

## Article

# Assessment of Water Resources Pollution Associated with Mining Activities in the Parac Subbasin of the Rimac River

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**Abstract:** The objective of this study is to evaluate the contamination of water resources in the Parac subbasin. The existing contamination by heavy metals due to the presence of mining companies is of great concern to the population that inhabits the area since health is being affected. A methodology has been used as an integrated approach based on pollution assessment indices. Five surface water samples and seven groundwater samples were collected in the Parac subbasin, in the vicinity of the Tamboraque tailings. Physicochemical parameters and heavy metals (Al, As, Br, Pb, Fe, Cd, Mn, Hg, B, Ni, Cu, and Se) were analyzed. The mean concentrations of Al, As, Ba, Cu, Fe, Pb, and Zn were 0.3 mg/L, 0.02 mg/L, 0.02 mg/L, 0.05 mg/L, 0.8 mg/L, 0.04 mg/L, and 0.12 mg/L respectively. HPI, HEI, and Cd indices were averaged around 1378.5, 134.5, and 126.5 respectively, HPI and Cd values were above 100 as a critical contamination index value, which indicates that the water samples are critically contaminated with respect to the heavy metals studied. The total variance was 88.11% of the water quality with two components according to the ACP analysis. Al, As, Cu, Fe, Pb, Zn, and Mn showed a high positive charge on PC1 (69.68%) while Ba and Mo had a high positive charge on PC2 (18.12%). The intensity of distribution of metals As, Fe, Mn, and Pb in surface and groundwater is an environmental concern and a more complete monitoring network is needed for the sustainable management of water resources.

**Keywords:** water resources; pollution; mining activities; heavy metals; water sample



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## 1. Introduction

The extraction of raw materials through the use of mining is essential for human development. Even so, it increases the probability of releasing toxic elements in areas near the worksites and accelerates the polluting processes that occur in the physical environment. Solid waste and wastewater produced by mining operations are potential sources of soil and water contamination since they contain metals that can be spread by purely natural circumstances, such as wind or rain, or accidentally. After all, they end up affecting the receiving environment [1]. Thus, the water resources become the point of greatest contamination by the mining industry. For instance, [2] assessed surface water quality using pollution indices in the Subarnarekha River, India can be observed. The results indicated that the elevated concentrations of certain metals in the Subarnarekha River near industrial and mining establishments can be attributed to anthropogenic contributions from industrial and mining activities in the area. The authors of [3] characterized the level of pollution of the water resources in the Vatukoula Goldmine and concluded that high pollution rates derived from gold mining in the area. They mentioned that some sources of contamination are associated with Cadmium (Cd), emissions from gold ore processing associated with Lead (Pb), and a mixed effect of mining and geogenic sources associated with Chromium and Zinc (Cr and Zn). The authors of [4] evaluated water resources in the Rimac river basin. Their results indicated that the quality of water resources in the upper part of the basin is being impacted by mining activities in the area.

Water is a fundamental element for the development of mining activities and is often the conduit through which pollutants are transported to the environment [5]. At some point, these polluted waters produced by the mines are discharged, so this becomes a fundamental factor in the dispersion and circulation of multiple chemicals that are harmful to the environment. Elements such as Cd, Cr, Pb, Ni, Mn, and Zn are considered potential heavy metals in aquatic environments due to their existence, and their toxic and nondegradable characteristics. Refs. [6–9] One of the sources of these pollutants is the mining inputs such as mine development, mineral processing, mining waste, and leaks from tailings dams, among others. In the same sense, the Congress of the Republic of Peru [10] establishes that the various operations carried out by the mining industry generate waste and emissions that are harmful to the environment, which is aggravated when a mine closes since the decline of rehabilitation programs only generates environmental mining liabilities caused by the abandonment or inactivity of mining operations, which makes them harmful to human health and ecosystems. On the other hand, the geochemical effects produced by the mining industry operations also generate detrimental consequences for the waters that are on the surface and groundwater on a regional magnitude even long after the mines have ceased their activities [11].

In both coastal and semidesert areas, water resources are highly sensitive to climatic transitions caused by seasonal changes [12], so freshwater resources are scarce, where groundwater is the most important natural resource and often the only source of water supply [13].

It is in these regions where the mining industry represents a major challenge in relation to water resources management, as the harmful consequences can be intensified by the unfavorable state of the climate and the pressure caused by mining on the water system, resulting in an obstacle to regional sustainable development [14].

Numerous surveys abound in the literature on heavy metal pollution of water sources. Such work includes [15–17]. All these workers concluded that there was a need to monitor water quality on a regular basis. The authors of [18] investigated trace element distributions and concentrations, specifically As. Their results showed that contamination reaches very high concentrations, and the impacts may be crucial for humans and ecosystems. We marked that some factors such as physicochemical properties, regional climate, and geological settings are controlling the occurrence and transport of As. In addition, [19] mentioned that the necessity of monitoring water quality has recently caused some to conclude that developing and applying index methods for water quality assessments regarding metal pollution are vital.

In Peru, the mining sector represents more than 50% of its export earnings, constituting one of the main sectors that favor the improvement of macroeconomic indicators. Contradictory to this situation, according to data from human development indices (HDI) in many of the departments, this activity has not contributed to the development and improvement of the living conditions of communities and populations in these areas but is related to environmental and social costs borne by populations and has had negative impacts on their living [20] conditions.

The extractive activities of the mines interact with most of the peasant communities (about 2900) located in the Peruvian highlands, so there is a constant risk of threat to the environment since it is a way of life that depends too much on the resources contained in an ecosystem, as is the case of the Peruvian highlands [21,22]. This circumstance is aggravated by the 8571 environmental liabilities generated by abandoned mines, [23] and the discharge of almost 13 billion m<sup>3</sup> of poorly processed wastewater [24]. Consequently, any mining exploitation above 3500 m above sea level is detrimental to water resource management [25,26]. The mining activity taking place in the Rimac River basin is present in the lower, middle (e.g., Cajamarquilla), and upper areas (e.g., Perubar, Coricancha, los Queñuales, Americana, Rosaura, among others) and generates pollution problems in the main tributaries [27]. In the lower and middle reaches (up to 3000 m.a.s.l.) mining activity occurs less frequently. In fact, the upper part of the Rimac basin can be considered the most

vulnerable since it is where most of the mining activity takes place. In this sense, ref. [28] indicated that mining, developed mainly above 3500 m.a.s.l, is a disruptive factor for water management.

The Rimac basin presents several problems regarding the quantity and quality of water resources, In the upper part, the mining activity has been developing since the decade of the 1930s with the exploitation of polymetallic deposits that have brought, as a consequence, the degradation of the quality of the waters of the river Rimac [29]. Among the main affected populations are San Mateo, Chicla, Casandapalca, and Matucana, located in the upper middle basin.

Given that the community is located in an area where mineral extraction activities are carried out, that the water they use comes only from surface or groundwater, and that these can be used by the population for drinking [30], irrigation, and food, it is clear that such mineral extraction activities are detrimental to water resources, human wellbeing and, in general, to the entire environment.

In this context, the purpose of this study was to assess water resources pollution in terms of surface and groundwater in order to know the possible impacts of mining on water resources in the Parac subbasin located in the upper Rimac river basin, by water facies identification of the studied samples, quantification of pollution in both surface and groundwater samples in the Tamboraque area located in the Parac subbasin and application of statistical approaches to identify the sources and risk of pollution in the river system [30]. The trace element concentrations were compared, not only to Peruvian legislation, but also with the reference estimates established by international organizations such as the Environmental Protection Agency (USEPA), the World Health Organization (WHO), and the Initiative for Responsible Mining Assurance (IRMA). In the present study, techniques such as Pearson's correlation coefficient were used to assist in the analysis of the statistics, with the intention of allowing the recognition of connections between elements and probable common sources of contamination [31]. On the other hand, the different indicators of contamination and risk were also evaluated to contrast the scale of contamination reached and the probable ecological impact on these aquatic ecosystems. It should be noted that the water resources of the region have never been the subject of such an exhaustive investigation; in this sense, both the data obtained in this study and the analysis will be very helpful tools when evaluating, contrasting, and reducing the harmful effects caused by the mining industry on the integrity of the water resources.

## 2. Materials and Methods

### 2.1. Study Area

The Parac river subbasin (see Figure 1), is located in the Rimac river basin, which, in turn, is part of the slope located on the Pacific. It is characterized by presenting a complex topographic relief, strongly predominant with slopes greater than 50% associated with softer relief areas. The altitudinal range is between 3000 to 5000 m.a.s.l. It has an area of 100 km<sup>2</sup>, from which downstream, the Parac stream, deposits its waters to the Rimac River, on the left bank. In the highest area is the snow-capped Chanape, the Suerococha lagoon, and streams such as Pucarral, and Musca, among others. It is bordered on the north and east by the Blanco River microbasin, on the south by the Mala river basin, and on the west by the microbasin of the Viso stream [32]. The study area is in the district of San Mateo de Huanchor in the province of Huarochirí, department of Lima. Geographically is in the region of the central coast of Peru between the geographical coordinates 11°49' S and 76°16' W.

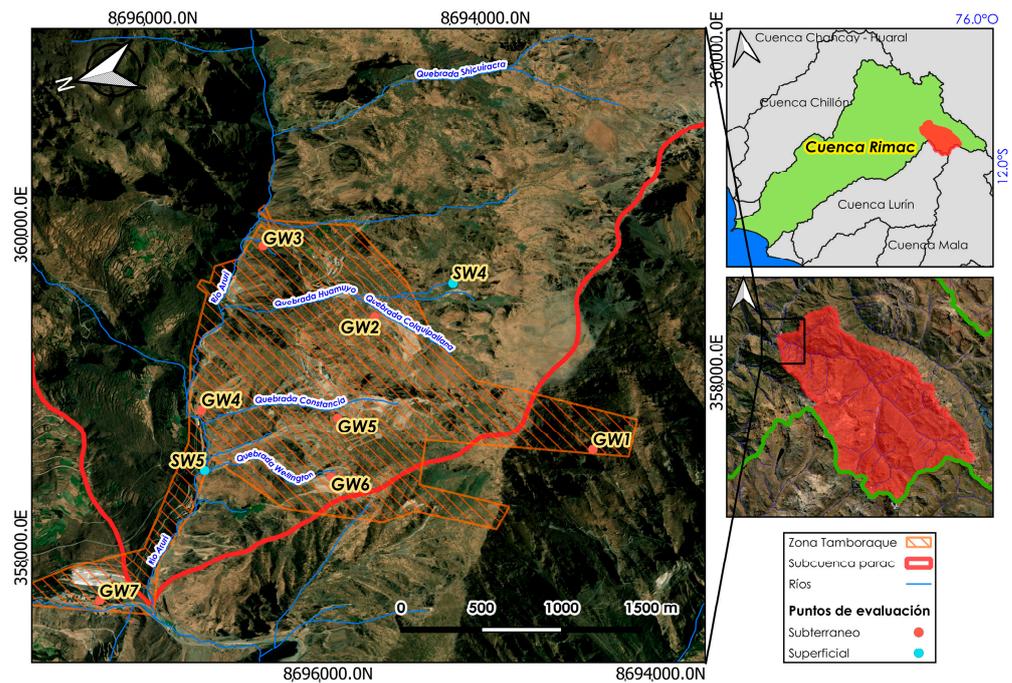


Figure 1. Study area and sampling locations.

### 2.2. Geology of the Area Studied

The Parac subbasin geological map was established by combining both 24-k geological papers mapping in October 2019 following onsite observations and experts’ advice to the Tamboraque area (see Figure 2).

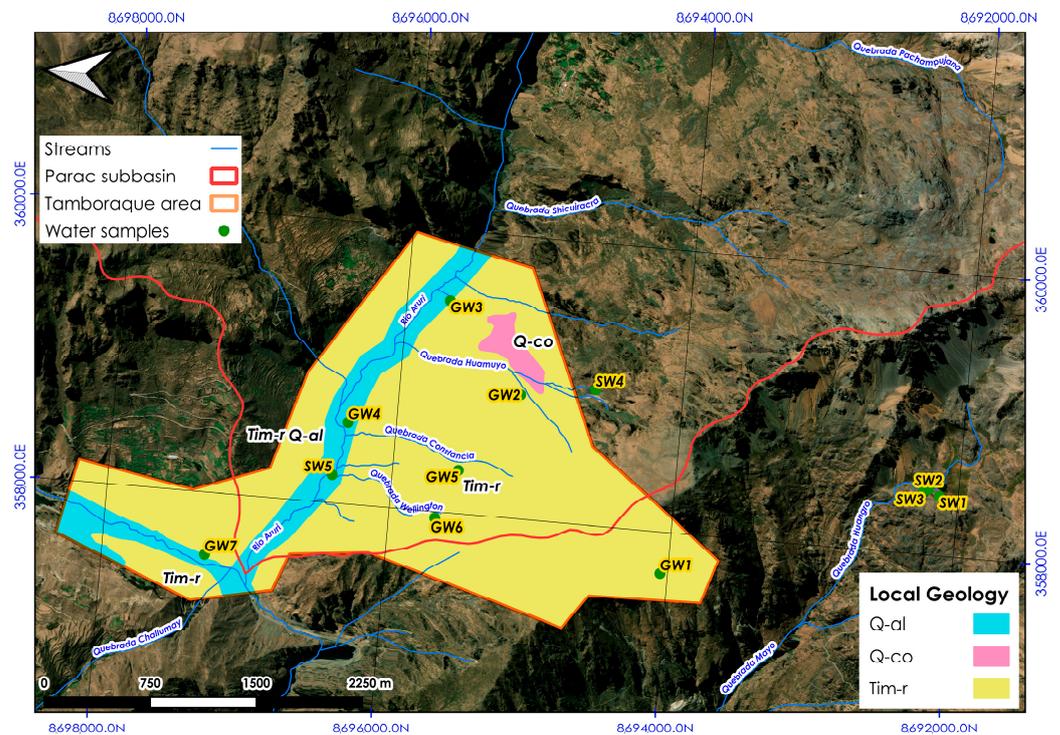


Figure 2. Geological map of the study area.

The Lower part of the Parac subbasin, where the Tamboraque area is located, is situated on rocks of the Quaternary system (Q) with alluvial deposits (al) formed by gravels and sands with boulders in the middle and lower reaches of the Aruri river and colluvial

deposits (co) at the foot of the escaped slopes of the hillsides as debris material consisting of gravels and subangular blocks with a matrix of sandstones and silts. Formations of the lower middle tertiary system (Tim) sedimentary rocks of the Rimac group (r) [33]. Andesite (Hypoabyssal) was found in the fieldwork. These outcrops are observed in the central and southern parts of the study area. They present an NS and NE trend, which cut the dacitic rocks and are aligned to the NS and NE fault system. According to [34], the andesite belongs to the middle tertiary.

Figure 3 shows the alluvial and colluvial material of Parac creek (a and b) and Hipoabisal andesite (c). The rains are abundant with an average annual rainfall of 500 mm, with a seasonal regime of the Peruvian Pacific vertient. The wet season begins in December and ends in March and the dry season begins in June and ends in the middle of August, the rest being transitional. With respect to temperature, it varies throughout the year and according to altitude. In the lower part, an annual average of 10 °C is reached, in summer it reaches 19 °C, and in winter up to 5 °C. In the valley, the temperature is not a limitation for agricultural activities. In the high areas, the presence of meteorological frosts only allows for the development of natural pastures.



**Figure 3.** Local geology in Tamboraque area, Parac watershed.

### 2.3. Collection and Processing of Samples

Surface water (SW) and groundwater (GW) samples were collected from the Tamboraque area located in the surroundings of the Aruri river and its main tributaries. The set of samples was collected in December 2019, and January and February 2020 from twelve (12) sampling stations, as presented in Figure 1. The sampling sites were georeferenced with a GPS device. Briefly, water samples were collected in pre-cleaned polyethylene and glass bottles followed by acidification and preservation correctly. One liter (1 L), five hundred milliliters (500 mL), two hundred and fifty milliliters (250 mL), one hundred and twenty milliliters (120 mL), and sixty milliliters (60 mL) polyethylene containers were used for sample storage. Only one glass bottle of 250 mL was used for each sample.

During water sampling, polyethylene and glass bottles were also rinsed with water from the studied site three times. The grab samples were taken in a single take to assess the quality of a water point at a given time. Finally, they have been rinsed three times then filled completely, and then sealed to avoid interfering reactions with the air.

### 2.4. Analytical Processes and Quality Control

Collections and preservations of samples were performed by following EPA SW-846, ASTM D 5903, *Standard Methods of Water and Wastewater 21st Edition* 2005, and the National Protocol for Monitoring the Quality of Peru's Water Resources. The metals in surface and groundwater samples were determined by inductively coupled plasma mass spectrometry (Expect ICP-MS) following the methods of EPA Method 200.8 Rev.5.4 (1994). Accuracy and precision were verified by triplicates analysis as quality assurance and quality control (QA/QC) procedures.

### 2.5. Quantification of Surface Water Pollution

Contamination index ( $C_d$ ): A contamination index summarizes the various consequences that degrade the quality of human drinking water, acting as an assessment of the degree of heavy metal contamination [35]. It can be defined by the following equation:

$$C_d = \sum_{i=1}^n C_{fi} \quad (1)$$

where:

$$C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1 \quad (2)$$

$C_{fi}$  = contamination factor for the umpteenth component.

$C_{Ai}$  = analytical value for the umpteenth component.

$C_{Ni}$  = maximum permissible concentration of the umpteenth component.

#### 2.5.1. Heavy Metal Pollution Index

According to [29], the heavy metals assessment index ( $HEI$ ) provides an improvement in the quality of the water, which presents a concentration of heavy metals and is calculated by the following formula:

$$HEI = \sum_{i=1}^n \frac{H_c}{H_{MAC}} \quad (3)$$

where:  $H_{MAC}$  and  $H_c$  are the maximum permissible concentrations and the monitored value of the  $i$ -th parameter, respectively.

#### 2.5.2. Heavy Pollution Index

The heavy metal contamination index ( $HPI$ ) analyzes the individual heavy metal composition of the water condition, as a model of disaggregation [36]. Each parameter that is chosen is assigned a weight ( $W_i$ ) that will allow the calculation and evaluation of the  $HPI$  index using the following formula.

$$HPI = \frac{\sum_{i=1}^n W_i Q_i}{\sum_{i=1}^n W_i} \quad (4)$$

where  $W_i$  and  $Q_i$  are the unit weight and the subscript of the  $i$ -th parameter, respectively. Therefore, the subscript ( $Q_i$ ) is calculated using the following equation.

$$Q_i = \sum_{i=1}^n \frac{(M_i - I_i)}{(S_i - I_i)} \times 100 \quad (5)$$

where  $M_i$ ,  $I_i$ , and  $S_i$  are the monitored heavy metals and the ideal and standard values of the  $i$ -th parameter, respectively. The unit weight ( $W_i$ ) is inversely proportional to the maximum permissible concentration of the selected parameter.

### 2.6. Statistical Analysis to Assess Surface and Groundwater Pollution

An analysis of the statistics was carried out to understand the mode of propagation of the metals and also to recognize the potential sources of heavy metals. Several techniques such as a Pearson correlation coefficient analysis with a significance scale equivalent to  $p < 0.05$  were also developed to obtain the association between the different heavy metals. On the other hand, to find the probable sources of contamination, the principal component analysis (PCA) technique was used to be able to correctly understand how the correlation of the variables is formed and to simplify the data search, since its dimensions are reduced and the hierarchical cluster analysis (HCA) of the set of samples using Rstudio software. All these techniques resulted in being able to differentiate the natural or anthropogenic origins

of the heavy metals obtained from the sampling of the water sections, thus improving the quality of the interpretation of the data obtained.

- Pearson correlation

It is a numerical measure of the correlation between two correlated variables or a pair of variables and is denoted by  $r$ , called the correlation coefficient. It measures the strength of the linear relationship between these variables. According to [36] the Pearson correlation coefficient is used to distinguish possible sources of heavy metals.

$$r = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 \sum_{i=1}^n (y_i - \bar{y})^2}} \tag{6}$$

where  $(x_i, y_i), i = 1, 2, 3, \dots, N$  represents  $n$  pairs of values. The value of  $r$  is between  $-1$  and  $+1$ . However, in the case of  $r = +1, -1$ , and  $0$ , it indicates the perfect positive correlation, perfect negative correlation, and noncorrelation, respectively, between the pair of variables [37].

- Principal Component Analysis

The dataset consisting of quantitative variables from different individuals can be analyzed and visualized by principal component analysis (PCA) as an efficient pattern recognition [38–42]. Group identification of samples, based on the similarity of heavy metal content, is used by cluster analysis (CA) [37,43–50]. CA was used to measure the distance separating groups characterized by similar concentrations of metals [51].

### 3. Results and Discussion

The data obtained with respect to the agglomeration of heavy metals found in ground-water and surface water are shown in Table 1.

**Table 1.** The concentration of heavy metals in the water systems belonging to the study area and reference values.

| Metals | Surface Water (mg L <sup>-1</sup> ) |              | Groundwater (mg L <sup>-1</sup> ) |               | Guidelines Values (mg L <sup>-1</sup> ) |         |       |       |       |
|--------|-------------------------------------|--------------|-----------------------------------|---------------|---|---------|-------|-------|-------|
|        | Range                               | Mean ± DS    | Range                             | Mean ± DS     | ECA MINAM                               |         | WHO   | IRMA  | EPA   |
|        |                                     |              |                                   |               | Cat1-A1                                 | Cat1-A2 |       |       |       |
| Al     | 0.071–1.229                         | 0.3 ± 0.51   | <LOQ–37.5                         | 9.5 ± 18.67   | 0.9                                     | 5       |       | 0.1   |       |
| As     | 0–0.05                              | 0.02 ± 0.02  | 0–1.9                             | 0.31 ± 0.71   | 0.01                                    | 0.01    | 0.01  | 0.01  | 0.01  |
| Ba     | 0.01–0.04                           | 0.02 ± 0.01  | <LOQ–0.03                         | 0.02 ± 0.01   | 0.7                                     | 1       | 1.3   | 1     |       |
| Be     | <LOQ                                |              | <LOQ–0.005                        |               | 0.012                                   | 0.04    |       | 0.06  |       |
| B      | <LOQ–0.03                           | 0.02 ± 0.005 | 0.01–0.15                         | 0.07 ± 0.06   | 2.4                                     | 2.4     | 2.4   |       |       |
| Cd     | <LOQ–0.003                          | 0.002        | <LOQ–0.75                         | 0.38 ± 0.53   | 0.003                                   | 0.005   | 0.003 | 0.005 | 0.005 |
| Cu     | <LOQ–0.1                            | 0.05 ± 0.07  | <LOQ–9.19                         | 2.31 ± 4.59   | 2                                       | 2       | 2     | 1     | 1     |
| Cr     | <LOQ                                |              | <LOQ–0.01                         | 0.001 ± 0.005 | 0.05                                    | 0.05    | 0.05  | 0.05  |       |
| Fe     | 0.2–1.7                             | 0.8 ± 0.75   | <LOQ–160.1                        | 28.01 ± 64.72 | 0.3                                     | 1       |       | 0.3   |       |
| Mn     | 0–0.2                               | 0.08 ± 0.07  | 0.04–12.78                        | 2.37 ± 4.65   | 0.4                                     | 0.4     |       | 0.05  | 0.05  |
| Hg     | <LOQ                                |              | <LOQ                              |               | 0.001                                   | 0.002   | 0.006 | 0.001 |       |
| Mo     | <LOQ–0.0003                         |              | 0–0.002                           | 0.001 ± 0     | 0.07                                    | **      |       | 0.05  |       |
| Ni     | <LOQ                                |              | <LOQ–0.1                          | 0.04 ± 0.06   | 0.07                                    | **      | 0.07  | 0.02  |       |
| Pb     | <LOQ–0.04                           | 0.04 ± 0.01  | 0–0.15                            | 0.05 ± 0.07   | 0.01                                    | 0.05    | 0.01  | 0.01  | 0.015 |
| Se     | <LOQ                                |              | <LOQ                              |               | 0.04                                    | 0.04    | 0.04  | 0.04  |       |
| U      | <LOQ                                |              | <LOQ                              |               | 0.02                                    | 0.02    | 0.3   | 0.03  |       |
| Zn     | 0–0.5                               | 0.12 ± 0.20  | <LOQ–123.52                       | 21.03 ± 50.22 | 3                                       | 5       |       | 3     |       |

Note(s): \*\* There is no value. ECA MINAM: (Ministerio del Ambiente—MINAM, 2017). WHO: (World Health Organization—WHO, 2017). IRMA: (Initiative for responsible mining assurance (IRMA), 2018). EPA: (United States Environmental Protection Agency—USEPA, 2019). LOQ: Limit of Quantification. DS: Deviation Standard.

The status of surface and groundwater has been evaluated with reference scales that can be obtained from Peruvian regulations [50] and with the laws dictated by international organizations such as the World Health Organization (WHO), the Initiative for Responsible Mining Assurance (IRMA), and the United States Environmental Protection Agency—USEPA [47–50]. In this sense, in Peruvian legislation, especially in the environmental

quality standards (EQS), reference values were used for water bodies of a natural origin of category one, subcategory A2—surface water intended for the production of drinking water, drinkable by conventional treatment, A2—water drinkable by disinfection, and category four—conservation of the aquatic environment of lakes and lagoons.

The result obtained from the water sampling concluded a slight acidity in the average pH with an amount of 6.7, which is an allowable amount when compared to the reference value of the regulations issued by the Ministry of Environment—MINAM [47]. The pH values of all the samples obtained from the water analysis can be seen in Table S1 (Supplementary Material). Of all the samples taken, the one with the lowest pH value was GW6, which was at level 690 in the sector where the mine's filters and perforations are located; the value obtained was 3.3. The magnitude of acidity in these water units is probably related to the wastewater discharged from time to time by the mining activity. When this action of discharge or release of water takes place, it would alter the chemical status not only of the rivers but also of the streams.

The average concentration of metals studied in groundwater followed a decreasing order of  $Fe > Zn > Al > Mn > Cu > Cd > Ar > B > Pb > Ni > Ba > Cr > Mo > Se > Hg > Be > U$ . In surface waters, Al took second place, Zn went up one position, and Ar dropped 2 positions.

It is observed that the values found for the metals Al, Ba, Br, B, Cd, Zn, Mn, Cu, and Pb found in the surface waters are lower than the estimated values established in the environmental protection regulations. Concentrations of metals such as Cr, Hg, Mo, Ni, Se, and U did not exceed the limit of quantification.

The highest concentration values of Al, Zn, and Cu were found at point SW5, located in the Aruri River, downstream of the Nv. 080 mine. The concentration values of As and Fe presented exceedances for the groundwater samples, the concentrations of B and Ba were lower than the required reference estimates, and the agglomerations of metals such as Be, Hg, Se, and U also obtained a lower result. Therefore, they did not exceed the LOQ that was intended to be obtained.

Of all the surface water samples that were analyzed, only 60% of them obtained a considerable amount of the metal As in their results, which, moreover, turned out to be an amount that did not exceed the reference estimates. However, the concentration of As obtained in samples SW5 and SW4 exceeded and even doubled the reference limit established by MINAM for freshwater in its freshwater quality for the population and for category A2, which is recreational. Therefore, these results clearly indicate that these water bodies are harmful to humans if consumed. On the other hand, the samples obtained from the waters located in the subsoil GW4 and GW5, which were also obtained in the same sectors as samples SW5 and SW4, go in the same direction, since the results in relation to the agglomeration of the metal As were exorbitant as estimated for category one freshwater, which also makes it impossible to be consumed as drinking water.

The average values obtained for As in localized surface water ( $0.02 \text{ mg L}^{-1}$ ) and groundwater ( $0.31 \text{ mg L}^{-1}$ ), and Pb in surface water ( $0.04 \text{ mg L}^{-1}$ ) and groundwater ( $0.05 \text{ mg L}^{-1}$ ), exceeded the estimated and authorized limits in the regulations of organizations such as the Ministry of the Environment (MINAM), the Initiative for Responsible Mining Assurance (IRMA), the United States Environmental Protection Agency (USEPA), and the World Health Organization (WHO) (see Table 1). Figures 4 and 5 show that 40% of the samples obtained from the surface water analysis exceeded the proposed limits, while 86% of the groundwater samples in which As was detected (6 samples) showed values above the recommended values.

On the other hand, Figure 5 shows that 43% of groundwater samples (three samples) exceeded the reference values for Pb.

Pearson's correlation analysis technique was used in the sampling of surface and subsurface waters or subsoil, in order to collect important data on the common sources and the existing similar behavior of the heavy metals examined in this research work. This correlation can be visualized in Figures 6 and 7 respectively.

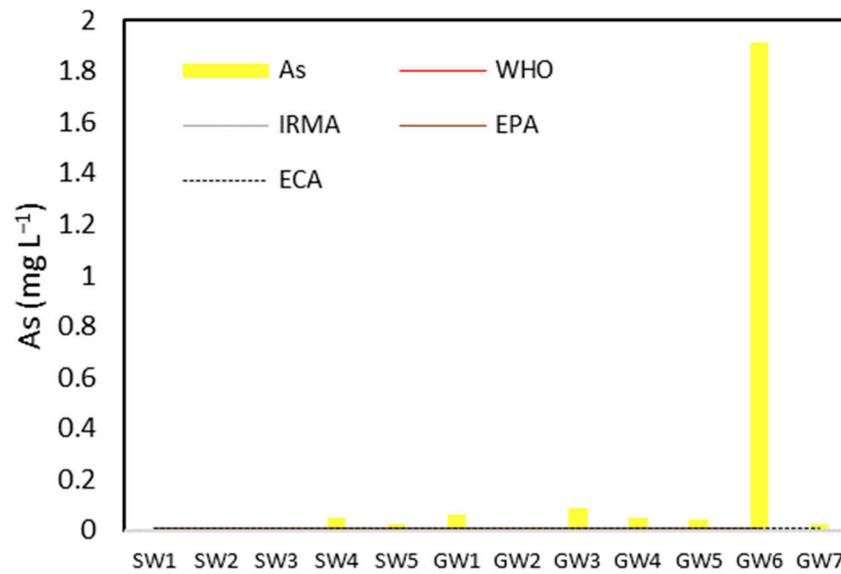


Figure 4. Arsenic concentrations were found in surface water (SW) and groundwater (GW) in the samples examined.

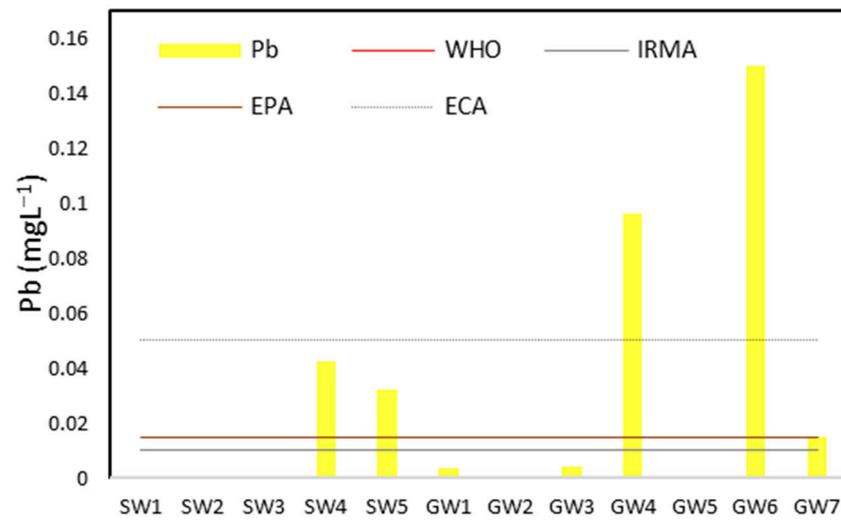


Figure 5. Lead concentrations in surface water (SW) and groundwater (GW) were obtained within the samples that were examined.

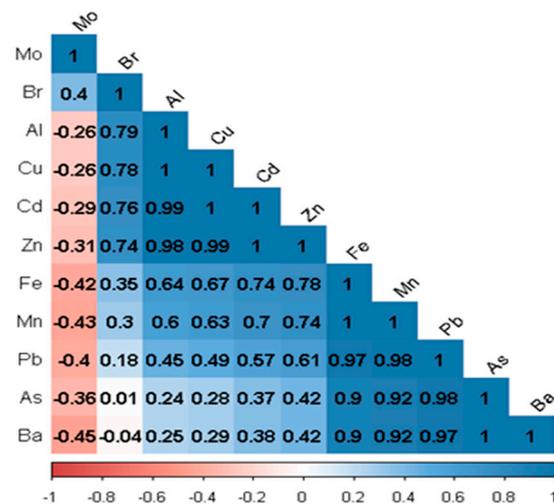
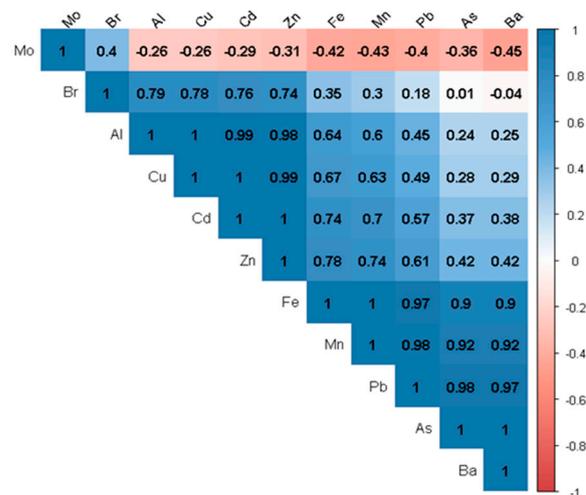


Figure 6. Surface water correlation matrix.



**Figure 7.** Groundwater correlation matrix.

In the chemical analysis results for the surface waters, significantly positive correlations were found ( $0.90 \leq r \leq 0.98$ ,  $p < 0.05$ ) between As–Fe–Mn–Pb, which would indicate that it may have common sources. Similarly, the metals Al–Cu–Cd–Zn evidenced very significant correlations ( $0.98 \leq r \leq 1$ ,  $p < 0.05$ ).

In the chemical analysis result of the groundwater sample, highly significant relationships were evidenced with positive correlation coefficients ( $0.82 \leq r \leq 1$ ,  $p < 0.98$ ) between As–Cu–Fe–Al–Cd–Zn–Mn–Pb, which shows that it is very likely that they come from common sources of contamination.

On the other hand, a correlation could be found for both surface water and groundwater samples. In these samples, a positive correlation was found between Al–Cd–Zn ( $0.90 \leq r \leq 0.99$ ,  $p < 0.05$ ). Likewise, a highly significant correlation was visualized in Fe–Pb–As–Ba–Mn, indicating that these contaminants behave similarly. In the same way that occurs with surface water, Mo is the only metal that does not present a connection with the other metals, thus showing that Mo comes from a different source of contamination, either natural or anthropogenic.

Principal component analysis (PCA) was applied to facilitate understanding and thus correctly examine the sources of origin of heavy metals in the samples obtained from both surface and groundwater. The PCA of samples obtained from surface and groundwater reduced the number of variables to only two principal components (see Figure 8), thus accounting for the variation in the data, as 88.10% was obtained. In other words, PC1 explained 69.98% of the variance and exhibited the highest loadings of Al, As, Cu, Fe (0.38), Mn (0.37), and Pb (0.31).

In relation to the mining industry, the key component is this. PC2 represents 18.12% of the total variety and was able to obtain higher loadings of the metal Br with an amount of 0.70, and also of the metal Mo (0.69). However, HR can also be recognized, although not to means associated with mining activity. The lower loadings generated for Ba (0.17) and Zn (0.04) indicate that these components evidently have no connections with either PC1 or PC2, so their sources of origin are purely natural (see Figure 9).

Results of the quantification of water resources pollution:

Figures 10 and 11 show the results of the surface and groundwater contamination indices (Cd, HEI, and HPI). The scale and average assessment of the HPI are from 23.5 to an amount of 13,305.24 and 1378.58. The demand originated by metal contamination was calculated using the Cd index in average values and a range of 126.5 and  $-5.47$  to 1403.5, respectively. HEI values ranged from 2.52 to 1411.56 (mean = 134.5).

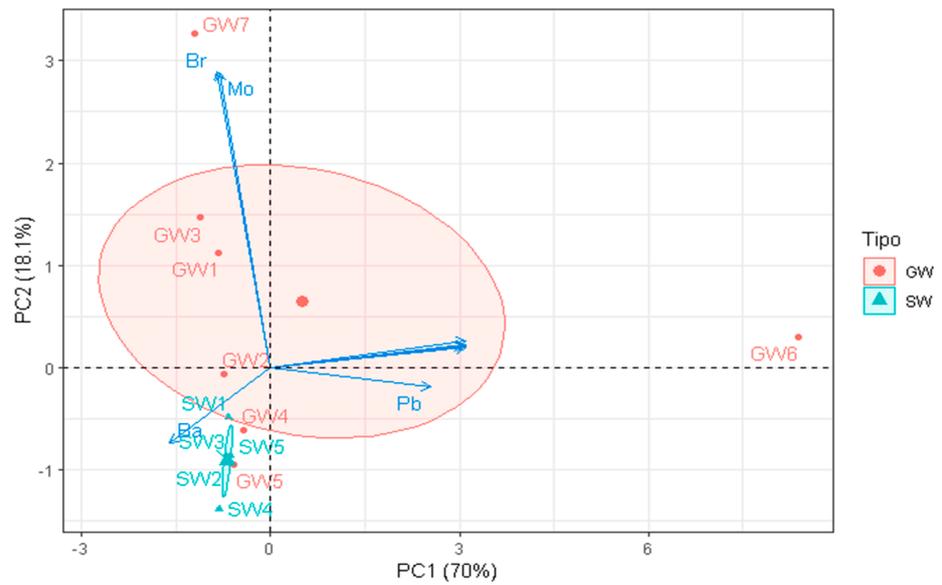


Figure 8. Metals examined in the sampling obtained by PCA.

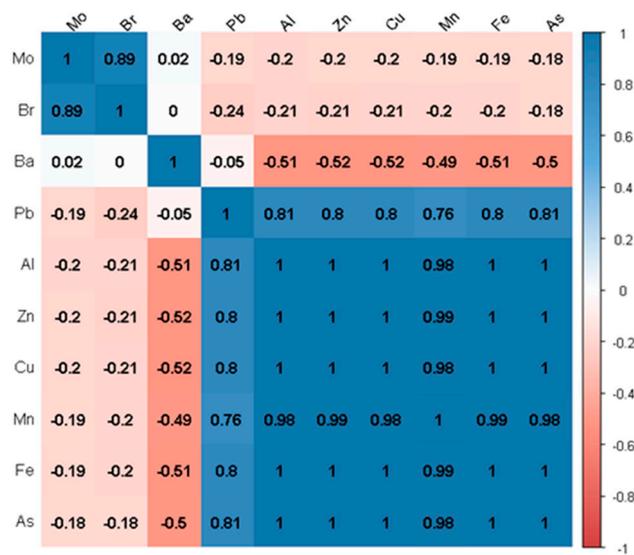


Figure 9. Surface and groundwater correlation matrix.

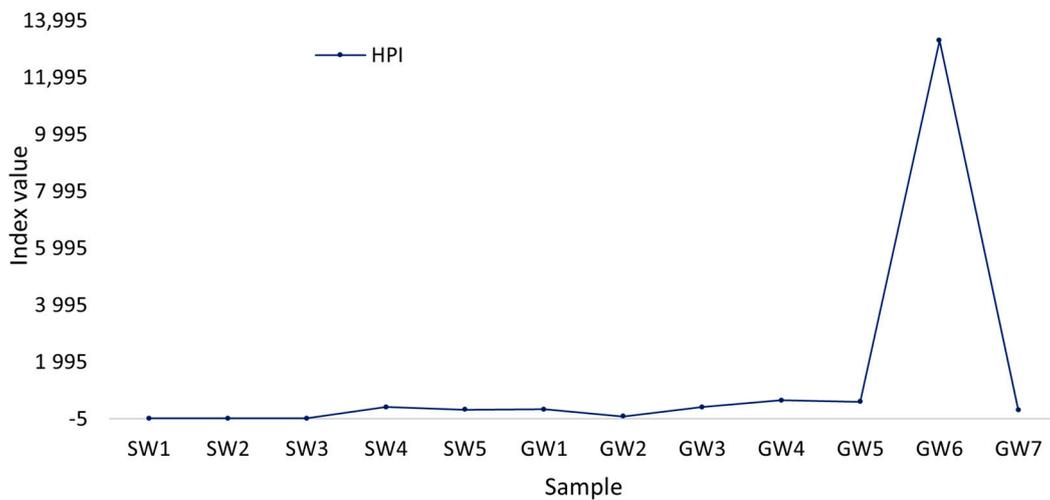


Figure 10. HPI samples studied.

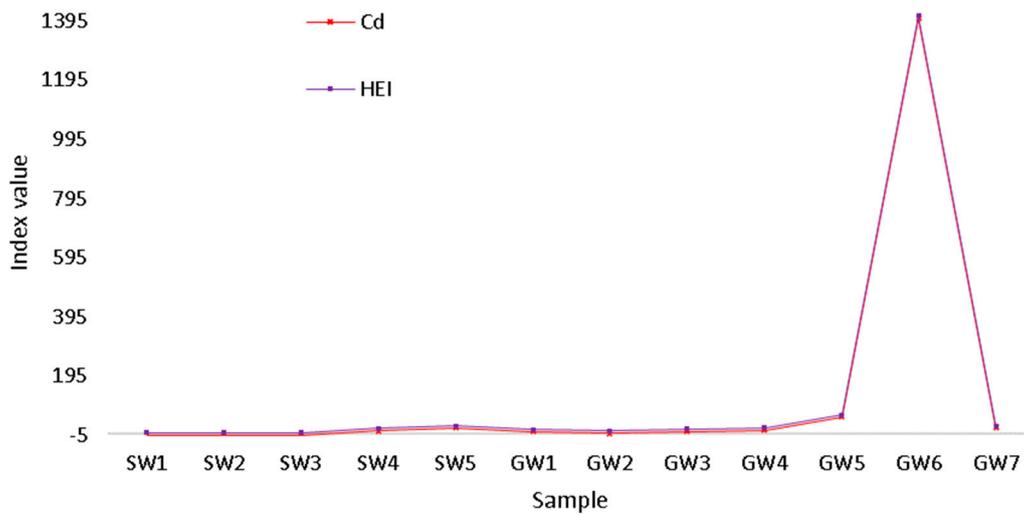


Figure 11. Cd and HEI of the samples studied.

Similar aspects that are related to the variation of the Cd, HEI, and HPI indices are presented in the sections that were analyzed in the investigation. Therefore, the difference between the HPI and the Cd in the developed points occurs through the variation in the water quality standards. The results show that the contamination indices for 90% are very much lower than the average value, which is (Cd = 126.5, HEI = 134.5, and HPI = 1378.6).

The lower part of the Parac subbasin is characterized by the presence of a large amount of contamination, which has a higher percentage due to the accumulation of water that comes from the flow that is loaded with heavy metals in the Tamboraque and Auri areas. Samples SW4, SW5, and GW1 to GW7 with contamination indices (HPI, Cd, and HEI) are higher than the critical value that presents contamination (100), for which greater importance and consideration are necessary (see Figure 12) [51].

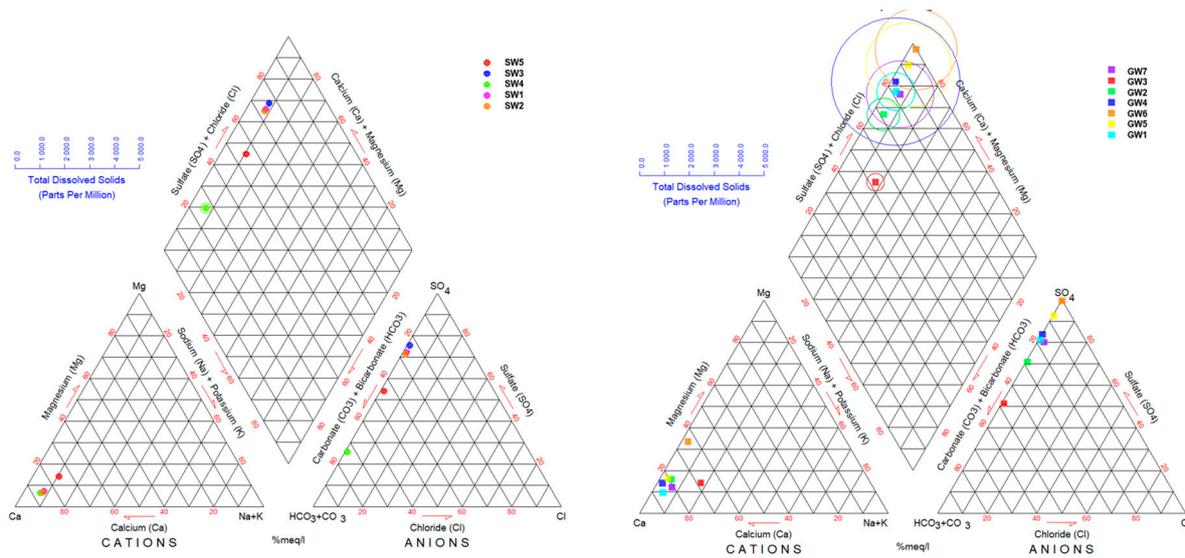
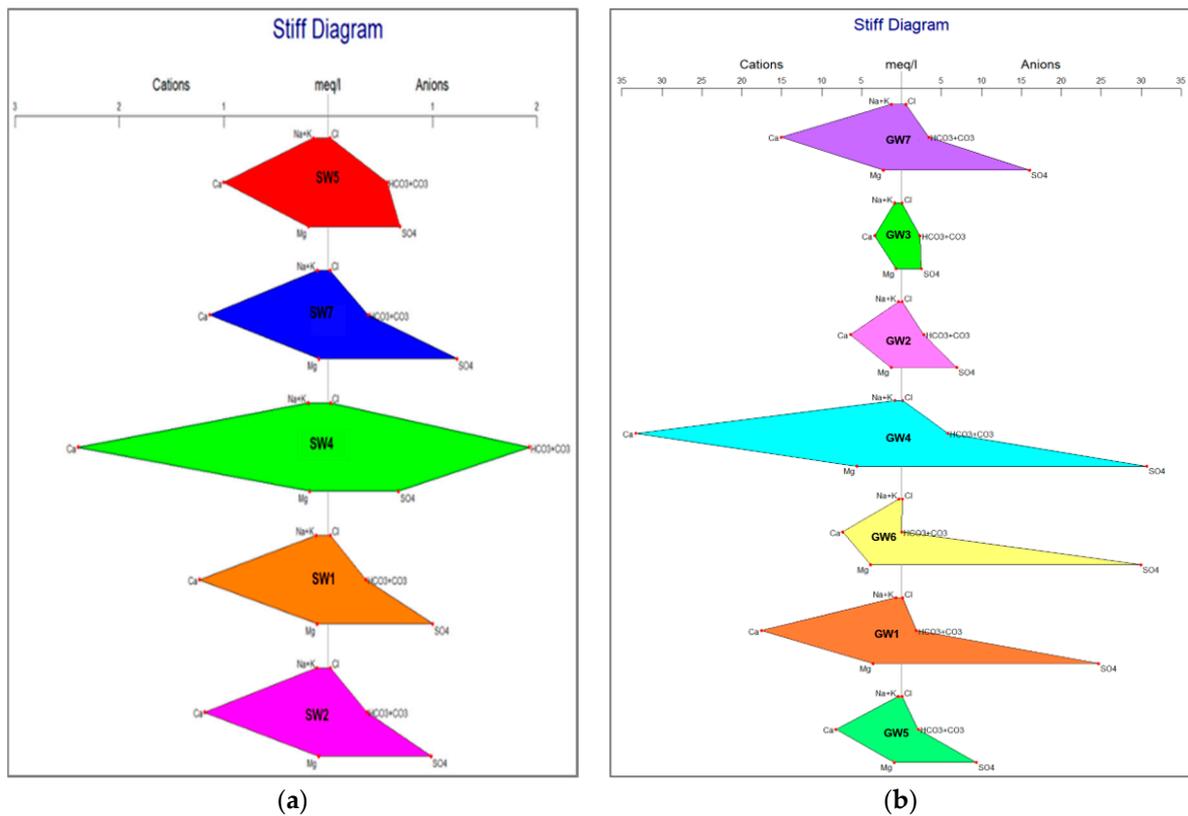


Figure 12. Piper diagram for the chemical composition of surface and groundwater samples.

The Piper diagram provides that the samples identified in the study area show multi-faceted surface water (a) which contains calcium sulfate for samples SW1, SW2, SW3, and SW5 and calcium bicarbonate for sample SW4. Additionally, groundwater (b) is calcium sulfate (see Figure 13) [52].



**Figure 13.** Stiff diagram for the chemical composition of surface and groundwater in water samples.

These waters are rich in bicarbonate and sulfate, and in the case of cations, they are composed of calcium.

The Stiff diagram was used to determine the concentration of cations and anions in each sample. The results indicate that surface water (a) is dominated by sulfate, except at point SW4 where bicarbonate is the predominant anion, and the predominant cation is calcium. In groundwater (b), sulfate is the predominant anion, and the predominant cation is calcium.

In areas where mining sectors and rural localities coexist, the harmful consequences of exposure to contaminants are reflected upon, and they affect not only the aquatic ecosystem but also human wellbeing. Ore piles that are usually in the open air are more reactive, which favors greater mobility of toxic material [53]. It is to these areas where these contaminants are moved by the physical process of surface water runoff as well as groundwater flow. Currently, most of the rivers located in Peru have been intensely damaged by the harmful effects of mining, such as the Rimac, Mantaro, Pisco, Madre de Dios, Llaucano, and Santa [54]. One of the areas impacted is the Rimac River basin, one of the three main tributary basins of the city of Lima (which concentrates about 30% of the national population), and its aquifer reserve, the main source of hydropower resources. It is also a main corridor (along the central road) for the provision of food and various products that arrive from the Amazon and the central highlands to the city of Lima. [55].

#### 4. Conclusions

The assessment of the water resources in terms of the surface and groundwater quality of the Parac river basin with the mining sites (Tamboraque area) was the aim of this study. The results provide valuable information on heavy metal contamination of the water resources. Consequently, the data obtained acquires great importance for the study of water resource contamination caused by heavy metals.

The analyses carried out with the samples obtained from both surface water and groundwater are located in neutral to extreme sectors that present a large number of

minerals in water bodies such as streams or water intakes. The results of the sampling process showed that the metals most detrimental to water resources are As, Mn, Fe, and Pb.

The result of the findings based on the contamination indices (HPI, Cd, and HEI) show that most surface water samples are above the critical contamination value (100), and special attention should be paid to these sampling sites. The HPI calculation demonstrated that around 75% of the water samples (surface and groundwater) fall in the high pollution classification category. The Cd index indicated that 16% of water samples (GW5 and GW6) qualify in the high pollution classification category. Finally, the HEI shows that only 8% of water samples (GW6) fall in high pollution. These indices represent the total quality of water with respect to heavy metals. According to the results, we could affirm that there is a pollution risk that is more pronounced in the groundwater. It is probable that the subway operations have a strong effect on this situation. The concept of the CI and HEI calculation is similar, due to the integration of the maximum permissible and the upper permissible concentration of the heavy metals, respectively.

The concept of calculation of both Cd and IHE are similar. Since it is possible to incorporate the maximum allowable concentration, and the maximum allowable concentration in relation to heavy metals. As a result, these indices represent the quality of water bodies with respect to heavy metals.

According to the statistical studies elaborated in the research, such as the Pearson correlation and the PCA, it was possible to determine two main sources of contamination origin. Those agglomerations of metals such as As, Mn, and Fe, were mainly associated with the mining industry. However, they were not very much related to sources of natural origin. Particularly, in the case of the metal Pb, the contamination found is probably due to the participation of some type of fertilizer, contrary to the metal Zn where the probability increases that the source of origin is both lithogenic and anthropogenic.

In conclusion, the researchers involved in the preparation of this study hope that it will be a very useful tool for the administrative entities in charge of environmental protection, particularly when addressing the problems related to the harmful consequences that the mining industry may have on the water resources of this region.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w15050965/s1>. Table S1. Concentration of heavy metals in surface water (SW) and groundwater (GW).

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