resources

MDPI

Article

Assessment of Environmental Pollution and Risks Associated with Tailing Dams in a Historical Gold Mining Area of Ecuador

Bryan Salgado-Almeida [1], Arián Briones-Escalante [1], Daniel Falquez-Torres [1], Karla Filián-Haz [1], Fredy Guzmán-Martínez [2], Kenny Escobar-Segovia [1], Elizabeth Peña-Carpio [1] and Samantha Jiménez-Oyola [1,*]

[1] Faculty of Engineering in Earth Sciences FICT, ESPOL Polytechnic University ESPOL, Km 30.5 Vía Perimetral, Guayaquil 090101, Ecuador; bryjosal@espol.edu.ec (B.S.-A.); jabrione@espol.edu.ec (A.B.-E.); dfalquez@espol.edu.ec (D.F.-T.); kfilian@espol.edu.ec (K.F.-H.); kescobar@espol.edu.ec (K.E.-S.); gepena@espol.edu.ec (E.P.-C.)

[2] Mexican Geological Survey (SGM), Boulevard Felipe Angeles Km. 93.50-4, Pachuca 42083, Mexico; fredyguzman@sgm.gob.mx

* Correspondence: sjimenez@espol.edu.ec

Abstract: Tailings are a significant concern due to their potential release of toxic elements into the environment, posing risks to ecosystems and human health. Therefore, understanding their polluting potential is crucial for effective mitigation strategies. This study evaluates the contaminating potential of eight tailing dams in the upper basin of the Puyango River in southern Ecuador. A physicochemical and mineralogical characterization of the tailings was conducted. The contents of As, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, V, and Zn were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The contamination index (IC) and the risk (R_I) to the environment and population were evaluated. As a result, it was found that As, Cu, Pb, Se, and Zn exceeded the maximum permissible limits in all the samples according to Ecuadorian regulations. Six of the eight tailing dams presented very high pollution levels (21.28 < IC < 298.61), indicating a severe contamination risk. As, Sb, and Se were the most significant contributors to the index, with 29%, 31%, and 20% contribution to the overall IC, respectively. However, the risk assessment indicated a low risk (R_I < 5) to both the population and the natural environment, mainly due to the distance between the tailing dams and the potential receptors. While the present risk associated with the studied tailing dams is low, there exists potential for long-term escalation.

Keywords: potentially toxic elements; mining environmental liabilities; contamination index; risk assessment

check for updates

Citation: Salgado-Almeida, B.; Briones-Escalante, A.; Falquez-Torres, D.; Filián-Haz, K.; Guzmán-Martínez, F.; Escobar-Segovia, K.; Peña-Carpio, E.; Jiménez-Oyola, S. Assessment of Environmental Pollution and Risks Associated with Tailing Dams in a Historical Gold Mining Area of Ecuador. *Resources* **2024**, *13*, 105. https://doi.org/10.3390/resources13080105

Academic Editor: Antonio A. R. Ioris

Received: 7 June 2024
Revised: 14 July 2024
Accepted: 17 July 2024
Published: 25 July 2024

1. Introduction

Mining is essential for societal development as it supplies essential raw materials for various industries. However, it can occasionally negatively impact ecosystems and populations [1–6]. One of the main concerns associated with mining activities is the potential release of high-toxicity pollutants into the environment [7–9]. Some potentially toxic elements (PTEs), such as As, Cd, Pb, and Zn, can cause severe damage to ecosystem resources [10]. Due to their toxicity, persistence, and bioavailability, the effects of some of the PTEs can persist indefinitely in contaminated environments, even after mining activities cease. These pollutants can adversely affect fields directly relevant to mining activities, including water resources, soil quality, and biodiversity [9,11–13]. Additionally, the impact on water bodies can have downstream effects on drinking water safety and aquatic life [14]. Understanding and mitigating the long-term effects of PTEs is crucial for ensuring sustainable mining practices and protecting interconnected sectors such as public health, environmental conservation, and industrial productivity.

In the upper basin of the Puyango River in southern Ecuador, important metallic mining activity is carried out, primarily artisanal and small-scale mining (ASM) [15,16]. Gold and silver have been extracted in this area since the early 1980s, with processing plants mainly located along the Calera and Amarillo Rivers [17]. Inadequate waste management and the lack of mining regulation and control have led to the direct discharge of mine tailings into rivers for many years, resulting in severe environmental damage [16,18]. Moreover, mining environmental liabilities (MELs) in the area, such as abandoned tailings and dumps, have facilitated the release and mobilization of pollutants due to wind or runoff [19]. Consequently, the upper basin of the Puyango River has been severely contaminated, affecting the water quality of the Tumbes River and leading to cross-border environmental conflicts with Peru [20].

In the past decade, several studies have assessed the environmental quality of the Puyango River Basin, revealing concerning findings. Ñuñez and Zegarra [21] reported high concentrations of Cu, Fe, and Pb, exceeding the maximum permissible limits (MPLs) according to Ecuadorian and Peruvian environmental regulations. Mora et al. [22] identified high concentrations of Cu, Fe, and Zn downstream from the confluence zone of the Calera and Amarillo Rivers. Delgado et al. [23] found significant contamination of water bodies in the area due to mining waste and effluents from mineral beneficiation plants. In the "Integral Reparation Plan for the Puyango River Basin", the Ministry of the Environment of Ecuador documented total As and Al concentrations exceeding permissible limits in water samples, soil samples showed high concentrations of Fe (71,129.60 mg/kg) and Al (44,402.10 mg/kg), and sediment samples from the lower basin of the Puyango River contained high concentrations of Ba, V, and Ni [19]. These impacts, linked to some mineralogical species, such as sulfides, sulfates, and oxides in abandoned waste deposits [24], show a long-standing legacy of pollution exacerbated by inadequate mitigation efforts. Consequently, MELs in the area, mainly tailing deposits [25], persist in the release and mobilization. Previous research in the area has shown the high contamination level in the Puyango River Basin. However, these studies lack information on the potential risk posed by mining waste deposits to the ecosystem and local population. Therefore, this study aims to evaluate the contaminating potential and associated risks of tailings in the upper basin of the Puyango River. The physicochemical and mineralogical characterization of the tailings and their surroundings help quantify the environmental and population risks these waste deposits pose. This study establishes a baseline for decision-makers, enabling the proposal of effective pollution control strategies in mining areas.

2. Materials and Methods

2.1. Study Area

The study area encompasses the upper basin of the Puyango River, situated in southern Ecuador (Figure 1). This area is considered one of the country's oldest and most important sites for artisanal and small-scale gold mining (ASGM) [16]. As an integral part of the Puyango–Tumbes Basin, this sector comprises key tributaries like the Calera, Amarillo, and Pindo Rivers, which feed into the Puyango River, eventually flowing into Peru [26].

The study area experiences two seasons: a rainy period from January to April and a dry season from May to November or December, with an average annual rainfall of 1160 mm. The climate is tropical, with an average yearly temperature of 24.5 °C in the plains and 22 °C in the mountainous area. During regular years, the dry season registers an average temperature of 26 °C, while the rainy season sees an average of 23 °C. However, during El Niño events, daily maximum temperature rises to 35 °C and 30 °C in the plains and mountainous regions, respectively [27].

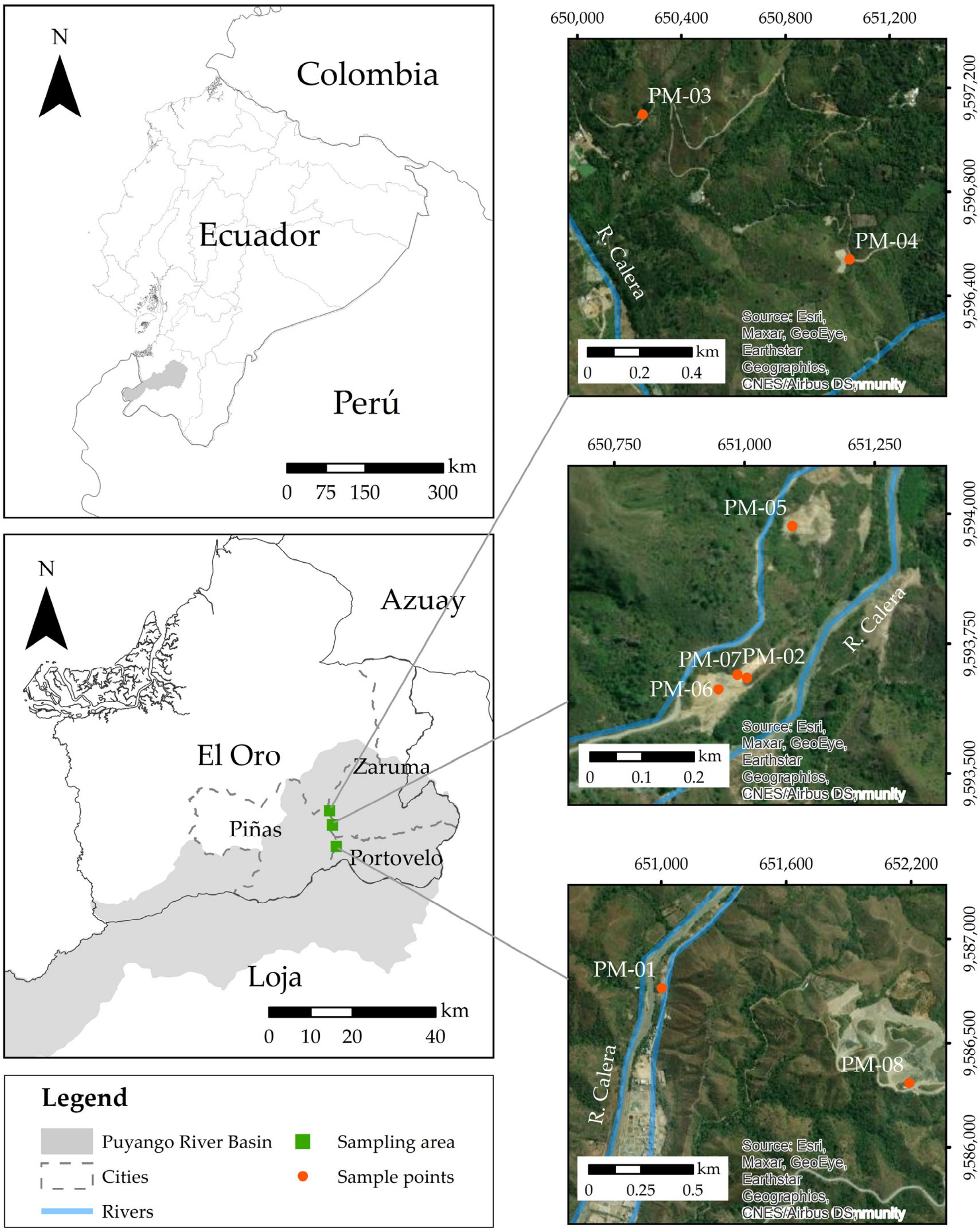

Figure 1. Geographical location of the study area and sample points in the upper river basin of the Puyango River, Ecuador.

Geologically, the upper basin of the Puyango River is formed by andesite rocks and tuffs associated with oxides and sulfides. This area exhibits three phases of mineralization: (i) quartz–pyrite–chlorite–hematite, (ii) quartz–pyrite–chalcopyrite, and (iii) polymetallic quartz rich in galena, sphalerite, and galena-chalcopyrite. Due to its geological resources, the region undergoes intense mining activity and treatment of gold and silver ores [17]. However, mining operations carried out near rivers have resulted in the degradation of natural resources caused by illegal discharges of highly polluting mining waste. In addition, inadequate waste management has resulted in the accumulation of MELs, mainly composed of tailings and abandoned galleries in the area [19,25]. Consequently, these sites have become potential sources of environmental contamination [16,28,29].

2.2. Sampling Campaign and Laboratory Tests

The sampling campaign collected samples from eight tailing dams; seven were identified as abandoned and inactive [19] and one as active—a community tailing dam receiving waste from different mineral recovery processes (from various mineral benefit plants). The sampling points were strategically located near the Calera River and the Puente de Buza–Piñas road, intersecting Zaruma, Portovelo, and surrounding Piñas (Figure 1). The samples were collected manually using shovels at depths of 30 to 40 cm. In addition, several samples were taken from the same tailing dam to obtain a composite and representative sample of the tailing material, according to the methodology proposed by Smith [30].

The laboratory analyses included physical, chemical, and mineralogical characterization of the samples. Particle size characterization was performed to identify the percentage of fine materials in the samples in accordance with the American Society for Testing and Materials (ASTM) standards. A portion finer than 0.075 mm was obtained by washing the material in a No. 200 sieve, per the ASTM D-1140 reference standard [31]. The portion retained in the 0.075 mm mesh was dried and analyzed based on the ASTM D-422 Standard [32], using sieves including No. 10 (2 mm), No. 16 (1.18 mm), No.30 (0.6 mm), No. 50 (0.3 mm), No. 100 (0.15 mm), and No. 200 (0.075 mm). The pH was measured with a HACH HQ40D multi-parameter meter in the supernatant of deionized water and tailing solution (L/S: 1/1). For the determination of Cd, Co, Ni, Mo, Sb, Se, and Pb, an Agilent 7700X Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was used, while for As, Cr, Cu, V, and Zn, an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) from Perkin Elmer® (Chatsworth, CA, USA) model AVIO 500, was employed [33]. Sample digestion was performed with four acids (HNO_3-HCl-$HClO_4$-HF, at concentrations of 69–70%, 36.5–38%, 69–72%, and 48–50%, respectively). The limits of detection (LoDs) for the analyzed PTEs were As = 4 mg/kg, Cd = 0.01 mg/kg, Co = 0.01 mg/kg, Cr = 3.33 mg/kg, Cu = 2.67 mg/kg, Mo = 0.06 mg/kg, Ni = 0.01 mg/kg, Pb = 0.02 mg/kg, Sb = 0.004 mg/kg, Se = 0.01 mg/kg, V = 6.67 mg/kg, and Zn = 0.41 mg/kg. The analysis used reference materials NCS DC 73,303 Rock and NCS DC 73,507 Ore for quality control. The mineralogical characterization to determine the content of mineral species was carried out using a Bruker Model D2 Phaser 2nd Gen diffractometer.

2.3. Statistical Analysis and Data Processing

Descriptive statistics were used to observe trends in the data set. The relationships among the PTEs were evaluated through Spearman's correlation coefficient. In addition, principal component analysis (PCA) was applied to investigate and extract the most significant groups that have a greater contribution to the variance [34]. Statistical analysis was performed with Statgraphics v19 software. For the processing of spatial information and the generation of maps, Geographic Information System software ArcMap 10.8.1 was used.

2.4. Pollution Assessment

The contamination index (IC) (Equation (1)) allowed the assessment of hazards associated with the presence of PTEs in mining tailings [35]. This indicator provides information on the geochemical composition of the soil and determines whether the presence of PTEs results from natural processes or anthropogenic contamination [9,36].

$$\mathrm{IC} = \frac{1}{\mathrm{n}}\left[\sum\nolimits_{\mathrm{i}=1}^{\mathrm{n}} \frac{\mathrm{C_i}}{\mathrm{B_i}}\right] \quad (1)$$

where C_i is the concentration of each analyzed element in the sample, B_i is the soil background level for element i, and n is the number of elements where the concentration in the tailings is greater than the respective B_i. The B_i values (mg/kg) used in this study were As (4.7), Cd (1.1), Co (6.9), Cr (42), Cu (14), Mo (1.8), Ni (18), Pb (25), Sb (0.62), Se (0.7), V (60), and Zn (62) [37]. The IC value was interpreted according to the following assessment scale: very low contamination potential ($1 \leq \mathrm{IC} < 3.5$), low contamination potential

(3.5 ≤ IC < 6.5), moderate contamination potential (6.5 ≤ IC < 10), high contamination potential (10 ≤ IC < 15.6), and very high contamination potential (IC ≥ 15.6) [35].

2.5. Risk Assessment

A risk assessment was carried out applying the methodology proposed by the Spanish Geological Survey [36], considering the scenario of polluting effluents affecting surface waters. The risk for this scenario was determined through the risk index (R_I), which results from multiplying the probability index (I_p) by the severity index (I_s). The probability index (I_p) was calculated by using Equation (2), considering factors such as proximity to water bodies (P_R), toxicity of mining wastes (F_{TOX}), and unprotected surfaces (F_{SD}). The valuation criteria of P_R are shown in Table 1. F_{TOX} was obtained from the average hazard quotient (AHQ) (Equation (3)), where X is the measured element concentration in the mining waste leachate using the U.S. Geological Survey Field Leaching Test method (USGS FLT) [38], MPL_i corresponds to the maximum allowable content of element $_i$, and n is the number of elements for which the concentration measured in the leachate is higher than the maximum permissible level. Table 1 provides the criteria for determining P_R, F_{TOX}, and F_{SD} values using Equations (2) and (3).

$$I_p = P_R \times F_{TOX} \times F_{SD} \tag{2}$$

$$AHQ = \frac{1}{n} \times \sum_{i=0}^{n} \frac{X}{MPL_i} \tag{3}$$

Table 1. Assessment criteria of parameters for the probability index (I_p) determination.

Parameter	Criteria	Value
Proximity factor to water bodies (P_R)	D ≤ 50 m 50 < D < 500 m D ≥ 500 m	P_R = 1.0 P_R = −0.0022 × D + 1.1 P_R = 0.0
Toxicity factor (F_{TOX})	AHQ ≤ 400 AHQ > 400	F_{TOX} = 0.0125 × AHQ F_{TOX} = 5
Unprotected surface factor (F_{SD}) *	S_{EX} ≤ 2 ha S_{EX} > 2 ha	F_{SD} = 0.5 × S_{EX} F_{SD} = 1

* Considering a surface of tailing deposit without vegetation. S_{EX} = exposed area of the tailing deposit in ha; D = distance from tailing deposit to water bodies; AHQ = average hazard quotient.

On the other hand, the severity index (I_s) evaluated the effects of contamination on the population (PO) and the natural environment (NA) through Equations (4) and (5), respectively. I_s for the population (I_s(PO)) considered the factor of the population exposed to toxic elements (P_{EX}), the exposure factor for the population ($F_{SUP\text{-}PO}$), and the vulnerability factor of the exposed population (V_P). Is for the natural environment (I_s(NA)) relied on the environmental exposure factor ($F_{SUP\text{-}NA}$) and the ecological vulnerability factor (V_E). Table S1 shows the criteria used in assessing each factor, using Equations (4) and (5).

$$I_s(PO) = 0.5P_{EX} + 0.5(F_{SUP\text{-}PO} \times V_P) \tag{4}$$

$$I_s(NA) = F_{SUP\text{-}NA} \times V_E \tag{5}$$

Both in the probability index (I_p) and the severity index (I_s), five categories are defined: very low (≥0 I_p/I_s < 1), low (≥1 I_p/I_s < 2), moderate (≥2 I_p/I_s < 3), high (≥3 I_p/I_s < 4), and very high (≥4 I_p/I_s ≤ 5). The risk of affectation (R_I) on the population (R_I(PO)) and the natural environment (R_I(NA)) was obtained by multiplying the probability of occurrence (I_p) and the severity of the consequences (I_s). This resulted in a three-degree scale based on the $I_p \times I_s$ product: low risk (0 ≤ R_I ≤ 5), moderate risk (6 ≤ R_I ≤ 15), and high risk (16 ≤ R_I ≤ 25).

3. Results

This section focuses on the results of the physical–chemical characterization of the eight tailing samples (PM-01 to PM-08). It also encompasses the findings related to the index of contamination (IC) and the risk assessment (R_I) for the ecosystem and the population. These results aim to pinpoint the tailing dam posing the most substantial contamination potential for both the environment and human populations.

3.1. Physical–Chemical Characterization

Regarding the physical characterization, it was observed that the average percentage of material finer than 0.075 mm was 49%, while the remaining percentage corresponded to sand size (Figure S1 in Supplementary Material). From an environmental point of view, smaller particle size means a greater surface area exposed to contact with water and oxygen, which favors sulfide oxidation processes [39] and, therefore, increases the likelihood of generating acid mine drainage (AMD) [40]. From a geotechnical perspective, a high percentage of material passing through the 0.075 mm sieve may cause structures to become less resistant to shear forces and foster the formation of saturated pockets, which can lead to rupture processes with a consequent release of PTEs into the environment [41].

Table 2 shows the pH values and total concentrations of the analyzed elements in the tailing samples (also see Table S2). The pH values ranged from 2.60 to 7.30, indicating acidic conditions in 75% of the analyzed samples. Conversely, the concentrations of trace elements, represented by the median (50th percentile), showed a decreasing behavior: Pb > As > Cu > Zn > V > Sb > Cr > Co > Ni > Se > Mo > Cd. Sample PM-08 presented the highest PTE content, mainly of Zn, Pb, As, and Cu. However, the pH value for this sample was 7.30, suggesting that the solubilization of these elements may not occur in the short term.

Table 2. PTE concentration (mg/kg) and pH values in tailing samples.

Parameter	MPL [a]	PM-01	PM-02	PM-03	PM-04	PM-05	PM-06	PM-07	PM-08
pH	6–8	6.4	4.5	2.9	3.0	3.2	2.6	3.3	7.3
As	12	23.6	129.6	4612	344.7	3940	418.1	470.3	5772
Cd	0.5	0.7	0.2	1.1	0.7	3.3	3.9	0.5	96.2
Co	10	23.0	6.9	22.1	11.6	14.9	2.8	2.4	42.9
Cr	54	88.3	31.3	75.6	25.1	63.5	26.3	43.6	45.4
Cu	25	64.9	119.9	1679	583.4	812.6	515.2	279.2	1834
Mo	5	3.0	3.0	1.0	4.6	25.8	7.6	10.5	5.1
Ni	19	42.4	6.2	19.6	6.7	15.4	3.1	6.7	23.3
Pb	19	37.4	178.7	85.9	584.4	699.1	1353	474.2	6196
Sb	-	14.6	25.3	93.8	36.7	156.9	166.1	72.8	78.7
Se	1	1.2	10.9	5.5	14.1	9.7	5.4	9.8	7.3
V	76	158.9	92.9	246.8	98.9	114.9	68.7	76.2	132.1
Zn	60	106.8	141.8	148.4	196.3	332.8	589.2	113.1	18,392

[a] Maximum permissible limit according to Ecuadorian regulations [42].

The concentrations of PTEs were compared with the MPL corresponding to the soil quality criteria outlined in Ecuadorian regulations [42]. Among the eight analyzed samples, the concentrations of As, Cu, Pb, Se, V, and Zn exceeded the MPL, representing a potential risk of environmental pollution. As was the contaminant of most significant concern, with concentrations in the tailings exceeding the MPL up to 481 times, followed by Pb and Zn, which exceeded the limits by over 300 times. To a lesser extent, Cu (up to 70 times the MPL), Se (up to 14 times the MPL), and V concentrations (up to 2 times the MPL) were also identified. Comparison with background values (Bis) [37] revealed significant enrichment of the analyzed elements resulting from mining activities. Notably, As emerged as one of the most concerning contaminants, surpassing Bis by up to 1228 times. These results align with previous studies conducted since the early 20th century in the upper basin of the Puyango River [17,29], which have consistently reported high concentrations of PTEs from mining activities. This environmental impact has even resulted in cross-border effects with Peru [20]. Studies by Tarras-Wahlberg et al. [16] and Appleton et al. [43] highlighted the influx of PTEs stemming from mining activities into the Puyango River Basin system before 1999, causing the water and sediments of the rivers in the area to be contaminated with toxic elements. Research carried out in the area has reported high levels of Pb (0.16 mg/L) in the water of the Puyango River [26], as well as concentrations of As, Cd, Cu, Pb, and Zn that exceed up to 3567 times the MPL in water and up to 740 times the recommended PTE limits in sediments within the vicinity of mineral processing plants along the Calera and Amarillo Rivers [44]. The upper reaches of the Puyango River Basin have displayed the most significant contamination, which has spread to the middle and lower parts of the basin [22]. Despite numerous studies and reports in the area, there has been a lack of timely intervention to mitigate the effects of contamination. Consequently, potentially toxic elements have accumulated in the soils, rivers, and sediments of the area over the years. This situation is exacerbated by MELs (mainly abandoned tailing deposits), which continue to release and mobilize toxic substances into the environment [25].

3.2. Mineralogical Characterization

The mineralogical analysis showed that quartz (SiO_2) is the predominant mineral species in the analyzed samples (Figure S2). This finding corresponds to the gold ore prevalent in the area, found in quartz veins associated with sulfides, mainly pyrite, chalcopyrite, sphalerite, and arsenopyrite. Jarosite ($KFe^{3+}{}_3(SO_4)_2(OH)_6$), gypsum ($CaSO_4{\cdot}2H_2O$), muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$), goethite ($FeO(OH)$), and chamosite ($(Fe^{2+}, Mg)_5Al(AlSi_3O_{10})(OH)_8$) were also identified, albeit in lesser proportions. These secondary minerals are known as byproducts of AMD-forming processes [39]. Of notable concern is the presence of sulfates, such as jarosite, in 75% of the samples, considering that the formation of this mineral indicates the oxidation of primary sulfides and a significant rise in acidity [45,46]. Therefore, this mineral can be a potential source of AMD [47]. In conjunction with gypsum and jarosite, the prevailing hot and arid climate conditions could favor the formation of efflorescent salts, known to retain PTEs [48–50]. Dissolving these salts in the presence of rainfall could release acidity and toxic elements [46,51], causing severe environmental damage. This process may result in the direct release of PTEs, such as As, Cd, Pb, and other toxic substances associated with the minerals in the region [24,52], triggered by the acidity induced by sulfide oxidation within the waste material.

3.3. Statistical Analysis

Spearman's correlation was used to assess the relationships among the studied PTEs. The high correlation between certain PTEs can be explained due to the presence of geologically associated minerals in the area, leading to their co-occurrence and therefore a high correlation. This occurs when minerals containing these metals were formed under similar conditions or deposited together during specific geological processes. In addition to geological processes, mining processes, such as mineral extraction and processing, can lead to the release of various metals/metalloids in tailings [53,54]. If extraction and treatment processes are similar for different minerals, it is likely that the metals/metalloids associated with these minerals are also present in similar proportions, resulting in a high correlation. Another factor, such as cross-contamination during milling processes, flotation, or other separation methods, may result in the presence of various metals/metalloids in similar concentrations in the tailings. This could be due to the difficulty of completely separating the different metals during ore processing.

Table 3 and Figure S3 shows the results of the Spearman correlation. Regarding the correlation of the PTEs with the pH, the results obtained showed a non-significant correlation. On the other hand, the following pairs of variables showed strong positive correlations for As-Cu and Pb-Zn (p-values < 0.05, $r \geq 0.90$); for Cd-Zn, Co-Ni, Co-V, Cr-Ni, and Ni-V (p-values < 0.05, $0.80 < r < 0.90$); and for Cr-V, Cd-Cu, and Cu-Zn (p-values < 0.05, $0.70 < r < 0.80$). The high correlations between some elements agree with the mineralogical species present in the study area. While As and Cu are associated with copper sulfide minerals such as chalcopyrite or arsenopyrite, Cd, Cu, Pb, and Zn are commonly found in sulfides such as sphalerite or galena [55,56].

Table 3. Spearman correlation matrix for the PTEs measured in tailing samples.

PTE	As	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sb	Se	V	Zn
Cd	0.67											
Co	0.29	0.43										
Cr	0.19	0.05	0.64									
Cu	0.90 *	0.76 *	0.43	0.05								
Mo	0.26	0.33	−0.33	−0.19	0.12							
Ni	0.26	0.17	0.83 *	0.86 *	0.21	−0.17						
Pb	0.52	0.74	−0.05	−0.48	0.57	0.64	−0.29					
Sb	0.67	0.74	−0.14	−0.10	0.62	0.48	−0.26	0.62				
Se	−0.05	−0.40	−0.40	−0.62	0.05	0.10	−0.45	0.14	−0.24			
V	0.26	0.17	0.88 *	0.79 *	0.36	−0.50	0.86 *	−0.40	−0.19	0.36		
Zn	0.62	0.88 *	0.19	−0.33	0.76 *	0.36	−0.19	0.90 *	0.71	0.00	−0.12	
pH	−0.07	−0.19	0.48	0.36	−0.17	−0.05	0.57	−0.07	−0.62	0.02	0.29	−0.21

* p-values < 0.05.

Regarding principal component analysis (PCA), four principal components (PCs) were extracted with eigenvalues > 1, of which PC1 explains 44.20% of the variance, while PC2, PC3, and PC4 explain 25.70%, 15.20%, and 8.60% of the variance, respectively (Table 4). In PC1, the elements with the greatest weight in the variance in decreasing order are Co, Cd, Zn, As, Cu, and Pb. Se and Pb had significant loading in PC2, while in PC3 and PC4, the elements with the greatest contribution to the variance were Sb and Mo, and Mo and Ni, respectively. These results suggest that the clustering of the data is related to sources of common origin. Additionally, significant loadings on the same component could indicate a correlation between the mobility of the analyzed elements [55].

Table 4. Principal component analysis (PCA) of PTE concentrations in tailing samples.

Parameter	PC1	PC2	PC3	PC4
As	0.368	0.089	0.313	−0.232
Cd	0.371	0.242	−0.176	0.169
Co	0.418	−0.064	−0.100	0.035
Cr	0.164	−0.478	0.228	0.126
Cu	0.363	0.111	0.190	−0.420
Mo	−0.061	0.175	0.558	0.382
Ni	0.238	−0.416	−0.074	0.338
Pb	0.343	0.306	−0.141	0.210
Sb	0.022	0.219	0.614	0.111
Se	−0.156	0.379	−0.068	−0.387
V	0.233	−0.377	0.136	−0.481
Zn	0.370	0.241	−0.190	0.163
Eigenvalues	5.304	3.084	1.824	1.033
% of variance	44.20	25.70	15.20	8.60
Cumulative %	44.20	69.90	85.10	93.70

3.4. Contamination Index

The results indicate potential environmental contamination in the studied area. Sample PM-01 presented a low index of contamination (IC = 4.56) followed by sample PM-02 with a high index of contamination (IC = 13.14), while the remaining samples exhibited a very high IC, ranging from 25.20 to 178.50 (Figures 2 and S4 and Table S3). Specifically, six out of the eight analyzed tailing dams present an increased risk of environmental contamination. The elements that contributed the most to the IC were As and Sb (between 56 and 89%) for the samples PM-01 to PM-07, while in sample PM-08, the main contribution to the IC was As (57%), followed by Zn (14%) and Pb (12%) (Table S4).

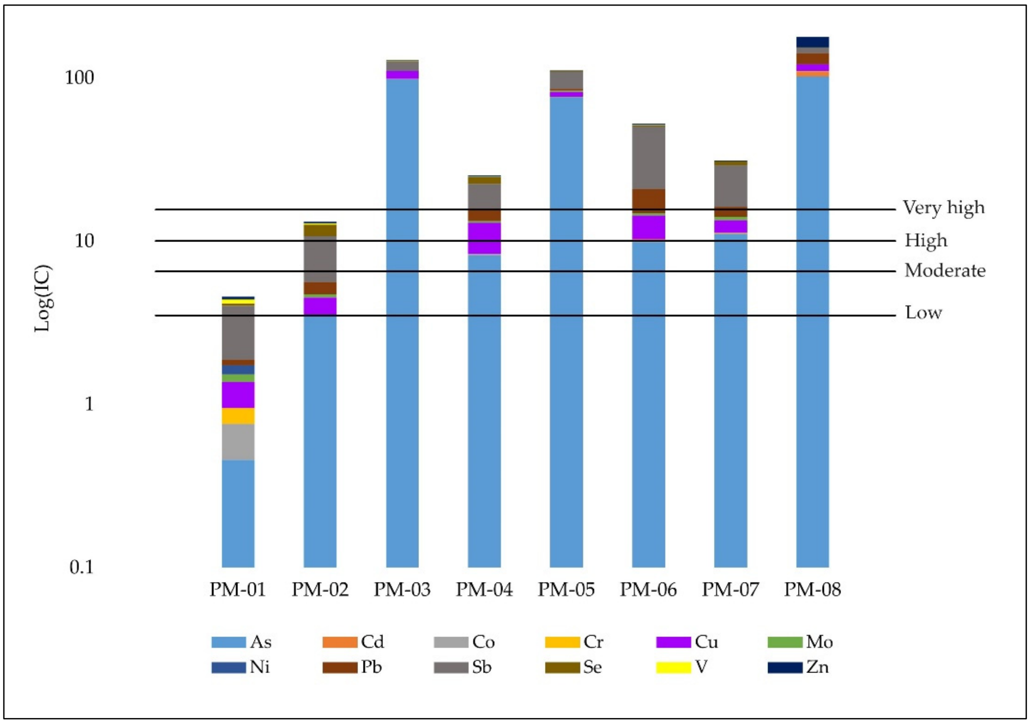

Figure 2. Contamination index calculated for tailing samples.

The results of this study are consistent with those of Guzmán-Martínez et al. [9], who reported high to very high IC levels (ranging from 11 to 220) in several abandoned tailing dams across different regions of Spain. Similarly, in the Riotinto Mining District in Spain, Arranz-González et al. [48] documented IC values > 13 in an abandoned sulfide tailing area, showing high contamination potential in the ecosystem.

3.5. Risk Assessment

The risk assessment showed low values ($R_I < 5$) for both the population and the natural environment (Table 5 and Figure S5). Despite the high content of PTEs in the samples analyzed, the low R_I values were attributed to the distance ($D \geq 50$ m) separating the tailing dams from potential receptors (the population or natural environment). This distance directly influenced the likelihood of contamination occurrence, resulting in an almost negligible probability ($I_p < 1$). Similarly, the risk index for the ecosystem was virtually insignificant ($R_I < 0.25$). Another contributing factor to the I_p outcome was the exposed surface area of the tailing dams. However, an exception was observed for tailing dam PM-08, where the exposed area was less than 1 ha. As a result, the severity index of the population I_s(PO) rated medium to high, falling within the range of $2 < I_s(PO) < 4$, considering an exposed population ($n > 40$) in 75% of the sampled sites. On the other hand, regarding population exposure to contaminants ($F_{SUP\text{-}PO}$), it remained below one due to the distance ($D > 300$ m) separating the population from the tailing dams. Consequently, this factor, linked with the population's vulnerability—especially in terms of water for recreational use, fishing, and irrigation—significantly influenced the severity index calculation. Regarding the effects of tailing dams on the natural environment, a moderate vulnerability factor was found in the ecosystem, considering the presence of surface water bodies with a deficient ecological status. In terms of the exposure of natural resources to contaminants ($F_{SUP\text{-}NA}$), a value ≤ 1 was observed due to the distance between the tailing dams and the rivers or streams in the area ($40 < D < 1300$ m). Finally, the severity of the consequences of waste deposits on the natural environment, akin to the population, resulted in medium to high values with $2 < I_s(NA) \leq 3$.

Table 5. PTE concentration (mg/kg) in tailing samples.

Sample	I_p [a]	$I_s(PO)$ [b]	$I_s(NA)$ [c]	$R_I(PO)$ [d]	RI(NA) [e]	Risk Level
PM-01	0.067	3.406	3.00	0.229	0.202	Low
PM-02	0.015	2.892	2.94	0.043	0.044	Low
PM-03	0.002	0.000	2.82	0.000	0.006	Low
PM-04	0.000	0.000	2.45	0.000	0.000	Low
PM-05	0.081	2.870	2.93	0.232	0.237	Low
PM-06	0.086	2.899	2.91	0.251	0.251	Low
PM-07	0.015	2.892	2.94	0.043	0.044	Low
PM-08	0.000	3.119	2.22	0.000	0.000	Low

[a] Probability index; [b] severity index of the population; [c] severity index of the natural environment; [d] risk to the population; [e] risk to the environment.

4. Discussion

This research has allowed us to identify and characterize PTE contamination in mining tailings in the southern area of Ecuador, highlighting the prevalence of heavy metals such as As, Pb, Zn, and Cu. The parameters determined in this study, such as PTE concentrations and pH, are essential to assess the risk to both humans and wildlife. The concentration of PTEs in environmental compartments provides critical information on direct and indirect exposure to these contaminants and on exposure pathways for wildlife and populations. Furthermore, bioaccumulation rates and transfer factors are useful for understanding how these PTEs move through the food chain, affecting both animals and humans [57,58].

A relevant finding in this study is that the distance from the pollution source (in this case, tailing deposits) to potential receptors is a key protective factor, especially for human populations [36,58]. However, this concept may not be as relevant for wildlife, which can move freely through contaminated areas. Therefore, it is crucial to consider additional parameters that consider the mobility and behavior of animals [4,8,59].

The significant correlation between certain PTEs, such as As-Cu and Pb-Zn, suggests the co-occurrence of these elements due to geological and mining extraction processes. This information is vital for designing more effective mitigation strategies, as it allows the most dangerous pollutants and their sources to be identified and prioritized.

The results of this study are consistent with previous research in other geographic contexts, underlining the universality and persistence of this environmental problem in abandoned and/or poorly managed mining areas. Guzmán-Martínez et al. [9] reported high to very high levels of contamination in several abandoned tailing deposits in different regions of Spain. Similarly, Arranz-González et al. [48] documented very high levels of contamination in abandoned mining areas in Riotinto, Spain. China is one country facing significant challenges due to the release of potentially toxic elements (PTEs) from mining and metallurgical activities. In 2017, China documented approximately 174 contaminated sites within its provincial capitals [60]. Specifically, the city of Hechi in Guangxi Province has experienced health risks for residents due to inadequate mining waste management, resulting in the presence of elements such as As and Cr [61]. Likewise, the Dahuangshan mining area, with abandoned mining facilities, has reported a high potential ecological risk attributed to elevated levels of As and Cd [62]. Similar research conducted by Chen et al. [59] in Shangluo, in Shaanxi Province, revealed potential ecological risks due to As soil pollution in an abandoned tailing deposit of the mining area. Furthermore, studies such as those by Uugwanga and Kgabi [63] in Namibia, particularly in areas like Klein Aub, have also analyzed tailings from abandoned mining sites, identifying significant contamination levels. In Slovakia, old mining areas have been designated as highly contaminated due to As, Cu, and Zn [64]. Despite the cessation of mining operations several years ago, these areas continue to pose a risk to the environment and the population. This shows the longlasting environmental impact caused by PTEs, characterized by their toxicity, persistence, and capacity to bioaccumulate in the environment.

In this sense, this study highlights the need for continuous evaluation and monitoring of mine tailing deposits to mitigate the risks of PTE contamination. Management strategies must incorporate both physical and chemical parameters, as well as ecological and human health factors, to effectively address environmental challenges and protect affected communities.

4.1. Implications for Public Policies and Sustainability

The management of mine tailing deposits requires comprehensive and sustainable policy action to mitigate environmental risks and protect public health [25]. It is crucial to implement policies that promote safer and more sustainable extraction and waste management practices [65,66]. These policies must include the following: (a) regulation and compliance, establishing strict regulations that govern the disposal of mining waste and promote rigorous compliance to prevent contamination; (b) continuous monitoring and evaluation, implementing continuous environmental monitoring programs to evaluate the quality of water, soil, and air in areas near tailing deposits. This will allow changes in contamination levels to be identified and timely corrective measures to be taken; (c) education and awareness, raising awareness among local communities about the risks associated with PTE exposure and promoting responsible consumption practices of natural resources; (d) restoration of contaminated sites, developing effective remediation and restoration strategies for contaminated areas to reduce long-term environmental impacts and restore the functionality of affected ecosystems.

To move towards sustainability in mine tailing management, it is essential to encourage interdisciplinary research and international collaboration. This includes the exchange of best practices and innovative technologies for the treatment of mining waste and the mitigation of environmental impacts. Furthermore, a continued commitment is required from governments, the mining industry, and civil society to address these challenges effectively and ensure long-term sustainable development. In summary, the study highlights the importance of integrating environmental, social, and economic considerations in the management of mining-related deposits, with the aim of protecting vulnerable ecosystems and ensuring the health and well-being of affected communities.

4.2. Rehabilitation and Remediation of Abandoned Tailing Dams

Rehabilitation involves restoring altered areas to achieve ecological stability, following a predefined plan to prevent further environmental damage. There are various alternatives for rehabilitation and remediation of disturbed lands, such as abandoned tailing deposits. Some of these alternatives use geosynthetic materials, vegetation, and soil encapsulation, as in Arranz-González et al. [67]. Figure 3 illustrates a remediation and rehabilitation proposal for the abandoned tailing areas highlighted in this study. The proposal consists of both physical and chemical stabilization. Physical stabilization aims to prevent potential slope failures. For the tailing dams requiring stabilization, a suggested approach involves benching through cut and fill techniques, as depicted in Figure 3a. Conducting a thorough slope stability analysis utilizing numerical and conventional methods during this phase is recommended. For chemical stabilization (Figure 3b), the aim is to avoid the generation of AMD by inhibiting the sulfide oxidation process. As the analyzed tailing deposits are considered potential long-term AMD sources, isolating the reactive materials from oxygen and water is necessary. Therefore, approximately 30 cm thick compacted clay soil should be placed on top of the contaminated material, covered by a high-density polypropylene geomembrane. This will allow a good seal and almost zero permeability. In addition, to facilitate drainage and prevent any pressure from filtered water, a thin layer (15 to 20 cm) of limestone and granular material, such as gravel, should be placed on top of the geomembrane. Finally, a 15 cm layer of vegetal or organic soil must be placed over this granular layer, facilitating vegetation growth.

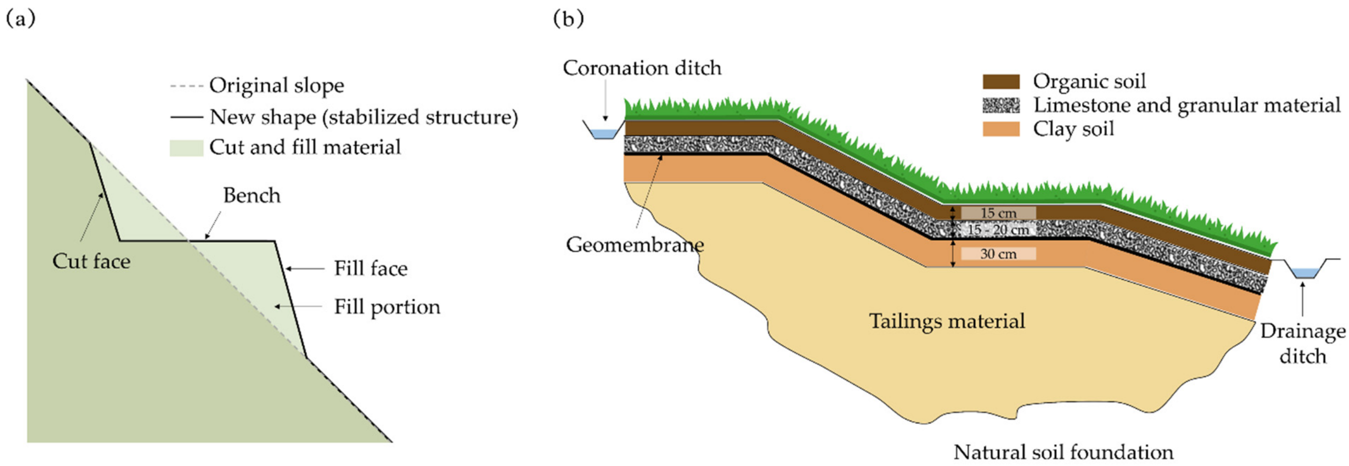

Figure 3. Proposal for rehabilitation and remediation that includes (**a**) physical and (**b**) chemical stabilization of the mining tailings.

Implementing measures to control runoff and prevent erosion caused by precipitation is equally crucial. This involves constructing perimeter channels around the tailing deposits and incorporating coronation and drainage ditches at the foot of the slope. In the same way, establishing an effluent collection system should be considered to manage any leachates due to groundwater levels. Regularly monitoring groundwater levels in the tailing area and controlling the water's physical and chemical parameters are recommended. Continuous monitoring of the growth of the implemented vegetation is also essential. It must be considered that while a management proposal is presented, the effectiveness of the rehabilitation strategies relies on the local climate, topography, surface hydrology, plant growth environment, and the nature and magnitude of the disturbance, according to Butler et al. [68]. Hence, the process requires meticulous planning and adherence to defined compliance parameters.

5. Conclusions

This study evaluated the potential contamination and associated risks posed by eight tailing dams in the Puyango River Basin. The results indicated that concentrations of As, Pb, and Zn in all analyzed samples exceeded the MPL by over 300 times. The IC showed a very high contamination potential in six out of the eight samples, with values exceeding the maximum limit (IC > 14) and with As, Cu, Pb and Sb as the PTEs with the most significant contribution. Risk assessment for the population and natural environment yielded very low values for both scenarios, mainly due to the distance between the tailing dams and the receptors. Even though the studied tailing dams represent a low risk for the population and natural environment, it is important to note potential long-term risks. The high PTE concentration in the environment and the local weather conditions can lead to acid drainage generation or mobilization of fine particles due to wind. The absence of an environmental and territorial management plan exacerbates this concern, potentially leading to different risk scenarios in the future. The insights provided in this study contribute to developing strategies for managing abandoned or inactive tailing dams and operational ones in the area. Future studies should conduct a detailed assessment of water and soil quality in the tailing dam environment and focus on bioavailability and contaminant mobility for a more comprehensive understanding.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/resources13080105/s1. Figure S1: Particle size distribution curves of tailings samples; Figure S2: Percentage of semi-quantitative minerals in the tailing's samples; Figure S3: Spearman correlation for the PTE measured in tailings samples; Figure S4: Contamination Index calculated for tailing samples; Figure S5: Risk map of tailing samples for population and environment; Table S1: Assessment criteria of parameters for the severity index (Is) determination on the population and the environment; Table S2: Statistical summary of the PTE concentration (mg/kg) and pH values in tailings samples; Table S3: Index of contamination (IC) calculated for the tailings samples; Table S4: Individual contribution of PTEs to the Index of contamination.

Author Contributions: Conceptualization, B.S.-A., A.B.-E. and S.J.-O.; methodology, B.S.-A., A.B.-E., F.G.-M. and S.J.-O.; validation and formal analysis, B.S.-A., A.B.-E., K.E.-S. and D.F.-T.; investigation and data curation, B.S.-A., A.B.-E. and K.F.-H.; writing—original draft preparation, B.S.-A., A.B.-E., F.G.-M., D.F.-T., K.F.-H. and S.J.-O.; supervision, S.J.-O.; writing—review and editing, K.E.-S., F.G.-M., E.P.-C. and S.J.-O. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data supporting the findings of this study are available upon reasonable request from the authors.

Acknowledgments: The experiments conducted in this study took place in the Geotechnics and Construction Laboratory of the Geosciences Engineering Faculty at ESPOL and in the Mexican Geological Survey Laboratory, both instrumental in this research. We express our gratitude to ESPOL and the Mexican Geological Survey for their support in providing the necessary facilities and scientific equipment. Additionally, we thank the ESPOL Research Dean and Academic Writing Center for supporting this research endeavor.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Nungesser, S.L.; Pauliuk, S. Modelling Hazard for Tailings Dam Failures at Copper Mines in Global Supply Chains. *Resources* **2022**, *11*, 95. [CrossRef]
2. Perdeli Demirkan, C.; Smith, N.M.; Duzgun, S. A Quantitative Sustainability Assessment for Mine Closure and Repurposing Alternatives in Colorado, USA. *Resources* **2022**, *11*, 66. [CrossRef]
3. Zhang, J.; Gu, H.; Chen, S.; Ai, W.; Dang, Y.; Ai, S.; Li, Z. Assessment of Heavy Metal Pollution and Preschool Children Health Risk in Urban Street Dusts from Different Functional Areas in a Typical Industrial and Mining City, NW China. *Environ. Geochem. Health* **2023**, *45*, 7199–7214. [CrossRef]
4. Moulatlet, G.M.; Yacelga, N.; Rico, A.; Mora, A.; Hauser-Davis, R.A.; Cabrera, M.; Capparelli, M.V. A Systematic Review on Metal Contamination Due to Mining Activities in the Amazon Basin and Associated Environmental Hazards. *Chemosphere* **2023**, *339*, 139700. [CrossRef] [PubMed]
5. Elwaleed, A.; Jeong, H.H.; Abdelbagi, A.H.; Quynh, N.T.; Agusa, T.; Ishibashi, Y.; Arizono, K. Human Health Risk Assessment from Mercury-Contaminated Soil and Water in Abu Hamad Mining Market, Sudan. *Toxics* **2024**, *12*, 112. [CrossRef] [PubMed]
6. Din, I.U.; Muhammad, S.; Faisal, S.; ur Rehman, I.; Ali, W. Heavy Metal(Loid)s Contamination and Ecotoxicological Hazards in Coal, Dust, and Soil Adjacent to Coal Mining Operations, Northwest Pakistan. *J. Geochem. Explor.* **2024**, *256*, 107332. [CrossRef]
7. Innis, S.; Ghahramani, N.; Rana, N.; McDougall, S.; Evans, S.G.; Take, W.A.; Kunz, N.C. The Development and Demonstration of a Semi-Automated Regional Hazard Mapping Tool for Tailings Storage Facility Failures. *Resources* **2022**, *11*, 82. [CrossRef]
8. Salazar, J.P.; Saldarriaga, J.F.; Zapata, D.; López, J.E. Determination of Bioavailability, Potential Ecological and Human Health Risks, and Biomonitoring of Potential Toxic Elements in Gold Mine Tailings from Four Areas of Antioquia, Colombia. *Water Air Soil Pollut.* **2024**, *235*, 122. [CrossRef]
9. Guzmán, F.; Arranz, J.C.; Ortega, M.; García, M.J.; Rodríguez, V. A New Ranking Scale for Assessing Leaching Potential Pollution from Abandoned Mining Wastes Based on the Mexican Official Leaching Test. *J. Environ. Manag.* **2020**, *273*, 111139. [CrossRef]
10. Bartoszek, L.; Gruca-Rokosz, R.; Pękala, A.; Czarnota, J. Heavy Metal Accumulation in Sediments of Small Retention Reservoirs—Ecological Risk and the Impact of Humic Substances Distribution. *Resources* **2022**, *11*, 113. [CrossRef]
11. Zhang, C.; Xia, T.; Zhang, L.; Chen, Z.; Zhang, H.; Jia, X.; Jia, L.; Zhu, X.; Li, G. Mercury Pollution Risks of Agricultural Soils and Crops in Mercury Mining Areas in Guizhou Province, China: Effects of Large Mercury Slag Piles. *Environ. Geochem. Health* **2024**, *46*, 53. [CrossRef] [PubMed]
12. Mao, L.; Ren, W.; Tang, Y.; Liu, X.; He, M.; Sun, K.; Zhang, B.T.; Lin, C.; Ouyang, W. Comprehensive Insight into Mercury Contamination in Atmospheric, Terrestrial and Aquatic Ecosystems Surrounding a Typical Antimony-Coal Mining District. *J. Hazard. Mater.* **2024**, *469*, 133880. [CrossRef] [PubMed]

13. Kumari, A.; Sinha, A.; Singh, D.B.; Pasupuleti, S. Source Apportionment and Health Risk Assessment in Chromite Mining Area: Insights from Entropy Water Quality Indexing and Monte Carlo Simulation. *Process Saf. Environ. Prot.* **2024**, *184*, 526–541. [CrossRef]
14. Mestanza-Ramón, C.; Jiménez-Oyola, S.; Montoya, A.V.G.; Vizuete, D.D.C.; D'Orio, G.; Cedeño-Laje, J.; Straface, S. Assessment of Hg Pollution in Stream Waters and Human Health Risk in Areas Impacted by Mining Activities in the Ecuadorian Amazon. *Environ. Geochem. Health* **2023**, *45*, 7183–7197. [CrossRef] [PubMed]
15. Sandoval, F. Small-Scale Mining in Ecuador. *Min. Miner. Sustain. Dev.* **2001**, *75*, 28.
16. Tarras-Wahlberg, N.H.; Flachier, A.; Lane, S.N.; Sangfors, O. Environmental Impacts and Metal Exposure of Aquatic Ecosystems in Rivers Contaminated by Small Scale Gold Mining: The Puyango River Basin, Southern Ecuador. *Sci. Total Environ.* **2001**, *278*, 239–261. [CrossRef] [PubMed]
17. Garcia, M.E.; Betancourt, O.; Cueva, E.; Guimaraes, J.R.D. Mining and Seasonal Variation of the Metals Concentration in the Puyango River Basin—Ecuador. *J. Environ. Prot.* **2012**, *3*, 1542–1550. [CrossRef]
18. Oviedo-Anchundia, R.; Moina-Quimí, E.; Naranjo-Morán, J.; Barcos-Arias, M. Contamination by Heavy Metals in the South of Ecuador Associated to the Mining Activity. *Bionatura* **2017**, *2*, 437–441. [CrossRef]
19. MAE-PRAS. Programa de Reparación Ambiental y Social—Plan de Reparación Integral de La Cuenca Del Río Puyango; Quito, Ecuador. 2015. Available online: http://pras.ambiente.gob.ec/documents/228536/737569/LIBRO_PRI_PUYANGO.pdf/94bcfdb4-bf26-4d3a-afa3-d5e87cf7398b (accessed on 14 March 2023).
20. Torres, W. Protesta en Perú por Contaminación de río por Minería en Ecuador. Available online: https://www.primicias.ec/noticias/economia/protesta-peru-contaminacion-rio-mineria-ecuador/ (accessed on 22 March 2023).
21. Nuñez, S.; Zegarra, J. *Estudio Geoambiental de La Cuenca Puyango—Tumbes*; Instituto Geológico, Minero y Metalúrgico—INGEMMET: Lima, Peru, 2006.
22. Mora, A.; Jumbo-Flores, D.; González-Merizalde, M.; Bermeo-Flores, S.A. Niveles de Metales Pesados En Sedimentos de La Cuenca Del Río Puyango, Ecuador. *Rev. Int. Contam. Ambient.* **2016**, *32*, 385–397. [CrossRef]
23. Delgado, J.; Ayala, D.; Páez, H. Sistema de Tratamiento Para Mejorar La Calidad de Aguas de Drenaje de Pasivos Ambientales Mineros En La Cuenca Del Río Puyango (Ecuador). *Soc. Geológica España* **2018**, *64*, 63–66.
24. Peña-Carpio, E.; Menéndez-Aguado, J.M. Environmental Study of Gold Mining Tailings in the Ponce Enriquez Mining Area (Ecuador). *DYNA* **2016**, *83*, 237–245. [CrossRef]
25. Salgado-Almeida, B.; Falquez-Torres, D.A.; Romero-Crespo, P.L.; Valverde-Armas, P.E.; Guzmán-Martínez, F.; Jiménez-Oyola, S. Risk Assessment of Mining Environmental Liabilities for Their Categorization and Prioritization in Gold-Mining Areas of Ecuador. *Sustainability* **2022**, *14*, 6089. [CrossRef]
26. Betancourt, O.; Narváez, A.; Roulet, M. Small-Scale Gold Mining in the Puyango River Basin, Southern Ecuador: A Study of Environmental Impacts AndHuman Exposures. *Ecohealth* **2005**, *2*, 323–332. [CrossRef]
27. INHAMI. Instituto Nacional de Meteorología e Hidrología | Ecuador. Available online: https://inamhi.wixsite.com/inamhi/novedades (accessed on 2 February 2022).
28. Oviedo-Anchundia, R.; Moína-Quimí, E.; Naranjo-Morán, J.; Barcos-Arias, M. Contaminación por metales pesados en el sur del Ecuador asociada a la actividad minera. *Bionatura* **2017**, *2*, 437–441. [CrossRef]
29. Carling, G.T.; Diaz, X.; Ponce, M.; Perez, L.; Nasimba, L.; Pazmino, E.; Rudd, A.; Merugu, S.; Fernandez, D.P.; Gale, B.K.; et al. Particulate and Dissolved Trace Element Concentrations in Three Southern Ecuador Rivers Impacted by Artisanal Gold Mining. *Water. Air. Soil Pollut.* **2013**, *224*, 1415. [CrossRef]
30. Smith, K.S.; Ramsey, C.A.; Hageman, P.L. Sampling Strategy for the Rapid Screening of Mine-Waste Dumps on Abandoned Mine Lands. In *Fifth. International Conference on Acid Rock Drainage*; USGS: Denver, CO, USA, 2000; 9p.
31. *ASTM D1140-17*; Standard Test Methods for Determining the Amount of Material Finer than 75-µm (No. 200) Sieve in Soils by Washing. ASTM International: West Conshohocken, PA, USA, 2017. Available online: https://www.astm.org/d1140-17.html (accessed on 11 March 2024).
32. *ASTM D422-63(2007)*; Standard Test Method for Particle-Size Analysis of Soils. American Society for Testing and Materials Standards: West Conshohocken, PA, USA, 2002. Available online: https://www3.epa.gov/hudson/pdf/sedc_2004-2005_append.pdf (accessed on 21 June 2023).
33. Meier, A.L.; Grimes, D.J.; Ficklin, W.H. Inductively Coupled Plasma–Mass Spectrometry: A Powerful Tool for Mineral Resource and Environmental Studies. In *USGS Research on Mineral Resources*; Carter, L., Toth, M.I., Day, W.C., Eds.; U.S. Geological Survey: Reston, VA, USA, 1994; pp. 67–68. [CrossRef]
34. Kurita, T. *Principal Component Analysis (PCA) BT—Computer Vision: A Reference Guide*; Springer International Publishing: Cham, Switerland, 2020; pp. 1–4. [CrossRef]
35. Arranz-González, J.C.; Guzmán-Martínez, F.; Tapia-Téllez, A.; Jiménez-Oyola, S.; García-Martínez, M.J. Polluting Potential from Mining Wastes: Proposal for Application a Global Contamination Index. *Environ. Monit. Assess.* **2022**, *194*, 792. [CrossRef] [PubMed]
36. del Campo, A.; Arranz-González, J.; Rodríguez-Gómez, V.; Vadillo, L.; Rodríguez, V.; Fernández, F. *Manual Para La Evaluación de Riesgos de Instalaciones de Residuos de Industrias Extractivas Cerradas o Abandonadas*, 1st ed.; Ministerio de Agricultura, Alimentación y Medio Ambiente España, Instituto Geológico y Minero de España: Madrid, Spain, 2014.
37. Kabata-Pendias, A. *Trace Elements in Soils and Plants: Fourth Edition*, 4th ed.; CRC Press: Boca Raton, FL, USA, 2010. [CrossRef]

38. Hageman, P.L. US Geological Survey Field Leach Test for Assessing Water Reactivity and Leaching Potential of Mine Wastes, Soils, and Other Geologic and Environmental Materials. *Geol. Surv. Tech. Methods B* **2007**, *5*, 14.
39. Gascón, R.C.; Soto, M.C.; Oblasser, A.; Calderón-Rosas, C.; Hoppe, J.; Farfán-Salazar, N.; Lavín, C.; Cruz, C.V.; Jorquera, J.R.; Guala, J.C.; et al. *Methodological Guide for the Chemical Stability of Mining Works and Facilities*; SERNAGEOMIN: Santiago, Chile, 2015.
40. Lemos, M.; Valente, T.; Marinho Reis, P.; Fonseca, R.; Delbem, I.; Ventura, J.; Magalhães, M. Mineralogical and Geochemical Characterization of Gold Mining Tailings and Their Potential to Generate Acid Mine Drainage (Minas Gerais, Brazil). *Minerals* **2021**, *11*, 39. [CrossRef]
41. Ramírez Morandé, N.A. *Guía Técnica de Operación y Control de Depósitos de Relaves*, National Geology and Mining Service: Santiago, Chile, December 2007.
42. TULSMA. *Texto Unificado de Legislación Secundaria Medio Ambiental. Ministerio de Ambiente de Ecuador*, TULSMA: Quito, Ecuador, March 2015.
43. Appleton, J.D.; Williams, T.M.; Orbea, H.; Carrasco, M. Fluvial Contamination Associated with Artisanal Gold Mining in the Ponce Enríquez, Portovelo-Zaruma and Nambija Areas, Ecuador. *Water. Air. Soil Pollut.* **2001**, *131*, 19–39. [CrossRef]
44. Marshall, B.G.; Veiga, M.M.; Kaplan, R.J.; Adler Miserendino, R.; Schudel, G.; Bergquist, B.A.; Guimarães, J.R.D.; Sobral, L.G.S.; Gonzalez-Mueller, C. Evidence of Transboundary Mercury and Other Pollutants in the Puyango-Tumbes River Basin, Ecuador–Peru. *Environ. Sci. Process. Impacts* **2018**, *20*, 632–641. [CrossRef]
45. Cogram, P. Jarosite. In *Reference Module in Earth Systems and Environmental Sciences*; Elsevier: Amsterdam, The Netherlands, 2018; pp. 1–9. [CrossRef]
46. Kirschbaum, A.; Murray, J.; Arnosio, M. Mining Environmental Liabilities in Northwest Argentina: Mineralogical, Geochemical Aspects and Environmental Consequences. *Rev. Mex. Ciencias Geológicas* **2012**, *29*, 248–264.
47. Swayze, G.A.; Desborough, G.A.; Smith, K.S.; Lowers, H.A.; Hammarstrom, J.M.; Diehl, S.F.; Leinz, R.W.; Driscoll, R.L. Chapter B: Understanding Jarosite—From Mine Waste to Mars. In *Understanding Contaminants Associated with Mineral Deposits*; Verplanck, P.L., Ed.; U.S. Geological Survey: Denver, CO, USA, 2008; pp. 8–13.
48. Arranz-González, J.C.; Rodríguez-Gómez, V.; Fernández-Naranjo, F.J.; Vadillo-Fernández, L. Assessment of the Pollution Potential of a Special Case of Abandoned Sulfide Tailings Impoundment in Riotinto Mining District (SW Spain). *Environ. Sci. Pollut. Res.* **2021**, *28*, 14054–14067. [CrossRef] [PubMed]
49. Hammarstrom, J.M.; Seal, R.R.; Meier, A.L.; Kornfeld, J.M. Secondary Sulfate Minerals Associated with Acid Drainage in the Eastern US: Recycling of Metals and Acidity in Surficial Environments. *Chem. Geol.* **2005**, *215*, 407–431. [CrossRef]
50. Dold, B. Evolution of Acid Mine Drainage Formation in Sulphidic Mine Tailings. *Minerals* **2014**, *4*, 621–641. [CrossRef]
51. Pi-Puig, T.; Solé, J.; Cruz, A.G. Mineralogical Study and Genetic Model of Efflorescent Salts and Crusts from Two Abandoned Tailings in the Taxco Mining District, Guerrero (Mexico). *Minerals* **2020**, *10*, 871. [CrossRef]
52. Sasaki, K.; Haga, T.; Hirajima, T.; Kurosawa, K.; Tsunekawa, M. Distribution and Transition of Heavy Metals in Mine Tailing Dumps. *Mater. Trans.* **2002**, *43*, 2778–2783. [CrossRef]
53. Rosario-Beltré, A.J.; Sánchez-España, J.; Rodríguez-Gómez, V.; Fernández-Naranjo, F.J.; Bellido-Martín, E.; Adánez-Sanjuán, P.; Arranz-González, J.C. Critical Raw Materials Recovery Potential from Spanish Mine Wastes: A National-Scale Preliminary Assessment. *J. Clean. Prod.* **2023**, *407*, 137163. [CrossRef]
54. Lemos, M.G.; Valente, T.; Marinho-Reis, A.P.; Fonsceca, R.; Dumont, J.M.; Ferreira, G.M.M.; Delbem, I.D. Geoenvironmental Study of Gold Mining Tailings in a Circular Economy Context: Santa Barbara, Minas Gerais, Brazil. *Mine Water Environ.* **2021**, *40*, 257–269. [CrossRef]
55. Borja, T.; Moreno, J. Estudio Para La Optimización de Un Circuito Flotación- Cianuración de Concentrados Sulfurosos En La Planta de Beneficio La López Para El Procesamiento Del Mineral de La Mina Jerusalén En El Cantón Camilo Ponce Enríquez, Escuela Superior Politécnica del Litoral. 2015. Available online: https://www.dspace.espol.edu.ec/handle/123456789/32270?locale=es (accessed on 20 March 2023).
56. Tepanosyan, G.; Sahakyan, L.; Belyaeva, O.; Asmaryan, S.; Saghatelyan, A. Continuous Impact of Mining Activities on Soil Heavy Metals Levels and Human Health. *Sci. Total Environ.* **2018**, *639*, 900–909. [CrossRef]
57. Romero-Crespo, P.; Jiménez-Oyola, S.; Salgado-Almeida, B.; Zambrano-Anchundia, J.; Goyburo-Chávez, C.; González-Valoys, A.; Higueras, P. Trace Elements in Farmland Soils and Crops, and Probabilistic Health Risk Assessment in Areas Influenced by Mining Activity in Ecuador. *Environ. Geochem. Health* **2023**, *45*, 4549–4563. [CrossRef]
58. González-Valoys, A.C.; Esbrí, J.M.; Campos, J.A.; Arrocha, J.; García-Noguero, E.M.; Monteza-Destro, T.; Martínez, E.; Jiménez-Ballesta, R.; Gutiérrez, E.; Vargas-Lombardo, M.; et al. Ecological and Health Risk Assessments of an Abandoned Gold Mine (Remance, Panama): Complex Scenarios Need a Combination of Indices. *Int. J. Environ. Res. Public Health* **2021**, *18*, 9369. [CrossRef] [PubMed]
59. Chen, R.; Han, L.; Liu, Z.; Zhao, Y.; Zhai, Y.; Li, R.; Xia, L. Analysis of Soil As Pollution and Investigation of Dominant Plants in Abandon Gold Mining Area. *Minerals* **2022**, *12*, 1366. [CrossRef]
60. Wang, Y.; Guo, G.; Zhang, D.; Lei, M. An Integrated Method for Source Apportionment of Heavy Metal(Loid)s in Agricultural Soils and Model Uncertainty Analysis. *Environ. Pollut.* **2021**, *276*, 116666. [CrossRef]
61. Wu, J.; Jia, R.; Xuan, H.; Zhang, D.; Zhang, G.; Xiao, Y. Priority Soil Pollution Management of Contaminated Site Based on Human Health Risk Assessment: A Case Study in Southwest China. *Sustainability* **2022**, *14*, 3663. [CrossRef]

62. Zeng, Q.; Shen, L.; Feng, T.; Hao, R. Investigation of the Distribution of Heavy Metals in the Soil of the Dahuangshan Mining Area of the Southern Junggar Coalfield, Xinjiang, China. *Minerals* **2022**, *12*, 1332. [CrossRef]
63. Uugwanga, M.N.; Kgabi, N.A. Assessment of Metals Pollution in Sediments and Tailings of Klein Aub and Oamites Mine Sites, Namibia. *Environ. Adv.* **2020**, *2*, 100006. [CrossRef]
64. Demková, L.; Jezný, T.; Bobuľská, L. Assessment of Soil Heavy Metal Pollution in a Former Mining Area—Before and after the End of Mining Activities. *Soil Water Res.* **2017**, *12*, 229–236. [CrossRef]
65. Mestanza-Ramón, C.; Ordoñez-Alcivar, R.; Arguello-Guadalupe, C.; Carrera-Silva, K.; D'orio, G.; Straface, S. History, Socioeconomic Problems and Environmental Impacts of Gold Mining in the Andean Region of Ecuador. *Int. J. Environ. Res. Public Health* **2022**, *19*, 1190. [CrossRef]
66. Mestanza-ram, C.; Paz-mena, S.; Carlos, L.; Jimenez-gutierrez, M.; Herrera-morales, G.; Orio, G.D.; Straface, S. History, Current Situation and Challenges of Gold Mining in Ecuador's Litoral Region. *Land* **2021**, *10*, 1220. [CrossRef]
67. Arranz-González, J.; Rodríguez-Gómez, V.; Rodríguez-Pacheco, R.; Fernández-Naranjo, F.J.; Vadillo-Fernández, L.; Alberruche del Campo, E. *Guía Para La Rehabilitación de Instalaciones Abandonadas de Residuos Mineros*; Ministerio para la Transición Ecológica: Madrid, Spain, 2019; p. 620.
68. Butler, L.; Mitchell, P.; Levin, E. *International Review of Environmental Rehabilitation Approaches for Artisanal and Small-Scale Mining. A Review of Best Practices for Frugal Rehabilitation of ASM in Mongolia*; The Asia Foundation: Ulaanbaatar, Mongolia, 2014.