harmonization of extraction techniques undertaken under the auspices of the bcr of the commission of the european communities. *Int. J. Environ. Anal. Chem.* **1993**, *51*, 135–151. [\[CrossRef\]](#)
30. Guillén, M.T.; Delgado, J.; Albanese, S.; Nieto, J.M.; Lima, A.; De Vivo, B. Heavy metals fractionation and multivariate statistical techniques to evaluate the environmental risk in soils of Huelva Township (SW Iberian Peninsula). *J. Geochem. Explor.* **2012**, *119–120*, 32–43. [\[CrossRef\]](#)
31. Huang, M.; Feng, H.; Shen, D.; Li, N.; Chen, Y.; Shentu, J. Leaching Behavior of Heavy Metals from Cement Pastes Using a Modified Toxicity Characteristic Leaching Procedure (TCLP). *Bull. Environ. Contam. Toxicol.* **2016**, *96*, 354–360. [\[CrossRef\]](#) [\[PubMed\]](#)
32. USEPA. *Liquid-Solid Partitioning as a Function of Liquid-solid Ratio for Constituents in Solid Materials Using an Up-Flow Percolation Column Procedure*; USEPA: Washington, DC, USA, 2013.
33. Jamali, M.K.; Kazi, T.G.; Arain, M.B.; Afridi, H.I.; Jalbani, N.; Memon, A.R.; Shah, A. Heavy metals from soil and domestic sewage sludge and their transfer to Sorghum plants. *Environ. Chem. Lett.* **2007**, *5*, 209–218. [\[CrossRef\]](#)
34. Yi, Y.; Yang, Z.; Zhang, S. Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin. *Environ. Pollut.* **2011**, *159*, 2575–2585. [\[CrossRef\]](#)
35. Muller, G. Index of Geoaccumulation in Sediments of the Rhine River. *Geojournal* **1969**, *2*, 109–118.

36. Loska, K.; Wiechuła, D.; Korus, I. Metal contamination of farming soils affected by industry. *Environ. Int.* **2004**, *30*, 159–165. [[CrossRef](#)]
37. Hakanson, L. An ecological risk index for aquatic pollution control: a sedimentological approach. *Water Res.* **1980**, *14*, 975–1001. [[CrossRef](#)]
38. Xiao, X.; Zhang, J.; Wang, H.; Han, X.; Ma, J.; Ma, Y.; Luan, H. Distribution and health risk assessment of potentially toxic elements in soils around coal industrial areas: A global meta-analysis. *Sci. Total Environ.* **2020**, *713*, 135292.
39. USEPA. *Exposure Factors Handbook (Final Report)*; US Environmental Protection Agency: Washington, DC, USA, 2011.
40. Kumar, V.; Parihar, R.D.; Sharma, A.; Bakshi, P.; Sidhu, G.P.S.; Bali, A.S.; Karaouzas, I.; Bhardwaj, R.; Thukral, A.K.; Gyasi-Agyei, Y.; et al. Global evaluation of heavy metal content in surface water bodies: A meta-analysis using heavy metal pollution indices and multivariate statistical analyses. *Chemosphere* **2019**, *236*, 124364. [[PubMed](#)]
41. Heydartaemeh, M.; Karamoozian, M.; Potgieter, H. Application of Nano High-Entropy Alloys to Reduce Energy Consumption and Wear of Copper Oxide and High-Grade Iron Ores in Heavy Mining Industries—A Case Study. *Minerals* **2019**, *10*, 16. [[CrossRef](#)]
42. Liu, S.; Hou, S.; He, K.; Yang, W. L-Kurtosis and its application for fault detection of rolling element bearings. *Measurement* **2018**, *116*, 523–532. [[CrossRef](#)]
43. Zhang, S.Q.; Zhang, X.; Guo, Z.; Ren, D.; Zhang, X.; Wang, S. Study on the remediation of heavy metal contaminated soils by citric acid and polyepoxysuccinic acid complex leaching. *Environ. Technol.* **2024**, *45*, 705–715. [[CrossRef](#)] [[PubMed](#)]
44. Faisal, M.; Wu, Z.; Wang, H.; Hussain, Z.; Azam, M.I.; Muzammil, M. Assessment and source apportionment of water-soluble heavy metals in road dust of Zhengzhou, China. *Environ. Sci. Pollut. Res.* **2022**, *29*, 68857–68869. [[CrossRef](#)]
45. Montoya-Mayor, R.; Fernández-Espinosa, A.; Seijo-Delgado, I.; Ternero-Rodríguez, M. Determination of soluble ultra-trace metals and metalloids in rainwater and atmospheric deposition fluxes: A 2-year survey and assessment. *Chemosphere* **2013**, *92*, 882–891. [[CrossRef](#)] [[PubMed](#)]
46. Zimmerman, A.J.; DWeindorf, C.; Cifuentes, A. Heavy Metal and Trace Metal Analysis in Soil by Sequential Extraction: A Review of Procedures. *Int. J. Anal. Chem.* **2010**, *2010*, 387803. [[CrossRef](#)] [[PubMed](#)]
47. Xu, J.C.; Wang, S.; Yao, T.; She, X.; Gan, Z. Vertical Distributions and Bioavailabilities of Heavy Metals in Soil in An-Tea Plantations in Qimen County, China. *Processes* **2022**, *10*, 664. [[CrossRef](#)]
48. Qing, X.; Yutong, Z.; Shenggao, L. Assessment of heavy metal pollution and human health risk in urban soils of steel industrial city (Anshan), Liaoning, Northeast China. *Ecotoxicol. Environ. Saf.* **2015**, *120*, 377–385. [[CrossRef](#)]
49. Gómez-Ariza, J.L.; Giraldez, I.; Sánchez-Rodas, D.; Morales, E. Metal readsorption and redistribution during the analytical fractionation of trace elements in oxic estuarine sediments. *Anal. Chim. Acta* **1999**, *399*, 295–307. [[CrossRef](#)]
50. Davranche, M.; Bollinger, J. Heavy Metals Desorption from Synthesized and Natural Iron and Manganese Oxyhydroxides: Effect of Reductive Conditions. *J. Colloid Interface Sci.* **2000**, *227*, 531–539. [[CrossRef](#)]
51. Meng, Q.P.; Zhang, J.; Zhang, Z.; Wu, T. Influence of ore deposits on river sediment compositions in Dan River drainage, China. *J. Geochem. Explor.* **2015**, *159*, 8–19. [[CrossRef](#)]
52. Ding, Q.; Cheng, G.; Wang, Y.; Zhuang, D. Effects of natural factors on the spatial distribution of heavy metals in soils surrounding mining regions. *Sci. Total Environ.* **2017**, *578*, 577–585. [[CrossRef](#)]

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