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Analysis of Heavy Metal Contamination in Surface Water Bodies in the Ponce Enriquez Mining District, Ecuador

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Abstract: Artisanal and small-scale mining (ASM) has become increasingly significant in Ecuador, contributing to rural employment and economic stability. However, its environmental consequences, particularly those related to illegal mining and the discharge of untreated waste into water bodies, have raised concerns regarding water quality deterioration. The present study investigates heavy metal contamination in six rivers (Siete, Pagua, Fermín, Villa, Guanache, and 9 de Octubre) within the Ponce Enríquez mining district, where elevated concentrations of heavy metals have been detected. To facilitate the development of effective remediation strategies, an integrated statistical analysis was conducted to elucidate the relationships between pollutants and their potential sources. The methodology encompassed (i) an extensive review of water quality data, (ii) a statistical correlation analysis of predominant heavy metals, and (iii) an evaluation of environmental management approaches. The findings indicate that the Villa, Siete, Fermín, and Guanache rivers exhibit particularly high concentrations of aluminium (Al), iron (Fe), lead (Pb), and zinc (Zn), with contamination levels intensifying during the wet season due to runoff and the influence of the geological composition of the study area. Strong positive correlations ($r>0.8$) were observed between Fe-Pb, Fe-Al, and Pb-Al in both dry and wet seasons, suggesting that mining activities, mineralogical characteristics of the region, and agricultural runoff contribute to heavy metal accumulation. Based on these findings, sustainable remediation techniques are proposed to mitigate contamination and enhance water quality. The implementation of these measures is expected to facilitate the gradual improvement of riverine ecosystems while promoting economic diversification within the Ponce Enríquez mining district.

Keywords: Heavy metal contamination; Artisanal and small-scale mining (ASM); Water quality degradation; Environmental remediation; Statistical correlation; Source identification; Ponce Enríquez mining district

1. Introduction

In low and middle income countries with great potential for mineral resources, the mining industry contributes significantly to the economic development of a territory (Ericsson & Löf, 2019). These minerals (gold, silver, copper, among others) are extracted on a large, small, or artisanal scale in approximately 168 countries (Morante-Carballo et al., 2022). ASM is an important source of income for rural sectors, where economic income alternatives are extremely limited (Verbrugge & Geenen, 2019). These activities generally lack standards to ensure health and safety, are labor-intensive, and have a significant environmental impact (Upadhyay et al., 2021).

Increased mining activities have released large amounts of unwanted toxic pollutants into the environment (Etteieb et al., 2020). Some elements (e.g., Cadmium-Cd, Chromium-Cr, Arsenic-As, Lead-Pb, Copper-Cu, Zinc-Zn, and Nickel-Ni) are classified as priority pollutants by the United States Environmental Protection Agency (USEPA) because of their effects on the environment and human health by entering media such as water or soil (Zerizghi et al., 2022). The decrease in pH and the formation of silicates, carbonates, and sulfides favor the leaching of heavy metals, causing environmental liabilities (e.g. Acid Mine Drainage (AMD) generation) (Guzmán-Martínez et al., 2020).

Pollution inevitably occurs during the extraction of mineral resources, and AMD is one of the most critical challenges in the global mining industry (Yang et al., 2022). AMD is mainly caused by sulfide oxidation during certain mining activities (Ighalo et al., 2022). Over the past decades, researchers have attempted to remediate AMD by decreasing acidity levels and removing metal ions to reduce its impact on the environment and human health (Magowo et al., 2020). For a correct analysis and the proposed solution, it is necessary to consider the identification and characterization of contamination sources (e.g. water or soil). This makes it possible to recognize the pollutants present and their composition in the environment (Jasmi & Hassan, 2024).

Water quality indices are mathematical mechanisms that summarize water data and results at different levels (e.g. physicochemical parameter measurements (Khadija et al., 2021)). A correlation or multivariate analysis of the assessed parameters generates crucial monitoring, which allows the long-term effects on water bodies to be analyzed (Amar et al., 2020; Chai et al., 2023). In recent years, multivariate statistical analysis has been among the most widely used methods for water quality assessment and environmental pollution analysis (Mokarram et al., 2020). Shrestha & Kazama (2007) in the Fuji River basin, Japan, and Zhang et al. (2009) in the Daliao River basin, China, used principal component analysis (PCA) to reduce the number of parameters for assessing water quality.

The quality of surface waters is becoming a serious concern worldwide, as they constitute the most crucial resource for subsistence (Kumar et al., 2020). Contamination by heavy metals causes serious health problems, disrupts the food chain, and disturbs biodiversity (Vasistha & Ganguly, 2020). Some metals (such as Mn, Zn, Cu, and Co) are necessary for human body function. In contrast, others (such as Cd, Pb, Ni, Cr, and As) are considered poisonous or non-essential, and contribute to numerous human health risks (e.g., damage to the central nervous function, cardiovascular and gastrointestinal systems, lungs, kidneys, liver, endocrine glands, and bones) (Ahmad et al., 2021; Hussain et al., 2019; Sankhla et al., 2016). Likewise, there are metals (e.g., Cd and Cu) that are easily absorbed by some plantations (e.g., cocoa (Engbersen et al., 2019)), which can cause toxic effects on the plant (no essential metabolic function) and have toxic traces in the human consumption chain (Chavez et al., 2015).

Latin America is historically linked to the mining industry and the exploitation of raw materials, being one of the economic pillars in colonial and modern times, and Ecuador is one of the leading countries where the economy is closely dependent on mining (Mestanza-Ramón et al., 2021). In Ecuador, gold and silver mining activities originated before the conquest (activities carried out by the Incas) (Rivera-Parra et al., 2021). Mining activities in Ecuador are currently administered by the Mining Regulation and Control Agency (ARCOM, by its acronym in Spanish) and the Electricity Regulation and Control Agency (ARCONEL, by its acronym in Spanish). The increase in mining activity in the Ecuadorian gold sector has brought natural resources under scrutiny in academic and social areas (Adler Miserendino et al., 2013). There is evidence of mining in multiple regions of Ecuador, including Nambija (Zamora) (González-Vásquez et al., 2023), Zaruma-Portovelo mining district (El Oro) (Carrión Mero et al., 2019), Buenos Aires (Imbabura) (Luzuriaga-Torres et al., 2022), Mira (Carchi) (Mestanza-Ramón et al., 2022), or Ponce Enríquez (Azuay) (Mestanza-Ramón et al., 2023).

The area of this study is the municipality of Camilo Ponce Enríquez, located to the west of the Andean province of Azuay. It borders the Guayas and El Oro provinces with an approximate area of 106 km^2 (Figure 1). Its population is approximately 22,000 (INEC, 2023), and its main activities are mining, quarrying, and other related activities (e.g., public administration, commerce, construction, and transportation). For this reason, this municipality is one of the leading mining districts in Ecuador. Approximately 5% of the population participates in activities such as agriculture, livestock, and forestry, which are all affected by the increasing pollution of the rivers that flow through this municipality.

The Ponce Enriquez mining district presents colluvial and alluvial deposits from the Quaternary, which show a lithology of sand, gravel, silt, and clay. These are overlain by Cretaceous geological formations such as the Pallatanga Unit, which corresponds to an ophiolitic association and is composed of a sequence of oceanic basalts, microgabbros, sandstones, peridotites, and tuffs (Calderón et al., 2023).

Historically, rivers that run through Ponce Enríquez (e.g., Siete, Fermín, Villa, Margarita, and Estero Guanache) present contamination in their waters and sediments, according to the Ecuadorian environmental regulations (Unified Text of Secondary Legislation of the Environmental Ministry-TULSMA). Regarding the water environment (rivers), several studies (e.g., Appleton et al. (2001), Carling et al. (2013), Jiménez-Oyola et al. (2021)) reported the presence of toxic elements, mainly due to anthropogenic activities in this area (mining and wastewater discharge).

In current research by Almeida-Guerra et al. (2023), field studies conducted at 29 sites on the rivers Siete, Fermín, Villa, Guanache, 9 de Octubre and Pagua, found that these freshwater sources present high concentrations of heavy metals such as Al, Cd, Cu, Fe, Pb, and Zn (Figure 1). The selection of the study area was determined by the following: i) the mining area of Ponce Enríquez is one of the mining districts with the highest metal extraction activity in Ecuador (Rivera-Parra et al., 2021), ii) from bibliographic references, it is known that it is an area where its rivers are highly affected by mining and other anthropic activities (e.g., agriculture) (Ramos et al., 2022; Salgado-Almeida et al., 2022), iii) the proximity of the Ponce Enriquez mining district to the geographical location of the ESPOL Polytechnic University, where the water quality data were processed (almost three hours by car); and iv) there was a mine opening within the study area that allowed water sampling, in addition to learning about its mining processes and activities.

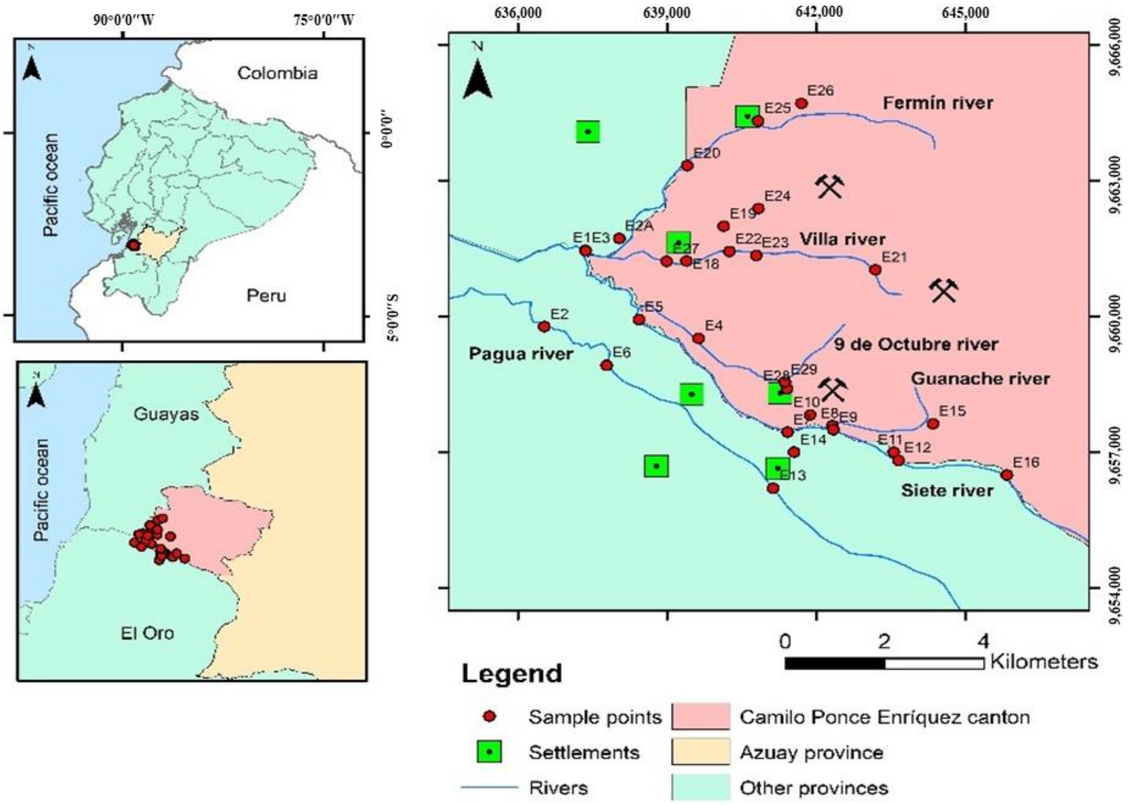


Figure 1. Geographical location of the Camilo Ponce Enríquez canton, with respect to the Azuay province, and the location of the water samples taken in the rivers by Almeida-Guerra et al. (2023)

Therefore, it is necessary to know the statistical correlation between the primary pollutants to propose strategies or suggestions that will allow decision-makers to reduce the current environmental damage. For instance, what contamination patterns are detected in surface waters, considering their origin? This study analyzes the heavy metal contamination of six rivers in the Ponce Enriquez mining district by correlating the primary pollutants present in the water bodies using non-parametric statistical approaches to understand the possible sources of contamination and enable decision-makers to implement environmental mitigation strategies.

2. Materials and Methods

This study proposes a non-parametric correlation between the pollutants detected in water samples taken from three rivers in the Ponce Enriquez canton (Spearman and PCA). These analyses were carried out during the wet and dry seasons to determine the level of relationship between the pollutants and discuss their possible origin and formation for environmental decision-making.

Figure 2 presents the outline and methodology followed by the authors: i) literature review of activities within the study area, ii) statistical correlation between the primary heavy metals found in the samples, and iii) approach to environmental strategies.

2.1 Baseline Data Analysis of the Study Area

A review of publications on the study area (e.g., scientific articles, conference papers, and graduate and postgraduate theses) revealed studies on a variety of relevant topics in the municipality of Ponce Enriquez, including an assessment of risk to human health due to heavy metals (e.g., Jiménez-Oyola et al. (2021)), risk assessment of contamination in water and soil resources (e.g., Salgado-Almeida et al. (2022)), effects on crops in the municipality (e.g., Ramos et al. (2022)), geochemical and isotopic characterization of surface water (Romero et al. (2012)), and remediation techniques in water or soil (e.g., Fernández Vélez (2022)).

The statistical analysis performed in this study is based on the data and results obtained by Almeida-Guerra et al. (2023), specifically the metals detected in high concentrations (Al, Cd, Cu, Fe, Pb and Zn) in 29 water samples (Figure 1) taken in two different seasons (dry and wet) in the Ponce Enriquez rivers. The samples taken in two different seasons of the year were essential to check the variability in the concentration of heavy metals in the rivers (due to seasonal differences in river flows). Seven samples were collected from the Siete River, three from the Pagua River, six from the Fermín River, seven from the Villa River, three from the Guanache River, and three from the Nine de Octubre River. Samples were taken at the locations shown in Figure 1 because of the openness of the mining concessions for this research and accessibility along the six rivers selected for this case study.

Field water samples were collected in 100 ml plastic containers, in triplicate at each sampling point, and stored in coolers for preservation until arrival at the laboratory. Within the laboratory, each (100 ml) sample was subdivided into a 30 ml filtered sample (using 0.45 µm Millipore™ cellulose syringe) and a 30 ml unfiltered sample. Both samples were preserved using 2% v/v HNO_3 for heavy metal analysis at the University of Colorado Laboratory (Boulder, Colorado, USA).

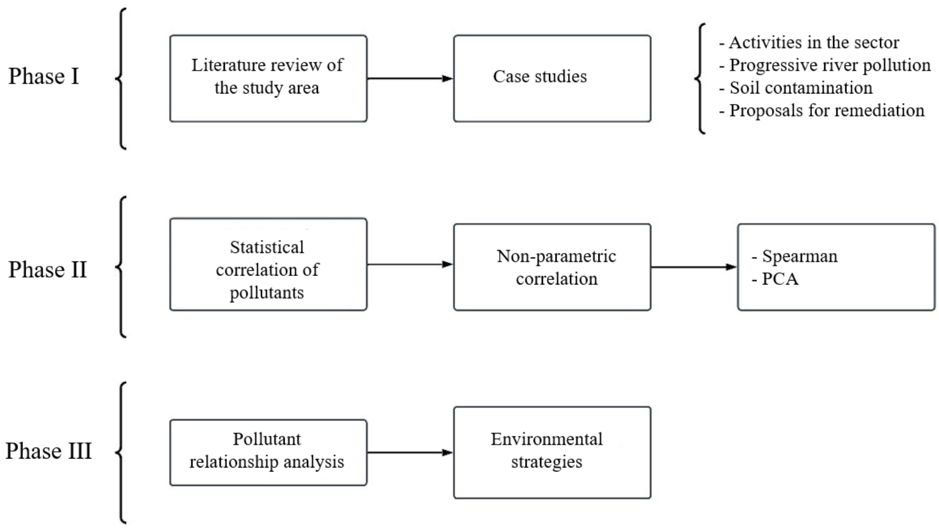


Figure 2. Three-phase methodological framework followed in this research

2.2 Statistical Correlation of Pollutants

In the second phase of the statistical analysis, a flat file (CSV) containing concentration data for the six heavy metals considered in this research (Al, Cd, Zn, Cu, Fe, and Pb) was used. Statistical analysis allowed the evaluation of the degree of correlation among the six primary pollutants (Al, Cd, Zn, Cu, Fe, and Pb) in surface water during the dry and wet seasons in the study area. Parametric tests, such as Shapiro, were used to verify data normality, with a significance level greater than 0.05 (Mohanraj et al., 2022). Due to the data distribution in this study, non-parametric samples were analyzed using the Wilcoxon-Mann-Whitney test (HongE et al., 2022). Correlation analysis among pollutants was performed using the non-parametric Spearman's correlation coefficient, with a probability of less than 0.05 (significant correlation), to establish the relationship between pollutants. Very high correlations between pollutants were considered with $r>0.8$ (Gupta et al., 2022), 0.60-0.79 (high), 0.40-0.59 (moderate), and 0.20-0.39 (weak) (Navada et al., 2021). Subsequently, PCA was used to analyze the distribution, relationship, and possible source of contamination between heavy metals (Rao et al., 2021). The proposed statistics were performed using the statistical program RStudio version R-4.1.2, using custom codes and program libraries.

Once the results of the statistical correlation between the pollutant concentration data (Al, Cd, Cu, Fe, Pb, and Zn) were obtained, analysis of the results and comparison with other studies was used to determine the relationship between pollutants (e.g., if by origin or by reactions due to contact with the environment).

2.3 Environmental Strategies Proposal

Finally, environmental impact identification and assessment were conducted using the Integrated Relevant

Criteria (IRC) methodology (Morante-Carballo et al., 2024). In Table 1, the positive and negative aspects are evaluated and rated according to the severity of their impact on the environment. In addition, environmental remediation strategies have been proposed for the case of contamination in the water bodies studied using the Strengths, Weaknesses, Opportunities, and Threats (SWOT) analysis (Benzaghta et al., 2021) of the mining activity in the Ponce Enriquez area. This analysis was conducted through the intervention and compilation of the opinions of the authors of this research. This allows decision-makers to have a reality check on water quality because of various activities around these water bodies.

Table 1. Environmental assessment with CRI methodology, through impact relevance

Qualification	Abbreviation	Relevance	Observation
Compliance	C	Positive aspect Not relevant	No remediation measures are necessary
Non-compliance	NC	Slightly significant	
Non-compliance (minor)	NC-	Moderately significant Highly significant	These activities should include monitoring and remediation plans
Non-compliance (major)	NC+	Very highly significant	

3. Results

3.1 Water Quality Status of Rivers

Within the analysis of historical results, we reviewed publications in the study area, where water samples were collected from the rivers of the study area. The following publications stand out.

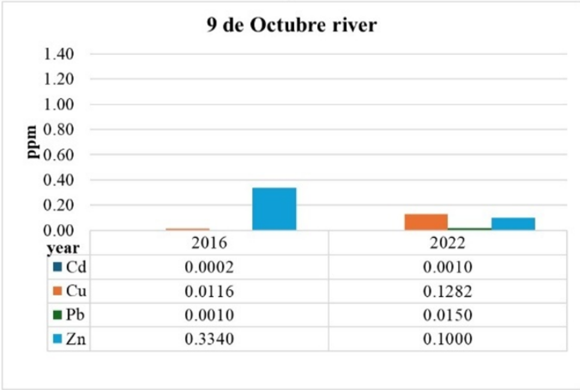
- 23 surface water samples were collected from the Siete, Margarita, Guanache, and Tenguel rivers in July 1996. Thirty milliliters of each sample were filtered through 0.45 μm Millipore™ cellulose acetate membranes (Appleton et al., 2001).
- In 2018, 13 water samples were taken from the Siete River. The samples were acidified with nitric acid and refrigerated until the analysis (Escobar-Segovia et al., 2021).
- 21 surface water samples were collected in September 2018. As, Cd, Cr, Cu, Ni, Pb, and Zn concentrations were analyzed in samples collected from rivers and streams used for recreational purposes. Water samples were acidified with nitric acid and refrigerated until analysis (Jiménez-Oyola et al., 2021).
- 18 water samples were collected from Guanache, Villa, Fermín, 9 de Octubre, Siete, and Tenguel. Sampling was carried out in May 2022, and the samples were stored in plastic bottles (Villamar Marazita et al., 2023).

The sampling methods used by the aforementioned authors are characterized by their standardized methodology (in terms of sampling, preservation, and sample transport), which was also applied during the research carried out in the present study. In addition, a higher number of samples (29) were taken in the present study than those analyzed in previous publications.

Figure 3 presents the results of historical heavy metal tests carried out on surface water samples in Siete, Fermín, Villa, and 9 de Octubre between 1996 and 2022. The levels of heavy metal contaminants have varied over time, as in the case of Pb (no presence in 1996 and 0.1543 ppm in 2018) and Cu (7.277 ppm in 1996 to 0.1282 ppm in 2022) in the Siete River, and in the 9 de Octubre and Fermín rivers, which have increased in Cd (2016: 0.0002 ppm, 2022: 0.001 ppm) and Cu (2016: 0.0116 ppm, 2022: 0.0150 ppm). This increase could be due to the rise in illegal mining and the expansion of agricultural areas in the Ponce Enriquez Mining District.

(a) (b)

(c)



(d)

Figure 3. Heavy metal analyses conducted in 1996 (Appleton et al., 2001), 2016 (Almeida-Guerra et al., 2023), 2017 (Sierra et al., 2017), 2018 (Escobar-Segovia et al., 2021; Jiménez-Oyola et al., 2021), and 2022 (Villamar Marazita et al., 2023); taken from various points in the rivers: (a) Siete; (b) Fermín; (c) Villa; and (d) 9 de Octubre

3.1.1 Water quality in rivers case study

The quality of 29 water samples taken from the rivers Siete, Pagua, Fermín, Villa, Guanache, and 9 de Octubre (Ponce Enríquez canton) were analysed during the dry and wet seasons (Figure 1). Table 2 presents a summary of the maximum results obtained in the analysis of six primary heavy metals (Al, Cd, Cu, Fe, Pb, and Zn), compared with the limit of the Ecuadorian standard (TULSMA) for environmental quality and effluent discharge for the preservation of flora and fauna in freshwater.

Table 2. Analysis of the maximum results of heavy metal tests in the Siete, Fermín, Villa, Guanache, 9 de Octubre y Pagua rivers in the municipality of Ponce Enríquez

Heavy Metals (ppm)		Sampled Rivers					
		Siete	**Fermin**	**Villa**	**Guanache**	**9 de Octubre**	**Pagua**
Dry season	pH	7.4600	7.3600	7.3100	5.7200	5.7000	7.1900
	Aluminum (Al)	2.9551	2.1500	3.6720	8.0883	0.6215	0.1168
	Cadmium (Cd)	0.0004	0.0005	0.0030	0.0011	0.0003	0.0002
	Copper (Cu)	0.1328	0.2050	1.2380	0.6046	0.0174	0.0049
	Iron (Fe)	19.7096	10.4120	9.6150	51.5734	0.9938	0.2054
	Lead (Pb)	0.0600	0.0300	0.0050	0.01770	0.0073	0.0018
	Zinc (Zn)	0.0921	0.0670	0.2240	0.09380	0.0412	0.0575
Wet season	pH	7.0500	7.4000	7.3900	7.6000	7.2600	7.4000
	Aluminum (Al)	11.5834	5.1783	2.9682	6.8312	0.5428	0.2442
	Cadmium (Cd)	0.0017	0.0006	0.0015	0.0015	0.0002	0.0001
	Copper (Cu)	0.2622	0.0894	0.8923	0.7662	0.0116	0.0082
	Iron (Fe)	46.4124	27.4733	7.9178	28.3185	0.9446	0.3792
	Lead (Pb)	0.0964	0.0300	0.0033	0.0659	0.0010	0.0003
	Zinc (Zn)	0.3994	0.0938	0.1803	0.1886	0.3344	0.0329

Note: Permissible TULSMA water quality limits for the preservation of flora and fauna in fresh waters (pH: 5-9; Al: 0.1 ppm; Cd: 0.001 ppm; Cu: 0.02 ppm; Fe: 0.3 ppm; Pb: 0.05 ppm; Zn: 0.18 ppm).

The data in Tables 1 and 2 indicate that the 9 de Octubre and Pagua were the least polluted rivers based on the heavy metal analyzed. Iron contamination occurred in four rivers (Siete, Fermín, Villa, and Guanache). The Siete River has a higher concentration of heavy metals (such as aluminum, iron, and lead) in the wet season than in the dry season, whereas the Fermin River has a higher concentration of aluminum and iron, and the Guanache River has a higher concentration of lead. This may be due to the transport of pollutants by runoff formed during the wet season from the mining sites to rivers or cultivated areas (Romero-Crespo et al., 2023). It is also possible that river sediments that contain these pollutants may be diluted or separated into exchangeable parts because of the pH level of the water (Equeenuddin et al., 2013).

3.2 Correlation Among Heavy Metal Content of the Study Area

There were highly significant correlations among the heavy metal contents within rivers in the study area. Figure 4 shows potentially associated pollutants (r>0.8). Fe and Al have the strongest relationship with the different pollutants (e.g., Pb) in the rivers during the two seasons (dry and wet). Fe content in the rivers was positively and significantly correlated with Pb content in both seasons. Similarly, Zn content showed highly positive and significant correlations with both Cu content in the dry season (subgraph (a) of Figure 4) and Cd content in the wet season (subgraph (b) of Figure 4). In addition, there was a moderately significant relationship between Cd and Cu contents during the dry and wet seasons. In gold and polymetallic mining in Ponce Enriquez, the processing of sulfide ores generates acid drainage and leachates rich in Cu and Cd. In agricultural areas near rivers, fertilizers and pesticides containing copper (Cu) are used as a fungicide (Romero-Crespo et al., 2023). In addition, higher concentrations of Cd and Cu in the dry season may be due to wastewater discharge from villages near the rivers and poor solid waste management in the sector (especially plastics and batteries) (Mekonnen et al., 2020).

The positive correlation between these pollutants is typical of an environmental pollution source that has geological, industrial, or anthropogenic impacts. In addition, the microorganisms in the system influence the pollution process. The correlations between Al-Fe, Al-Pb, and Pb-Fe were the highest among all the heavy metals analyzed. During the rainy season, increased river flow causes soil erosion and entrainment of particles from the geological substrate, many of which contain Fe, Al, and Pb. During the dry season, some heavy metals are trapped in river sediments, whereas in the rainy season, increased water velocity can suspend these sediments and release the metals into the water (Paz-Barzola et al., 2022). The flow in the rivers of the study area varies from approximately 2.05 m^3/s (in the wet season) to 0.28 m^3/s (in the dry season) (Valverde-Armas & Galarza-Romero, 2012). Mining activities generate tailings deposits and waste dumps that can release heavy metals into water bodies when receiving heavy rainfall.

In contrast, the river water samples showed a relatively normal pH in both seasons ($3.3<pH<7.6$). The pH values had low positive correlations with all the pollutants ($r<0.45$) which means that pH does not play a significant role in the concentration of these heavy metals. Higher pH values are typically associated with heavy metal ions forming precipitates or complexes with other substances.

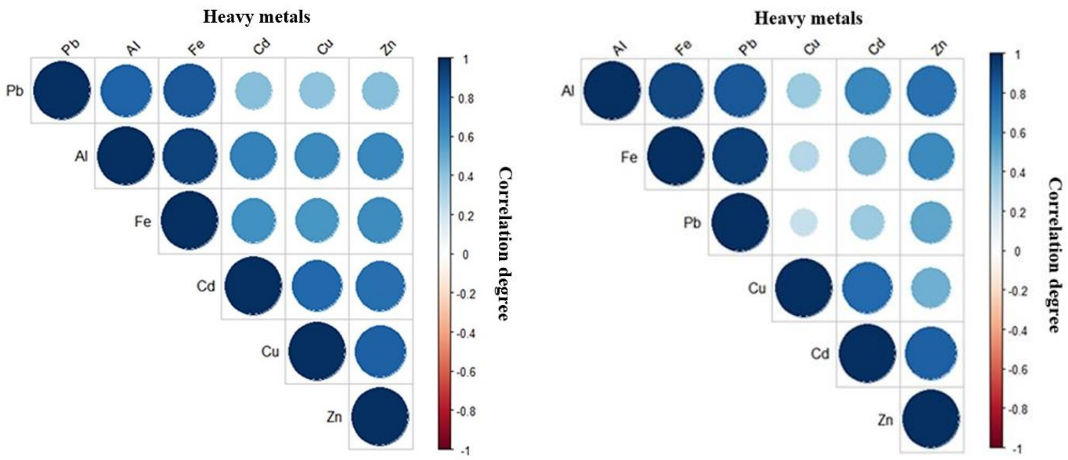


Figure 4. Correlation analysis between pollutants: (a) Dry season correlation; (b) Wet season correlation
Note: Aluminum (Al), Cadmium (Cd), Copper (Cu), Iron (Fe), Lead (Pb), Zinc (Zn)

3.3 Interpreting Pollution Sources

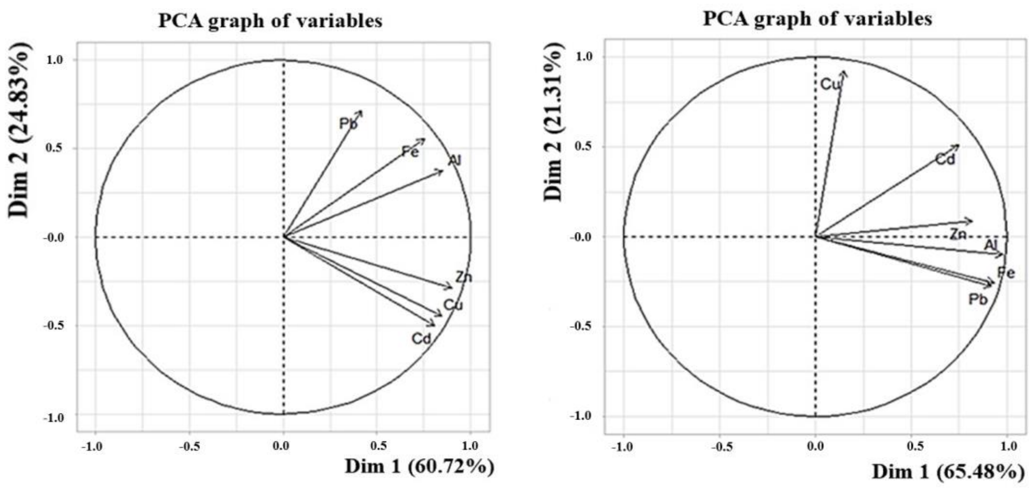
PCA was used to analyze the possible sources of heavy metal contamination. Table 3 shows the most significant factors (aka Dimensions or Dims) that are descriptive of the total variance in pollutant concentrations, i.e., those with eigenvalues greater than 1. During the dry season, 85.55% of the variance in the samples was explained by two fundamental factors. Similarly, 86.79% of the variance of pollutants can be represented by two critical factors for the wet season.

Table 3. Importance of the main components in dry and wet season

Season	Statistics	Dim 1	Dim 2	Dim 3	Dim 4	Dim 5	Dim 6
Dry	Variance	3.64	1.49	0.56	0.16	0.09	0.05
	Variance (%)	60.72	24.83	9.39	2.70	1.48	0.89
	Cumulative %	60.72	85.55	94.93	97.63	99.11	100.00
Wet	Variance	3.93	1.28	0.47	0.26	0.05	0.02
	Variance (%)	65.48	21.31	7.87	4.28	0.81	0.26
	Cumulative %	65.48	86.79	94.66	98.94	99.74	100.00

3.3.1 Dry season

Factor 1 (Dim 1), which accounted for 60.72% of the variance in the data, was highly associated with the concentration of the contaminants Zn, Cu, and Cd. These contaminants explain similar sources of contamination and are related to gold mining activities and the auriferous geology-mineralisation of the study area (corresponding to pyrrhotite, arsenopyrite, and chalcopyrite as the most common minerals (Paz-Barzola et al., 2022; Salgado-Almeida et al., 2022)). Factor 2 (Dim 2) explained 24.83% of the total variance, indicating sources of contamination other than factor 1 associated with Pb, Fe, and Al (subgraph (a) of Figure 5). Pb is usually present in gold and silver mining activities, as mercury (Hg) is used in the mineral extraction process (inappropriate use of Hg in amalgamation releases contaminants such as Pb) (Ramos et al., 2022). Meanwhile, the presence of Fe and Al is abundant in the soil and rock of the study area (geology), increasing their concentration depending on the volumes extracted during mining activities in the area (mines or quarries) (Villamar Marazita et al., 2023). The high concentrations of these pollutants are possibly associated with the generation of acid drainage or tailings from mines located along the studied rivers (Marcillo Guillen, 2023).



(a) (b)

Figure 5. Heavy metal concentrations chart: (a) Dry season pollutants; (b) Wet season pollutants

3.3.2 Wet season

During the wet season, two factors explained 86.79% of the total variance in pollutants (subgraph (b) of Figure 5). Factor 1 explains 65.48% of the variance between Fe, Pb, Al and Zn concentrations. This was mainly due to the contamination of rainwater and the activities of the mining and agricultural sectors in the municipality of Camilo Ponce Enriquez. Heavy rainfall causes erosion of soils, mine dumps, and tailings, moving Fe, Al, Pb, and Zn-rich particles into rivers (oxidation of metal sulfides such as galena (PbS), sphalerite (ZnS), and pyrite (FeS_2)) (Peña Carpio & Menendez-Aguado, 2016). In addition, rain-eroded agricultural soils may contain trace amounts of Zn and Pb from fertilizers and pesticides (Romero-Crespo et al., 2023).

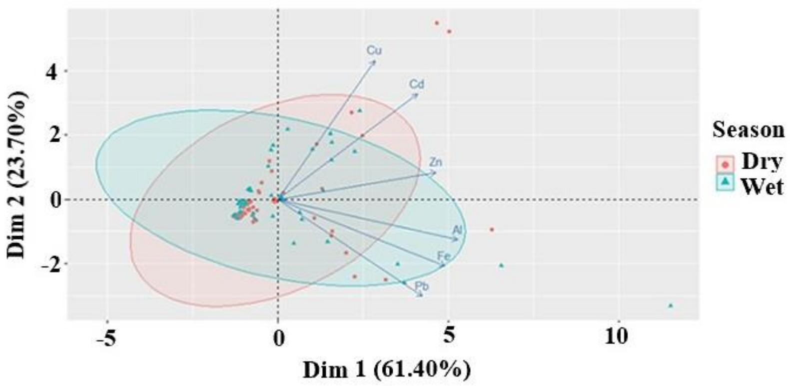


Figure 6. Biplot for ACP loadings of heavy metals in the dry and wet seasons

Additionally, Factor 2 accounted for 21.31% of the total variation. The heavy metals Cu and Cd suggest sources of contamination other than Factor 1 in the wet season, which is associated with illegal mining in the rivers (e.g., Guanache). Surface runoff mobilizes soil particles, tailings, and mining debris rich in Cu and Cd (sulfide minerals such as chalcopyrite $CuFeS_2$) (Jiménez-Oyola et al., 2021).

Figure 6 shows the concentrations and Global Warming Potential (GWP) scores of pollutants in the two clusters associated with the dry and wet seasons. The intersection of the clusters indicates the highest concentration of pollutants in both seasons in the study area.

3.4 Environmental Strategies

The authors conducted an environmental impact assessment, analysing different physical, biodiversity, and socio-economic aspects affected by various sources of contamination (Table 4). As observed in Section 3.3 (Interpretation of pollution sources), water is one of the most contaminated media due to sources such as tailings deposits, geology of the study sector, and mineral processing plants. In addition, the importance of mining sources within the socio-economic impact is highlighted, as the Ponce Enriquez community has an ancient mining history (mining district). Another factor that is highlighted is the serious situation of insecurity within the mining district owing to criminal groups and growing illegal mining.

Table 4. Results of the environmental assessment carried out between the activities within the river path and the environmental parameters

Parameters		**Tailing Deposit**	**Minerology**	**Activities Mineral Processing Plant**	**Insecurity**	**Infrastructure**
Physical	Air	Slightly significant	Not relevant	Slightly significant	Not relevant	Not relevant
	Soil	Slightly significant	Slightly significant	Slightly significant	Not relevant	Not relevant
	Water	Moderately significant	Moderately significant	Moderately significant	Not relevant	Not relevant
Biodiversity	Flora	Slightly significant	Not relevant	Slightly significant	Not relevant	Not relevant
	Fauna	Slightly significant	Not relevant	Slightly significant	Not relevant	Not relevant
Socioeconomic	Economic	Positive impact	Positive impact	Positive impact	Moderately significant	Positive impact
	Social	Slightly significant	Slightly significant	Slightly significant	Moderately significant	Positive impact

Table 5. SWOT matrix analysis of mining in Ponce Enriquez

Strengths	**Opportunities**
1. The Ponce Enriquez Mining District has a wide range of mineral resources. 2. Ponce Enriquez, as well as surrounding communities, enjoys the benefits of mining-related employment or commerce. 3. Ponce Enriquez is a large mining industry owing to its long and extensive mining history. 4. The existence of a road network and access to essential services for mining operations.	1. Implementing new and modern mining technologies would improve the efficiency of production and extraction and reduce environmental impact. 2. Improved mining infrastructure within quarries or mines (e.g., occupational health and safety). 3. Attraction to foreign investment in economic development and new business opportunities in the region. 4. Various studies and university projects have been conducted to identify sustainable mining techniques and practices.
Weaknesses	**Threats**
a) Mining causes adverse environmental effects (e.g. contamination of water sources, soil degradation, and contamination). b) Risks to human health due to exposure to toxic substances from mining activities. c) The populations are economically dependent on mining activities. d) The economically active population of Ponce Enriquez changed its work activity (e.g., from agriculture to mining).	a) Restrictions on mining activities owing to changes in environmental regulations. b) Socioeconomic impact of changes in mineral resource prices. c) Current insecurity (e.g., criminal gangs) may generate social conflict, affecting the economic activity of the sector. d) The operation and logistics of the mining industry are affected by wet seasons (e.g., destruction of road networks and flooding of rivers). e) Presence of illegal mining in different areas of Ponce Enriquez.

Table 6. Proposed environmental strategies and guidelines for their implementation

Environmental Strategies	Guidelines	Cases
Use new and modern technologies in mining activities to improve the efficiency of the production and extraction of mineral resources. This will reduce or minimize exposure to and contamination of environmental media (e.g., water and soil), which affects the health and activities of the population (e.g., agriculture) and other living organisms (e.g., animals and plants).	a. Initial diagnosis The initial environmental status of the mining concessions in Ponce Enriquez should be assessed to identify the current processing systems and technologies. b. Technical and economic evaluation c. Implementation strategies The Ministry of Environment, Water, and Ecological Transition (MAATE) and other ministries that oversee mining issues will promote the adoption of environmental impact reduction technologies.	• Automation and digital mining (Autonomous mining, remote sensing and monitoring, and artificial intelligence) (Brzychczy et al., 2025) • Mine Water Management and Treatment (Reverse osmosis and Nanofiltration, Biological reactors, and Constructed wetlands) (Kianoush et al., 2024) • Tailings Management (Filtered and dry tailings, Tailings reclamation and Recycling, and Predictive geochemistry)
Implement passive and active treatment systems to reduce acidity and remove heavy metals from the rivers of the Ponce Enriquez mining district, allowing for ecological restoration and the application of control measures and management of contaminating sources.	a. Diagnosis and characterization of water sources. b. Selection and implementation of treatment technologies. c. Monitoring and evaluation of pollutant sources d. Community participation and environmental education	• Passive (Low Cost and Sustainable) Treatment (Wetland Systems or Passive Bioreactors) (Almeida-Guerra et al., 2023) • Active Treatment (Increased Control and Efficiency) (Treatment Plants, or Electrocoagulation and Phytoremediation)
Organize workshops between mining companies, mining unions or associations, and governmental entities to propose new environmental regulations or laws to control mining liabilities or waste. This will reduce soil contamination in Ponce Enriquez, helping to promote agriculture in the sector, and therefore, decrease the dependency on mining activity.	a. Identification of key stakeholders Examples: MAATE, Ministry of Energy and Mines, Municipality of Ponce Enriquez, El Oro prefecture, representatives of mining companies, NGOs and local communities. b. Organization of workshops and working groups c. Monitoring and enforcement of regulations	• Multi-sectoral approach with active participation (dialogue roundtables, training, and environmental awareness) • Implementation of Pilot Projects • Community and business participation methods
Strengthen the relationship between academia-business-government-community by providing opportunities for investment in research projects focused on the proposal of new options and improvement in the development of mining activity in Ponce Enriquez.	a. Identification of research needs and opportunities Conduct a working group to develop a diagnosis of problems and identify priority research topics. b. Promote the creation of cooperative agreements between companies and Higher Education Institutions. c. Implementation of pilot projects Further research should be conducted on the implementation of modern and clean mining technologies. In addition, they seek financing from NGOs or lending institutions (Inter-American Development Bank or World Bank).	• Public-Private Innovation Funds (environmental monitoring and control laboratories, pilot plants, or internship program links) (Bamber et al., 2024) • Community participation and environmental education programmes • Development of economic and productive alternatives (Research on Alternative Use of Mining Waste or Promotion of agroforestry in degraded mining areas) (Luzuriaga-Torres et al., 2022)
Develop and promote sustainable tourism (e.g., visits to sites of geological and mining interest) in the mining district of Ponce Enriquez, taking advantage of its rich mining history, the vast and varied existence of mineral resources, and the existence of a road network. This will allow the population not to be subject to the price variation of mineral resources, in addition to carrying out an activity that does not negatively affect the environment or human health.	a. Identification of points or areas of geological and mining interest. b. Evaluation of environmental impact and tourism capacity c. Encourage the creation of tourism products Tourist guides should be trained in geotourism to promote new routes.	• Development of Ecotourism Infrastructure and Services (Mining Museum, Geological Interpretation Center, Geotourism Trails or Routes) (Carrión-Mero et al., 2025b) • Education and Community Participation (Training of Local Specialized Guides, Mining and Geology Events and Festivals, Incentives and Regulations for Sustainable Tourism).

The authors of this research present a SWOT matrix for mining in the municipality of Ponce Enriquez as a reference for decision-makers within the scope of mining activities in this district. This SWOT analysis provides a broader view of the internal and external environments for implementing strategic plans. Table 5 shows the SWOT of the current mining activities in the study sector.

As part of the environmental strategy, the authors propose the following in Table 6.

4. Discussion

The Ponce Enriquez mining district is known for its Cu, Au, and Mo deposits in veins, breccias, stockworks, and epithermal deposits that developed within andesitic volcanic rocks (Paz-Barzola et al., 2022). In this zone, gold is associated with iron sulphides, arsenic sulfides, copper sulphides, and other sulphides such as galena (SPb) and sphalerite (SZn) (Jiménez-Oyola et al., 2021). Furthermore, Ponce Enriquez, Peña Carpio y Menéndez-Aguado (2016) determined that gold paragenesis is associated with pyrite (FeS_2), chalcopyrite ($CuFeS_2$), arsenopyrite (FeAsS), and silica (SiO_2). Thus, the high levels of heavy metals such as iron (Fe), lead (Pb), and zinc (Zn) can be related to mining around the case study rivers (Table 1). Akhtar et al. (2021) recognise that to understand and analyse surface and groundwater quality, it is necessary to know the anthropogenic activities (e.g., agriculture and urban activities) and natural processes (e.g., climate change, natural disasters, geological factors), which can influence this process.

From the results in Table 1, Siete, Fermín, Villa and Guanache rivers show high concentrations of heavy metals, as they exceed the permissible limits proposed in the TULSMA (water quality for the preservation of flora and fauna in fresh waters). The contamination of rivers (case studies) is highest in the heavy metals iron (Fe) and Aluminum (Al), as they exceed the TULSMA permissible limits by up to 172 times and 116 times, respectively. Additionally, high levels of Copper (Cu) are found in the same four rivers, with concentrations of up to 62 times the TUSLMA permissible limits. Several authors (Jiménez-Oyola et al., 2021) have characterized the water of the same rivers and obtained results that also exceeded the permissible limit for the same heavy metals. A similar case is the Tarkwa Mining Area (Ghana), where when extracting the gold and manganese characteristics of the area, the Efuanta and Bonsa rivers present high concentrations (contamination) of iron (Fe), lead (Pb), and sulphides (Ewusi et al., 2017). Similarly, in the Pahang mining district (Malaysia), two abandoned mines (Kuala Lipis and Bukit Ibam) were monitored by measuring the Water Quality Index (WQI), denoting contamination by Copper (Cu), Pb, Zinc (Zn) and Arsenic (As) (Madzin et al., 2017).

Comparing the results of this study with previous studies carried out in the mining district, a decreasing trend in heavy metal content was observed, especially for Cu in the Siete river (Paz-Barzola et al., 2022; Salgado-Almeida et al., 2022)). Appleton et al. (2001) reported values between 17-7277 μg/L, whereas Carling et al. (2013) reported values between 0.2-208 μg/L. The recent decreasing trend in heavy metal content in the mining area of Ponce Enriquez can be related to the development of public policies aimed at protecting and preserving the environment (since 2009). Sanga Suárez (2020) indicates that approximately 15 mining sites affect the characteristics of these rivers. Zhou et al. (2020) collected data on heavy metals (e.g. Cd, Pb, Zn, Cu, and Fe) in 240 surface water bodies worldwide between 1972-2017. They showed that heavy metal concentrations above permissible limits were the highest in countries in Africa, Asia, and South America, with significant sources of mining, manufacturing, and rock erosion. In Brazil, de Mello et al. (2020) proposed proper watershed management and a correlation between Land-Use/Land-Cover (LULC) and water quality to maintain a site's ecosystem services. In general, agriculture, urban areas, and mining activities are responsible for water quality degradation in this catchment, especially as their effects can vary seasonally. The proposed forest restoration method can improve water quality, but more studies are needed.

Figure 4 shows the results of the non-parametric Spearman's correlation for both the dry and wet seasons. Strong positive correlations ($r>0.8$) were detected between Fe-Pb, Fe-Al and Pb-Al and moderate positive correlations ($0.6<r<0.8$) between Cd-Cu, Cd-Zn and Cu-Zn. This is related to the geology and mineralisation of the area, which corresponds to a sulfide-rich deposit, including pyrrhotite, arsenopyrite, galena, and chalcopyrite as the most common minerals (Escobar-Segovia et al., 2021). In this context, the exploitation, extraction, and processing of minerals may have resulted in the release and transport of these elements in addition to the generation of waste into the environment and into the surrounding soils. This was added to the transport by precipitation during the wet season. In analysing the relationship between the concentration and sources of heavy metals in the dry season, the first principal component (Dim 1) had the highest contribution (60.72 %), which explains the relative influence of Cd, Cu, and Zn (Figure 5). Similarly, Tu et al. (2023) in the Huangpu River, Shanghai (China), indicated a 52.88% relationship between Cu, Zn, and Cr and industrial activity. In the wet season, Dim 1 contributed 65.48%, and it also contained Al, Fe, and Pb. The concentrations of these metals could explain the source of contamination from agricultural activity and soil erosion during the wet season. Similar to the study by Fadlillah et al. (2023), an urban river in Indonesia showed a 38.17% ratio of Al, Fe, and Pb owing to agricultural activity.

Based on the proposed environmental strategies (Section 3.4), the aim was to strengthen or encourage agriculture in the study area, as this activity is the most significant other than mining. If the results of Table 1 are compared with the permissible limits of the Ecuadorian environmental standard (TULSMA) for water quality for agricultural irrigation, only the heavy metals Aluminum (Al), Iron (Fe) and Copper (Cu) would present problems (permissible limits of 5.0 ppm, 5.0 ppm and 0.05 ppm, respectively). This can be controlled by implementing proposals to regulate and improve the mining techniques. Jiménez-Oyola et al. (2021) found high concentrations of Cu, Cd, As, Pb, and Ni in soil samples collected within the study area. Globally, soil contamination problems can also be perceived. In China, several researchers (Li et al., 2020) conducted 1731 analyses of agricultural soil samples between 1985 and 2016, demonstrating the contamination of farming soils with Cu, Pb, and Cd. Qin et al. (2021) proposed removal technologies for soil remediation, such as soil amendments, phytoremediation, and foliar sprays.

The environmental strategies presented in Table 5 include guidelines for their correct and progressive implementation within the Ecuadorian mining industry, particularly in the mining district of the study area. Implementing advanced technologies in mining activities improves the efficiency of mineral resource extraction and processing, thus reducing environmental impacts. In a review conducted by Nursamsi et al. (2024), the use of remote sensors for environmental and forest control and monitoring in mining areas was proposed, indicating the importance of a periodic analysis of such data, which can guide policymakers and companies in decision-making, but with the need for the participation of the community and people in situ to validate the information collected. Mining exploration continues to cause environmental damage, and the use of passive and active treatment systems is fundamental to reducing acidity and removing heavy metals in the rivers of the Ponce Enriquez mining district. Boi et al. (2023) analyzed native Mediterranean plants for the phytoremediation of water bodies and soil by metal contamination related to mining exploitation, ensuring high biodiversity and landscape value. Similarly, Almeida-Guerra et al. (2023) proposed bioremediation techniques for AMD using bacteria from a wastewater biodigester and sugarcane bagasse (95-99% reduction in heavy metal concentrations).

During the research period, there were limitations in collecting water samples from the rivers of the study area. One of the main limitations was the accessibility to the sampling sites due to insecurity in the mining concessions (criminal gangs within and related to mining activity), in addition to the openness of the mining companies in revealing the internal processes of extraction and processing of metals. Another limitation was the use of samples during the wet season because, due to the increase in precipitation in the study area, the flow of the rivers increased, threatening the safety of personnel taking samples.

As future lines of research, the authors propose:

a) Monitoring campaigns in surface water bodies (rivers) and groundwater (aquifers): periodic sampling in strategic stations (dry and wet) to assess the evolution of contamination (Carrión-Mero et al., 2024). This can be done by collecting samples at strategic points in rivers, streams, or wells, real-time monitoring (e.g., sensors and implementation of Internet of Things (IoT) technology), pollutant dispersion modelling (e.g., HEC-RAS, MODFLOW software), and the use of natural tracers and isotopic modelling to assess the source of contamination (Campoverde-Muñoz et al., 2022).
b) Impact of contamination in agriculture: Analysis of metal bioaccumulation in agricultural crops or evaluation of the loss of fertility of agricultural soils due to mining contamination. This can be performed by analyzing plant tissues (leaves, roots, and fruits) in agricultural crops (Argüello et al., 2019).
c) Bioremediation and biological studies for contamination assessment: Determine the degree of water contamination by studying macroinvertebrates within the water body (e.g., indices such as BMWP/Col, ABI, and EPT) (Adams, 2002), and develop bioremediation strategies with microorganisms (sulfate-reducing bacteria) and aquatic plants (Vetiver, Eichhornia crassipes) (Vetiver, Eichhornia crassipes) (Almeida-Guerra et al., 2023).
d) Promotion and incentives for geotourism: An inventory and evaluation of sites of geological and mining interest for the development of geotourism is proposed (Carrión-Mero et al., 2025a), environmental evaluation and tourism carrying capacity of geological and mining sites (Carrión-Mero et al., 2025b), and conditioning exploration mines for tourist visits and presentation of mining heritage.

5. Conclusions

This study presents an analysis of the state of the Siete, Pagua, Fermín, Villa, Guanache, and 9 de Octubre rivers (Ponce Enríquez mining district), where mining activities have started since the beginning of the 21st century. The authors performed a physicochemical analysis (heavy metals, e.g., Al, Cd, Cu, Fe, Pb and Zn) and a statistical correlation analysis (Wilcoxon-Mann-Whitney test, Spearman's non-parametric correlation coefficient, and PCA); where substantial concentrations of heavy metals (Fe and Pb) were detected, as well as positive correlations ($r>0.8$) between Fe-Pb, Fe-Al and Pb-Al. Additionally, the PCA showed possible sources of contamination related to gold and other mining and exploitation (main contamination activity), anthropogenic activities (e.g. agriculture), and the geological conditions of the study area (existence of minerals such as pyrite (FeS_2), chalcopyrite ($CuFeS_2$), arsenopyrite (FeAsS), and silica (SiO_2)).

The presence of high concentrations of heavy metals in the case study rivers during the dry season is influenced by sources of contamination, such as waste discharges from mining activities and the auriferous geology-mineralisation of the study area (volumes of soil and rock mined, presence of iron sulphides, copper sulphides, galena, sphalerite, pyrite, and chalcopyrite in the study area). In the wet season, in addition to the sources that affect the dry season, there is also pollution caused by runoff. Possible sources of contamination are agricultural land adjacent to rivers (due to the presence and use of fertilisers in the soil) and the poor disposal of waste dumps and tailings from illegal and artisanal mining.

According to the water quality analysis to preserve flora and fauna in fresh waters of the TULSMA standard (Ecuador), the Villa, Siete, Fermín, and Guanache Rivers are the most contaminated by heavy metals, especially during the wet season. The Siete River has 11.58 and 46.41 ppm of Aluminum and Iron, respectively, while the Villa River contains 1.24 and 0.003 ppm of Copper and Cadmium, respectively. On the other hand, the Pagua River has the lowest water quality contamination (only aluminum and iron originate from geological formations in the study area).

This study proposes five environmental strategies for the gradual improvement of water quality in rivers and the diversification of economic activities in the Ponce Enriquez mining district: 1) the use of new and/or modern technologies in mining activities; 2) organising working groups or forums between mining companies, mining guilds or associations, and government bodies; 3) implementing proposals for the regulation of mining activities; 4) strengthening the relationship between academia-business-government-community; and 5) developing and promoting sustainable tourism, taking advantage of the historical mining wealth in the study area.

The research can be extended or completed with future lines of research, such as: a) Monitoring campaigns in surface water bodies (rivers) and groundwater bodies (aquifers) (e.g., use of sensors, sample collection, or modelling of contaminant dispersion); b) impact of contamination on agriculture (bioaccumulation of metals in crops and fertility of agricultural soils); c) bioremediation and biological studies for contamination assessment (application of biological indices and application of passive bioreactors); and d) promoting and encouraging geotourism in the mining district (inventory and evaluation of sites of geological and mining interest).

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Data Availability

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Conflicts of Interest

The authors declare no conflict of interest.

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