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Human Risk from Exposure to Heavy Metals and Arsenic in Water from Rivers with Mining Influence in the Central Andes of Peru

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Abstract: Water pollution by heavy metals is one of the leading environmental concerns as a result of intense anthropogenic pressure on the aquatic environment. This constitutes a significant limitation to the human right of access to drinking water. In this context, the risk to humans from exposure to heavy metals and arsenic in water from rivers subject to mining influence in the Central Andes of Peru was assessed. Water samples were collected from seven rivers at 63 sampling sites, and concentrations of Cu, Fe, Pb, Zn, and As were determined using flame atomic absorption spectrophotometry. Cluster analysis was used to group 21 sampling sites into four groups with similar chemical characteristics, and principal component analysis was used to simplify the complex relationship between the toxic elements by generating two main components with a total percentage of variation of 86%. Fe, Zn, and As had higher percentages of contribution in the Mantaro, Cunas, and Chia rivers. The hazard quotient was highest for children and adults. The hazard index for ingestion of all the studied heavy metals and As was higher than the threshold value ($HI_{ing} > 1$). HI_{ing} in 43% of the rivers indicated that the adult population is at risk of non-carcinogenic effects, and HI_{ing} in 14% of the rivers revealed a very high health risk. The risk of cancer by ingestion for children varied from medium to high risk and for adults from low to high risk.

Keywords: river water; heavy metals; metalloids; hazard index; non-carcinogenic risk; carcinogenic risk

1. Introduction

Water pollution by heavy metals is one of the leading global environmental problems. Heavy metals enter aquatic ecosystems through geogenic or anthropogenic sources. Geogenic sources with significant metal inputs are erosion of rocks, mineral deposits, and volcanic activities [1]. However, the most significant anthropogenic sources are poorly treated or untreated municipal and industrial effluent discharges [2,3]. Heavy metals released into the aquatic environment can enter food chains, persist in the environment, bioconcentrate, and biomagnify [4–6]. However, some metals, such as copper, zinc, iron, and cobalt, play an important role in the metabolic processes of living beings and are only considered a danger when they reach higher concentrations than required [7].

Concentrations of heavy metals and metalloids in surface waters exceeding the limits set by WHO and US EPA are indicators of risks to human health and ecosystems [8]. In humans, heavy metals can enter via the digestive, respiratory, and skin pathways. The effects of metal toxicity on human health are of great concern because they can cause liver and kidney disease and carcinogenic effects [9,10].

Rapid population growth, increasing urbanization, and rapid industrial development have accelerated water pollution. Many studies on water quality, health risks, and human rights point out that different development activities, particularly mining, constitute a great restraint on the human right to access clean drinking water. Fan et al. [11] analyzed river water quality in the Pearl River Delta in China using multivariate statistical techniques. They found that water quality is increasingly deteriorating due to anthropogenic pollution and accelerated economic development. Abdel-Satar et al. [12] evaluated the water quality of the Nile River in Egypt using environmental indices (Heavy metal pollution index and Contamination index). They revealed that Nile waters are significantly contaminated with heavy metals. Othman et al. [13] investigated the distribution, source, and environmental risk of heavy metals in the Selangor river basin in Malaysia. They found elevated concentrations of As, Fe, and Mn that exceeded standard values. Saha et al. [14] evaluated heavy metal contamination of the Bangshi River in Bangladesh, showing heavy metal concentrations above drinking water quality guidelines and a non-carcinogenic risk with mean hazard index (HI) values that were >1.0 for ingestion and dermal contact pathways.

In Latin America, Flores et al. [15] analyzed the concentrations of heavy metals in water and surface sediment of the Ilusiones Lagoon in Mexico. They found that the heavy metals in water do not exceed the standard limits of the Mexican regulations. On the other hand, the heavy metals content in sediment exceeded the limit values of the Canadian and U.S. standards, posing a risk to biota. Salazar-Lugo et al. [16] studied heavy metals in the Orinoco River aquatic environment. They found concentrations within limits for unpolluted water and sediment; however, in fish the concentrations of Cd and Pb were high. Barra-Rocha et al. [17] monitored the concentration of heavy metals in the waters of the main tributaries of the São Mateus stream basin in Brazil, finding pollution rates that were of concern due to contents of Hg, Cu, Pb, and Zn above environmental regulations.

In Peru, mining has been one of the main economic activities for more than a century. This has had negative effects on the quality of water bodies. Gammons et al. [18] monitored the levels of mercury and other heavy metals in the headwaters of the Ramis River, finding very high concentrations of Hg and other heavy metals in the headwater streams near mining centers. Monroy et al. [19] determined the concentrations of heavy metals in Lake Titicaca. This study documented high concentrations of Pb, Cu, Zn, Cd, and Hg, in the water at the discharge points of the main tributary rivers, which exceeded the safety thresholds established by international legislation. Guittard et al. [20] characterized the variability of trace metals in the Santa River Basin through a large-scale synoptic sampling, finding higher Mn concentrations than international standards, and this implies possible detrimental effects on human and ecosystem health.

Heavy metals have the ability to replace some cations in the metabolism, resulting in health effects [21]. Lead (Pb) tends to replace bivalent cations such as magnesium (Mg^{2+}), calcium (Ca^{2+}), and iron (Fe^{2+}), interfering with various biological processes such as ion transport, protein folding, cell signaling, cell adhesion, and vitamin D metabolism [22,23]. Consumption of water contaminated by toxic elements or of unknown quality puts consumers at risk of possible diseases [20,24]. Many studies report that exposure to heavy metals and metalloids is associated with various chronic diseases ranging from dermatitis to carcinogenic effects [25].

In response to growing concern regarding the health effects of heavy metal contamination of water, many countries have implemented a water policy in their legislation [26]. However, in developing countries, this policy focuses on major cities and not on most cities where the population does not have access to safe drinking water or where the water supply is intermittent. In Peru, the logistics of good water use are being deployed; however, this is not enough if this resource is not managed efficiently. Priority must not only be on availability but also on quality.

Peruvian government institutions still use conventional methods to evaluate the effect of heavy metals on health, comparing the concentrations of these contaminants with the maximum permissible limits in Peruvian regulations. However, these methods are not reliable for estimating detailed risk levels. In order to achieve an effective assessment of the impact of water quality on health, health risk assessments should be carried out using techniques that allow for the estimation of risks based on the toxicity burden of heavy metals in water [27]. The Mantaro River basin plays a very important role in the economy of Peru and the agricultural production of this basin provides food to several regions of the country. The main objective of this study was to analyze the concentration of heavy metals and arsenic in water from seven rivers subject to mining influence in the Central Andes of Peru and assess these data using multivariate statistical methods. Based on the concentrations of heavy metals and arsenic detected, the human risk was then evaluated.

2. Materials and Methods

2.1. Study Area

The rivers included in the study are located in the Mantaro river watershed located in the Andes Mountains, central region, between the parallels 10°34′30″ and 13°35′30″ south latitude and the meridians 73°55′00″ and 76°40′30″ west longitude. This basin is characterized by a complex topography that gives rise to a variety of contrasting climatic conditions. In the northern sector of the basin, the semi-frigid humid climate predominates with a rainy season in summer and a dry season in winter. In the central sector, the climatic conditions vary between a cold wet climate and a semifrigid wet climate, and in the south (2000–2500 masl) rainfall can be >1500 mm [28].

The Mantaro river, the main river in the basin, runs through areas subject to significant mining influence, from the city of Cerro de Pasco to the Cobriza mine (located in the southeast of the basin). Three sampling sites were established in the Mantaro river. The first site is located downstream of the city of La Oroya, where one of the most important metallurgical centers in South America is located [29]. At the second site, south of the village of San Juan de Pachacayo, the main economic activity is livestock. The third site, in Jauja, is located in an area with substantial agricultural activity in the Mantaro Valley. In the tributary rivers Cunas, Shullcas, Chía, Chilca, Miraflores, and Chanchas, the sampling sites were located in the upper, middle, and lower zone of each river (Figure 1).

2.2. Sampling, Analytical Determination, and Quality Control

The water sampling was carried out in autumn 2019. The water samples were obtained in triplicate at each site in the opposite direction of the flow of the stream at a depth of 20 cm. The sample containers were two-liter plastic bottles, previously treated with a 10% nitric acid solution for 24 h and rinsed with distilled water and water from the sampling site, repeatedly. The conservation of each of the samples was achieved by adding 1.5 mL of concentrated nitric acid to one liter of water [30]. Then, the samples in refrigerated conditions were sent to the Laboratory of Chemistry and Environment of the National University of Central Peru for the determination of Cu, Fe, Pb, Zn, and As.

The laboratory methods used for analytical determinations corresponded to those specified in the American Public Health Association's International Analytical Standards [31]. The digestion of the samples was carried out from 250 mL of water, brought to a boil to obtain 100 mL. Then, 5 mL of nitric acid and 5 mL of concentrated hydrochloric acid were added for the destruction of organic matter, and it was again brought to a boil until the water was consumed and a residue of pasty consistency was obtained. This was left to cool, and then, 10 mL of distilled water was added, filtered, and measured in a 100 mL vial, with 1% nitric acid. The concentration of Cu, Fe, Pb, Zn, and As (mg/L) was determined using atomic absorption spectrophotometry by flame, with an Atomic Absorption Spectrophotometer, Varian AA240.

Quality control was performed through the application of standard laboratory measurements and quality control methods that included replication, the use of standards for each metal investigated, and the determination of the accuracy of the instrument [30]. Standard solutions for Pb, Cu, iron (Fe), zinc (Zn), and As were supplied by Merck (Germany) with the highest purity level (99.98%). With the

1000 mg/L standard for Pb, Cu, Fe, Zn, and As, an average standard of 100 mg/L concentration was prepared. Then, working standards of 0.001, 0.01, 0.1, 1.0, and 2.0 mg/L were prepared, with 1% nitric acid. The detection limits varied from 0.001 to 0.0015 mg/L.

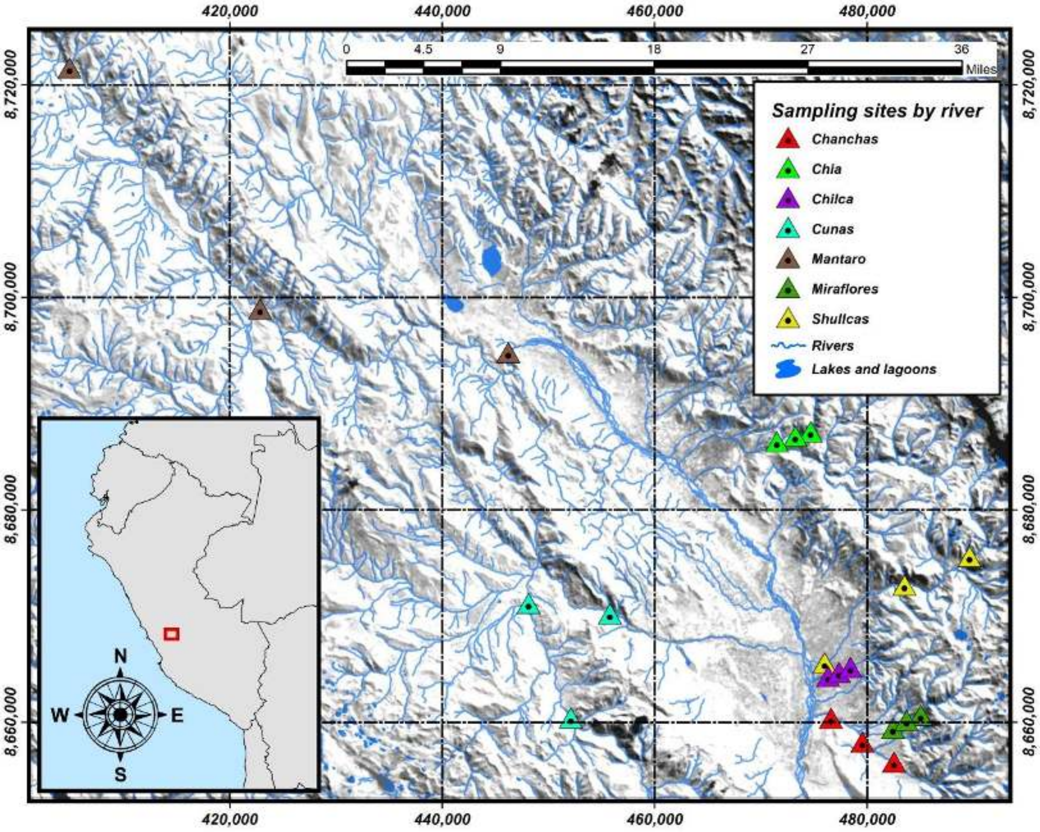

Figure 1. Location of the Mantaro river basin, tributary rivers, and sampling sites.

2.3. Statistical Analysis

The correlation structure between variables was analyzed using Spearman's coefficient because the data for heavy metal and arsenic concentrations were not normally distributed. Principal component analysis was performed with standardized z-scale data to avoid erroneous classification [32,33]. Cluster analysis by the Ward method was performed to group samples according to Euclidean distances with similar multivariate trends [34]. Multivariate analysis of permutational variance was used to contrast differences between fixed groups (rivers). The p-value generated permutation was made from 1000 iterations of the algorithm.

2.4. Human Health Risk Assessment

2.4.1. Exposure Dose

The human health risk assessment estimate the health effects that could arise from the combined exposure to carcinogenic and non-carcinogenic chemicals [35,36]. The risk assessment was performed on the basis of exposure doses (D) to heavy metals and arsenic in water by ingestion and dermal pathways using Equations (1) and (2).

$$\mathrm{D_{ing}} = \frac{\mathrm{C_{agua}} \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \tag{1}$$

$$\mathrm{D_{der}} = \frac{\mathrm{C_{agua}} \times \mathrm{SA} \times \mathrm{KP} \times \mathrm{ET} \times \mathrm{EF} \times \mathrm{ED} \times \mathrm{CF}}{\mathrm{BW} \times \mathrm{AT}} \tag{2}$$

where D_{ing} is the exposure dose through water ingestion (µg/kg/day); D_{der} is the exposure dose through dermal absorption (µg/kg/day); C is the measured metal concentration in water (µg/L); IR is the ingestion rate per unit time (L/day), 2.2 L/day for adults, 1.8 L/day for children; EF is the exposure frequency (350 days/year); ED is the exposure duration (70 years for adults, 6 years for children); BW is the average body weight (70 kg for adults, 15 kg for children); AT is the average exposure time (25,550 days for adults, 2190 days for children); SA is the exposed skin area (18,000 cm^2 for adults, 6600 cm^2 for children); ET is the exposure time (0.58 h/ day for adults, 1 h/ day for children); CF is the unit conversion factor (0.001 L/cm^3); and KP is the dermal permeability coefficient (cm/h). The coefficients of dermal permeability for Cu, Pb, Zn, Fe, and As are given as 0.001, 0.004, 0.006, 0.001, and 0.001, respectively [37].

2.4.2. Non-Carcinogenic Risk Assessment

Non-carcinogenic risk was evaluated using the hazard quotient (HQ), which was calculated by dividing the exposure value by the reference dose [38].

$$\mathrm{HQ}_{\mathrm{ing/der}} = \mathrm{D}_{\mathrm{ing/der}} / \mathrm{RfD}_{\mathrm{ing/der}} \tag{3}$$

where $HQ_{ing/der}$ is the hazard quotient for ingestion or skin contact. $RfD_{ing/der}$ is the oral/dermal reference dose (µg/kg/day) obtained from the literature [39,40].

A value of $HQ \leq 1$ indicates that adverse health effects are unlikely. $HQ > 1$ reveals probable adverse health effects. $HQ > 10$ indicates high chronic risk.

The general potential for non-carcinogenic effects has been assessed by integrating the HQs calculated for each element and expressed as a hazard index [40].

$$\mathrm{HI} = \sum_{i=1}^{n} \mathrm{HQ}_{\mathrm{ing/der}} \tag{4}$$

where $HI_{ing/der}$ is the hazard index for ingestion or dermal contact. *n* is the total number of chemical elements considered.

If $HI < 1$, the non-carcinogenic adverse effect due to a particular route of exposure or chemical is assumed to be insignificant.

2.4.3. Carcinogenic Risk Assessment

Carcinogenic risk was assessed taking into account the United States Environmental Protection Agency's risk assessment guidance [37]. Previously, the chronic daily intake (CDI) was calculated using the formula:

$$\mathrm{CDI}_{\mathrm{ing}} = \mathrm{C}_{\mathrm{water}} \times \mathrm{DI} / \mathrm{BW} \tag{5}$$

where Cwater, DI, and BW represent the concentration of metal trace in the water (µg/kg), mean daily water intake, and body weight, respectively.

The cancer risk (CR) was calculated using the formula:

$$\mathrm{CR}_{\mathrm{ing}} = \mathrm{CDI}_{\mathrm{ing}} / \mathrm{SF}_{\mathrm{ing}} \tag{6}$$

where SF_{ing} is the slope factor of cancer. SF_{ing} for Pb is 8.5, and As is 15.0×10^2 µg/kg/day [35].

A value of $CR > 1.0 \times 10^{-4}$ is considered unacceptable; $1.0 \times 10^{-4} < CR < 1.0 \times 10^{-6}$ is considered an acceptable range depending on the exposure conditions; $CR < 1.0 \times 10^{-6}$ is considered not to have significant health effects.

3. Results

3.1. *Analysis of Heavy Metals and Arsenic in River Water Subject to Mining Influence*

Table 1 shows the mean concentration, standard deviation, and the maximum and minimum values of heavy metals and arsenic determined in water from rivers subject to mining influence in the Central Andes of Peru. The mean copper concentration ranged from 0.99 to 14.60 µg/L, in the Chanchas and Mantaro rivers, respectively. The maximum concentration of copper was registered in the Mantaro River. This value did not exceed the environmental quality standards (EQS) for water in the Peruvian regulations for its various uses (except EQS for water intended for recreational use), nor those of the WHO and US EPA (2×10^3 µg/L). The mean lead concentration in the rivers showed similar features as Cu, as these did not exceed the EQS for drinking water (10 µg/L), fish farming (200 µg/L), and irrigation (200 µg/L). Waters from the Mantaro and Chilca rivers had mean Pb concentrations that exceeded the EQS water for recreation (8.1 µg/L) and fish farming (2.5 µg/L). The Mantaro river had maximum lead values of 20 µg/L. This far exceeds the environmental water quality standards for its various uses. The mean concentrations of Zn and Fe did not exceed national and international water quality standards. However, the mean As concentrations exceeded the EQS for water in 40% of the rivers evaluated. The Chia river showed maximum As values of 23.00 µg/L, while the Mantaro river showed a maximum value of 21.10 µg/L. In both rivers, the average concentrations exceeded the WHO drinking water guidelines and the EQS for water in Peru (10.0 µg/L).

Table 1. Heavy metal and arsenic concentrations in river waters in the Central Andes of Peru and limit values for various uses, expressed in µg/L.

Rivers	Cu	Pb	Zn	Fe	As
	Mean ± SD Max − Min	Mean ± SD Max − Min	Mean ± SD Max − Min	Mean ± SD Max − Min	Mean ± SD Max − Min
Chanchas	0.99 ± 0.12 8.70 − 1.00	4.00 ± 0.10 4.10 − 3.90	13.20 ± 3.50 16.70 − 9.70	217.00 ± 72.00 289.00 − 145.00	nd
Chía	1.37 ± 0.06 1.40 − 1.30	nd	15.30 ± 0.30 15.60 − 15.00	14.40 ± 4.40 18.80 − 10.00	17.67 * ± 4.73 23.00 − 14.00
Chilca	1.20 ± 0.20 1.40 − 1.00	2.80 ± 2.14 4.50 − 0.40	6.30 ± 50 6.80 − 5.80	157.10 ± 10.10 167.20 − 147.00	0.70 ± 0.01 0.71 − 0.69
Cunas	1.90 ± 0.20 2.10 − 1.70	nd	9.30 ± 0.80 10.10 − 8.50	9.50 ± 2.40 11.90 − 7.10	8.00 ± 1.00 9.00 − 7.00
Mantaro	14.60 ± 7.37 21.60 − 6.90	9.50 ± 9.10 20.0 − 4.0	58.30 ± 32.10 90.7 − 26.6	1140 * ± 1488.0 2841.0 − 502.5	21.10 * ± 7.82 26.2 − 12.1
Miraflores	1.70 ± 0.10 1.80 − 1.60	nd	11.20 ± 0.60 11.80 − 10.60	183.20 ± 5.20 188.40 − 178.00	nd
Shullcas	1.13 ± 0.15 1.30 − 1.00	0.73 ± 0.06 0.80 − 0.70	13.30 ± 1.50 14.80 − 11.80	91.00 ± 4.70 91.00 − 86.30	1.67 ± 1.16 1.00 − 0.70
WHO Drinking water guidelines	2×10^3	10	3×10^3	300	10
US EPA Drinking Water Standards	1×10^3	0.0	5×10^3	300	0.0
Peruvian Drinking water EQS	2×10^3	10	3×10^3	300	10
Recreational water	3.1	8.1	81	na	50
Water for fish	200	2.5	1×10^3	na	100 farming
Water	200	50	2×10^3	5×10^3	100 irrigation

* Significantly higher than the maximum permissible standard ($p < 0.05$) nd: not detected na: not applicable.

The decreasing order of metal molar concentrations in the Chanchas river was Fe (3.89×10^{-3}) > Zn (2.02×10^{-4}) > Pb (1.9×10^{-5}) > Cu (1.6×10^{-5}); in the Chia river: Fe (2.58×10^{-4}) > As (2.36×10^{-4}) > Zn (2.34×10^{-4}) > Cu (2.2×10^{-5}); in the Chilca: Fe (2.81×10^{-3}) > Zn (9.6×10^{-5}) > Cu (1.9×10^{-5}) > Pb (1.4×10^{-5}) > As (9×10^{-6}); in the Cunas: Fe (1.7×10^{-4}) > Zn (1.42×10^{-4}) > As (1.07×10^{-4}) > Cu (3×10^{-5}); in the Mantaro: Fe (2.04×10^{-2})> Zn (8.92×10^{-4})> As (2.82×10^{-4}) > Cu (2.3×10^{-4}) > Pb

(4.6 × 10^{-5});in the Miraflores: Fe (3.28 × 10^{-3}) > Zn (1.71 × 10^{-4}) > Cu (2.7 × 10^{-5}); and in the Shullcas: Fe (1.63 × 10^{-3}) > Zn (2.03 × 10^{-4}) > As (2.2 × 10^{-5}) > Cu (1.8 × 10^{-5}) > Pb (4 × 10^{-6}). Pb was not detected in the Chía, Cunas, and Miraflores rivers; in the rivers Chanchas and Miraflores, no As was detected.

Figure 2 shows the correlation matrix between heavy metals and arsenic in river water subject to mining influence. This figure reveals that As is significantly ($p < 0.05$) correlated with Cu and Zn and significantly negatively correlated with Fe. The correlation between As and Cu exhibited a high correlation coefficient (rho = 0.52), denoting that their concentrations are related. Pb showed a positive correlation trend with Fe (rho = 0.61) and a non-significant negative correlation trend with Cu (rho = −0.13).

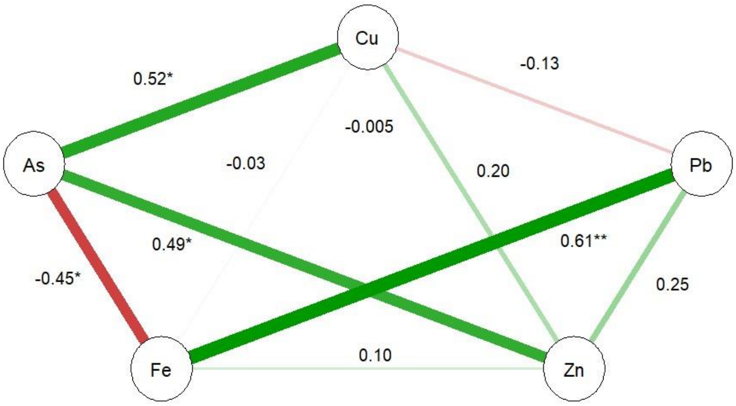

Figure 2. Spearman correlation matrix between heavy metals and arsenic in river water with mining influence.

PERMANOVA analysis rejected the null hypothesis ($p = 0.01$) that the groups would be statistically homogeneous, with the location of the sampling sites as a factor, with an R^2 of 0.92 and a pseudo-F of 61.9. Cluster analysis identified four distinct groups among the observation sites (Figure 3). Group 1 is made up of the Mantaro River sampling sites. Compared the other groups, this is the most influenced by heavy metals and arsenic. At the other end of the spectrum, Group 3 represents the sites most impacted by arsenic. The rivers that make up this group are the Cunas and Chia. The former has experienced urban expansion in the areas adjacent to the river margins, as well as intensive agriculture, and subsistence fishing activity. Chía river has consolidated human settlements around the aquaculture industry [41]. Groups 2 and 4 represent mixed conditions with surface disturbances to varying degrees. The heavy metals that tend to differentiate them are zinc and lead, but they are not significantly different.

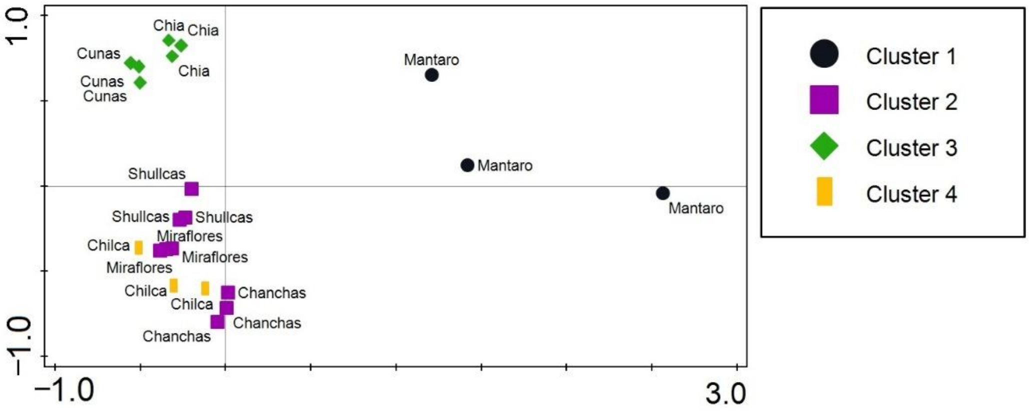

Figure 3. Distribution of observations and hierarchical clustering by river.

The result of the principal component analysis showed that the first two components accounted for 86% of the variation in the data. This implies that the variance of the variables studied is mainly explained by these two extracted components. The first component represented 63.9% of the total variance. A correlational component loading (CCL) >0.75 means "strong" association with the component under study; values of $0.50 < CCL < 0.75$ indicate "moderate" association, and values of $0.30 < CCL < 0.50$ denote "weak" association [42,43]. The first component showed a strong positive load for Zn, Fe, Cu, Pb, and As and the second component for As (Figure 4).

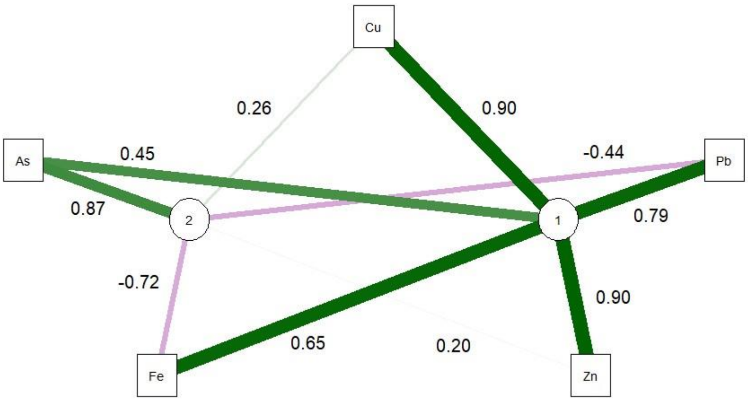

Figure 4. Correlation of heavy metal and arsenic vectors with major components.

The first principal component indicates that the waters of the Mantaro river have higher concentrations of Cu, Zn, and Pb. This is due to the proximity of the sampling sites to the metallurgical center of La Oroya. The sites in the Cunas and Chia rivers have similar chemical element concentrations as the Shullcas, Miraflores, Chanchas, and Chilca rivers, but they differ in arsenic concentrations. This is due to the fact that the sites in the Cunas and Chia rivers have higher arsenic values in contrast to the other less contaminated rivers. Principal component 2 shows a much lower eigenvalue and total variance compared to Principal component 1 (Figure 5).

Figure 6 shows the percentage molar distribution of heavy metals and arsenic, by sampling site, from the downstream to the upstream of each river. Iron, zinc, and arsenic constituted the highest percentages of contribution in the Mantaro, Cunas, and Chia rivers. In the Mantaro River, at the sampling site nearest the metallurgical center of La Oroya (site 3), the percentage contributions of iron, zinc, and arsenic were 58.23%, 16.98%, and 13.93%, respectively. In the Cunas River, the highest contributions of iron (43.69%) and zinc (31.67%) were recorded at Site 2, and that of arsenic (26.90) at Site 3. In the Chia River, the highest contributions of iron (37.68%) and arsenic (34.36%) were recorded in Site 3 and that of zinc (36.52%) in Site 2.

Table 2 shows the generalized linear model (GLM) analysis conducted to determine whether any of the heavy metals had a significant functional relationship with arsenic. The analysis indicates that only copper shows a direct and significant relationship with arsenic.

3.2. Human Health Risk Assessment

The non-carcinogenic health risks for various heavy metals and arsenic in both children and adults were determined based on hazard quotient (HQ) values. Ingestion HQ values were higher than dermal HQ values in both children and adults, due to Pb and As. In the Mantaro river, the HQ_{ing} values decreased in the following order: As > Pb > Fe > Cu > Zn. Similar trends were observed in the rivers Shullcas and Chilca. In the rivers Cunas, Miraflores, and Chía, the HQ_{ing} values in descending order were As > Cu > Zn > Fe, while in the Chanchas river the HQ_{ing} values decreased in the following order: Pb > Fe > Cu > Zn (Table 2).

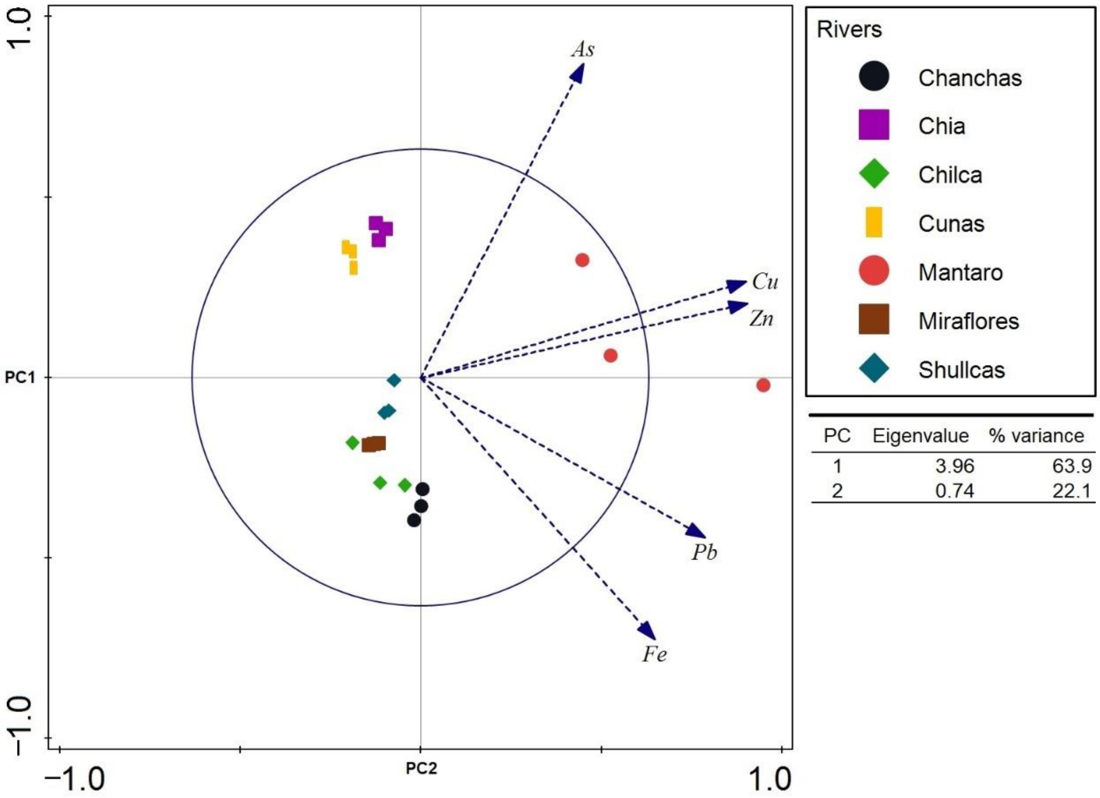

Figure 5. Perceptual map of the sampling sectors and heavy metal vectors in the principal component analysis.

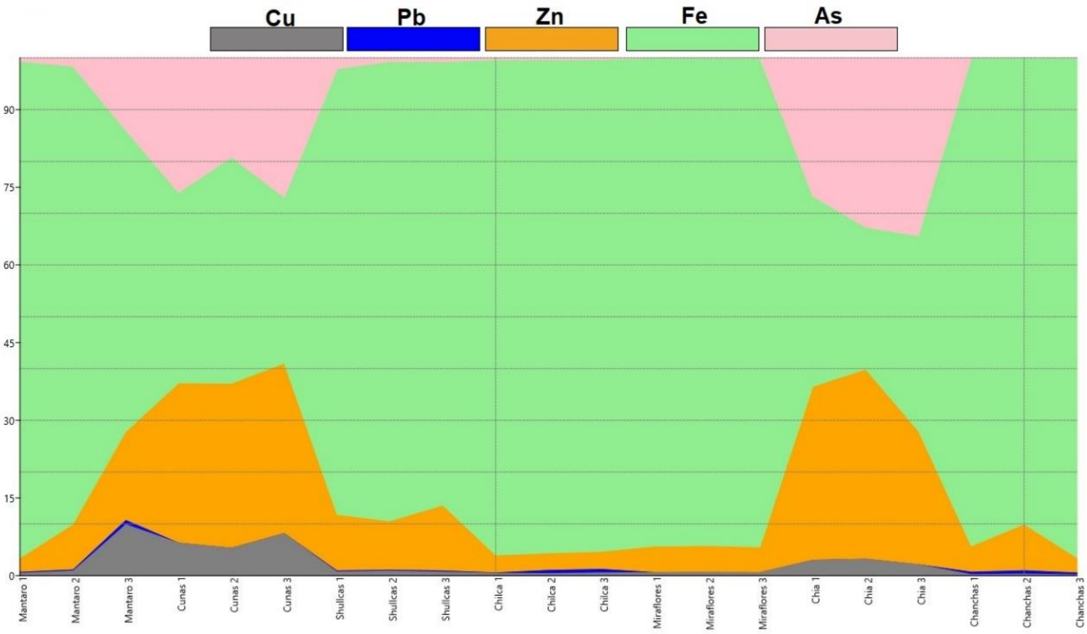

Figure 6. Distribution of the percentage contribution of heavy metals and arsenic by sampling site and river.

Table 2. Analysis of generalized linear models of heavy metals and arsenic in river water in the Central Andes of Peru.

Response Variable		**As**		
Expected distribution	Gaussian	with identity link function		
Fitted model deviance	607.74	with 16 residual DFs		
Null model deviance	1610.70	with 20 residual DFs		
Parsimony (AIC-like)	148.27			
F statistic	6.60	(DF = 4.16)		
p(F)				0.00246
Term	b	SE	T	p(T)
(Intercept)	1.416	2.228	0.640	0.534
Cu	1.519	0.534	2.840	**0.012**
Pb	−0.902	0.956	−0.940	0.360
Zn	0.219	0.176	1.250	0.230
Fe	−0.004	0.008	−0.580	0.573

For children, the HQ_{ing} values of As in the Mantaro River were significantly higher than the HQ_{ing} values of heavy metals; this is due to the high concentrations of this metalloid in the waters of this river. At site 1, As HQ_{ing} values indicated high chronic risk ($HQ_{ing} > 10$), while in the other two sites they HQ_{ing} indicated probable adverse health effects ($HQ_{ing} > 1$). Pb HQ_{ing} values indicated probable adverse health effects at site 1 and unlikely adverse health effects in the other two sites. The HQ_{ing} values for Cu, Zn, and Fe indicated that adverse health effects are unlikely ($HQ_{ing} < 1$). The HQ_{ing} values of As in the Cunas and Chia rivers indicated probable adverse health effects (Table 3), while the heavy metal HQ_{ing} values determined for these rivers indicated that adverse health effects are unlikely. Similarly, HQ_{ing} values obtained for heavy metals from the rivers Shullcas, Chilca, Miraflores, and Chanchas indicated that adverse health effects are unlikely. For adults, As HQ_{ing} values in the Mantaro river were higher than heavy metal HQ_{ing} values ($1 < HQ_{ing} < 10$), indicating probable adverse health effects. Similar trends were found for the values of As HQ_{ing} in the Chia river. The heavy metal HQ_{ing} values studied were below the permitted limit and indicated that adverse health effects are unlikely. However, the combined hazard index for ingestion registered HI > 1 values in 43.0% of the rivers evaluated, indicating that the adult population are at risk of suffering non-carcinogenic effects due to the combined effects of heavy metals and As. HI > 10 values were recorded in 14.0% of the rivers; this revealed a very high risk to health.

Table 4 shows the non-carcinogenic skin contact risk of heavy metals and arsenic in water for children and adults. The results reveal a risk considerably below the permitted limit (HQ and HI less than 1), indicating that there is no evident risk to the population in the study area via the dermal pathway [35]. Overall, the results reveal that children are most vulnerable to acute and chronic effects of heavy metal and arsenic intake. This is due to the fact that children consume more water per unit of body weight than adults [37].

Table 3. Non-carcinogenic risk by ingestion (HQ$_{\text{ing}}$ and HQ$_{\text{ing}}$) of heavy metals and arsenic in river water subject to mining influence (children and adults).

River	Sector	Cu	Pb	Zn	Fe	As	HQ$_{\text{ing-children}}$	Cu	Pb	Zn	Fe	As	HQ$_{\text{ing-adults}}$
Mantaro	S1	0.06	1.64	0.03	0.47	10.05	**12.26**	0.02	0.43	0.78	0.12	2.63	**3.98**
	S2	0.02	0.37	0.02	0.08	4.64	**5.14**	0.01	0.10	0.50	0.02	1.22	**1.83**
	S3	0.04	0.33	0.01	0.01	9.59	**9.98**	0.01	0.09	0.23	0.00	2.51	**2.83**
Cunas	S1	0.01	nd	0.00	0.00	3.45	**3.46**	0.00	nd	0.08	0.00	0.90	**0.98**
	S2	0.00	nd	0.00	0.00	2.68	**2.70**	0.00	nd	0.09	0.00	0.70	**0.79**
	S3	0.01	nd	0.00	0.00	3.07	**3.08**	0.00	nd	0.07	0.00	0.80	**0.88**
Shullcas	S1	0.00	0.06	0.01	0.01	1.15	**1.23**	0.00	0.02	0.11	0.00	0.30	**0.43**
	S2	0.00	0.06	0.00	0.02	0.38	**0.47**	0.00	0.02	0.10	0.00	0.10	**0.22**
	S3	0.00	0.07	0.01	0.01	0.38	**0.47**	0.00	0.02	0.13	0.00	0.10	**0.25**
Chilca	S1	0.00	0.03	0.00	0.03	0.27	**0.33**	0.00	0.01	0.05	0.01	0.07	**0.14**
	S2	0.00	0.29	0.00	0.02	0.26	**0.58**	0.00	0.08	0.05	0.01	0.07	**0.20**
	S3	0.00	0.37	0.00	0.03	0.27	**0.68**	0.00	0.10	0.06	0.01	0.07	**0.23**
Miraflores	S1	0.00	nd	0.00	0.03	nd	**0.04**	0.00	nd	0.10	0.01	nd	**0.10**
	S2	0.01	nd	0.00	0.03	nd	**0.04**	0.00	nd	0.10	0.01	nd	**0.11**
	S3	0.00	nd	0.00	0.03	nd	**0.04**	0.00	nd	0.09	0.01	nd	**0.10**
Chía	S1	0.00	nd	0.01	0.00	5.37	**5.38**	0.00	nd	0.13	0.00	1.41	**1.54**
	S2	0.00	nd	0.01	0.00	6.14	**6.15**	0.00	nd	0.13	0.00	1.61	**1.74**
	S3	0.00	nd	0.01	0.00	8.82	**8.83**	0.00	nd	0.13	0.00	2.31	**2.44**
Chanchas	S1	0.00	0.33	0.01	0.04	nd	**0.37**	0.00	0.09	0.11	0.01	nd	**0.21**
	S2	0.03	0.32	0.01	0.02	nd	**0.38**	0.01	0.08	0.14	0.01	nd	**0.23**
	S3	0.00	0.34	0.00	0.05	nd	**0.39**	0.00	0.09	0.08	0.01	nd	**0.18**

nd: not determined.

Table 4. Non-carcinogenic risk by dermal contact (HQ_{derm} and HI_{derm}) of heavy metals and arsenic in river water with mining influence (children and adults).

River	Sector	Cu	Pb	Zn	Fe	As	$HI_{derm\text{-}children}$	Cu	Pb	Zn	Fe	As	$HI_{derm\text{-}adults}$
Mantaro	S1	0.00	0.08	0.00	0.01	0.04	**0.13**	0.00	0.03	0.00	0.00	0.01	**0.04**
	S2	0.00	0.02	0.00	0.00	0.02	**0.04**	0.00	0.01	0.00	0.00	0.01	**0.01**
	S3	0.00	0.02	0.00	0.00	0.04	**0.05**	0.00	0.01	0.00	0.00	0.01	**0.02**
Cunas	S1	0.00	nd	0.00	0.00	0.01	**0.01**	0.00	nd	0.00	0.00	0.00	**0.00**
	S2	0.00	nd	0.00	0.00	0.01	**0.01**	0.00	nd	0.00	0.00	0.00	**0.00**
	S3	0.00	nd	0.00	0.00	0.01	**0.01**	0.00	nd	0.00	0.00	0.00	**0.00**
Shullcas	S1	0.00	0.00	0.00	0.00	0.00	**0.01**	0.00	0.00	0.00	0.00	0.00	**0.00**
	S2	0.00	0.00	0.00	0.00	0.00	**0.00**	0.00	0.00	0.00	0.00	0.00	**0.00**
	S3	0.00	0.00	0.00	0.00	0.00	**0.01**	0.00	0.00	0.00	0.00	0.00	**0.00**
Chilca	S1	0.00	0.00	0.00	0.00	0.00	**0.00**	0.00	0.00	0.00	0.00	0.00	**0.00**
	S2	0.00	0.01	0.00	0.00	0.00	**0.02**	0.00	0.00	0.00	0.00	0.00	**0.01**
	S3	0.00	0.02	0.00	0.00	0.00	**0.02**	0.00	0.01	0.00	0.00	0.00	**0.01**
Miraflores	S1	0.00	nd	0.00	0.00	nd	**0.00**	0.00	nd	0.00	0.00	nd	**0.00**
	S2	0.00	nd	0.00	0.00	nd	**0.00**	0.00	nd	0.00	0.00	nd	**0.00**
	S3	0.00	nd	0.00	0.00	nd	**0.00**	0.00	nd	0.00	0.00	nd	**0.00**
Chía	S1	0.00	nd	0.00	0.00	0.02	**0.02**	0.00	nd	0.00	0.00	0.01	**0.01**
	S2	0.00	nd	0.00	0.00	0.02	**0.02**	0.00	nd	0.00	0.00	0.01	**0.01**
	S3	0.00	nd	0.00	0.00	0.03	**0.03**	0.00	nd	0.00	0.00	0.01	**0.01**
Chanchas	S1	0.00	0.02	0.00	0.00	nd	**0.02**	0.00	0.01	0.00	0.00	nd	**0.01**
	S2	0.00	0.02	0.00	0.00	nd	**0.02**	0.00	0.01	0.00	0.00	nd	**0.01**
	S3	0.00	0.02	0.00	0.00	nd	**0.02**	0.00	0.01	0.00	0.00	nd	**0.01**

nd: not determined.

Table 5 shows the carcinogenic risk for children and adults by ingestion of arsenic measured in river water subject to mining influence. The carcinogenic risk of As to children through ingestion of river water varied from 6.49×10^{-5} (medium cancer risk) in the Chilca River to 2.63×10^{-3} (high cancer risk) in the Mantaro River. However, the Chia, Cunas, and Shullcas rivers also revealed cancer risk associated with this metalloid. The risk levels of As-induced cancer for children through the ingestion of water from the Chia, Cunas, and Shullcas rivers were high, with maximum values of 2.31×10^{-3}, 9.04×10^{-4}, and 3.01×10^{-4}, respectively, while, the risk level of As-induced cancer through the water of Chilca river qualified as medium risk. These results suggest that the carcinogenic risk of As from ingestion of water contaminated by this metalloid is higher in children than in adults.

Table 5. Carcinogenic risk by ingestion arsenic and lead in river water subject to mining influence (children and adults).

River	Sector	As		Pb	
		Children	Adults	Children	Adults
Mantaro	S1	2.63×10^{-3}	1.12×10^{-3}	1.14×10^{-5}	6.73×10^{-2}
	S2	1.22×10^{-3}	5.20×10^{-4}	2.56×10^{-6}	1.51×10^{-2}
	S3	2.51×10^{-3}	1.07×10^{-3}	2.28×10^{-6}	1.35×10^{-2}
Cunas	S1	9.05×10^{-4}	3.86×10^{-4}	nd	nd
	S2	7.04×10^{-4}	3.00×10^{-4}	nd	nd
	S3	8.04×10^{-4}	3.43×10^{-4}	nd	nd
Shullcas	S1	3.02×10^{-4}	1.29×10^{-4}	3.99×10^{-6}	2.36×10^{-3}
	S2	1.01×10^{-4}	4.29×10^{-5}	3.99×10^{-7}	2.36×10^{-3}
	S3	1.01×10^{-4}	4.29×10^{-5}	4.56×10^{-7}	2.69×10^{-3}
Chilca	S1	7.04×10^{-5}	3.00×10^{-5}	2.28×10^{-7}	1.35
	S2	6.94×10^{-5}	2.96×10^{-5}	1.99×10^{-6}	1.18×10^{-2}
	S3	7.14×10^{-5}	3.05×10^{-5}	2.56×10^{-6}	1.51×10^{-2}
Chía	S1	1.41×10^{-3}	6.01×10^{-4}	nd	nd
	S2	1.61×10^{-3}	6.86×10^{-4}	nd	nd
	S3	2.31×10^{-3}	9.87	nd	nd
Chanchas	S1	nd	nd	2.28×10^{-6}	1.35×10^{-2}
	S2	nd	nd	2.22×10^{-6}	1.31×10^{-2}
	S3	nd	nd	2.34×10^{-6}	1.38×10^{-2}

The adult carcinogenic risk of As through ingestion of water from the rivers ranged from 2.96×10^{-5} (medium cancer risk) to 1.124×10^{-3} (high cancer risk). Adult As-induced cancer risk levels were also high for the waters of the Chía and Cunas rivers and a sector of the Shullcas (in urban sectors). The results also revealed a low cancer risk for this metalloid for the waters of the Chilca and Shullcas rivers (two sectors). The risk of Pb-induced cancer for children varied from 2.28×10^{-7} (very low cancer risk) in the Chilca river to 1.14×10^{-5} (low cancer risk) in the Mantaro river, while in adults the risk varied from 2.63×10^{-3} (high cancer risk) in the Shullcas river to 6.73×10^{-2} (very high cancer risk) in the Mantaro river. Carcinogenic risk of Pb to children from ingestion of water from the rivers Shullcas, Chilca, and Chanchas ranged from a very low cancer risk to a low cancer risk. In adults, the carcinogenic risk of Pb from water intake of 80% of the rivers studied qualified as very high cancer risk. It should be noted that the waters from several of the studied rivers are raw water sources for water works supplying tap water through simple disinfection or sedimentation.

4. Discussion

4.1. Assessment of Heavy Metals and Arsenic in River Water Subject to Mining Influence

Continental aquatic systems are experiencing strong natural (weathering and erosion of bedrock, volcanoes, and atmospheric transport) and anthropogenic pressures. Monitoring the levels of chemicals is becoming increasingly urgent as a critical measure to ensure water quality [44–46]. The results obtained in the current study reveal that the heavy metals and arsenic measured in the rivers of the central region of Peru vary between the river basins. This variability is due to soil heterogeneity and anthropogenic activities, such as mining and agriculture, which are the main economic activities. However, variability in heavy metal and metalloid concentrations is also governed by the sampling season. Water samples were collected in April, after the summer rainy season. In the Peruvian Andes, heavy rainfall in the Mantaro watershed could increase the pollution load that reaches the rivers through runoff carrying mining waste. In other parts of the basin, the contribution of large volumes of water not contaminated by these chemicals tended to decrease the concentration of pollutants [46].

The main Mantaro river (with a length of 724 km) had mean concentrations of heavy metals and arsenic that exceed national and international standards [46–48]. There is a decrease in the concentrations of these contaminants compared with to the from the National Water Authority of Peru [49].

Spatial distribution of heavy metals in aquatic ecosystems depends on natural and anthropogenic sources, as well as on meteorological, hydrological, and geochemical factors [50]. The high concentration of Fe in the studied rivers may be due to the abundance of Fe-containing minerals in much of the sedimentary rocks of the Andean Mesozoic belt in the Central Andes [51] as well as the contribution of anthropogenic activities. The results shown in this study corroborate the results obtained by Abdel-Satar et al. [12] that indicate that Fe values that exceeded aquatic life and drinking water guidelines were associated with anthropogenic sources.

The high Cu and Zn values measured in the Mantaro River could be attributed to the contribution of industrial (mining-metallurgical) activities and agricultural and municipal wastewater effluents in the study area. In addition, Goher et al. [52] note that soil erosion and leaching and atmospheric deposition can add heavy metals to water bodies. However, the Cu and Zn concentrations in the other rivers of the study were low. The values of Pb and As in the Mantaro River exceeded the maximum permissible values of national and international standards, revealing that this river is experiencing strong pressure from mining-metallurgical activity. The high concentrations of As registered in the Chia River in line with the results reported for this river by the Peruvian National Water Authority.

Understanding the conditions that specifically affect the distribution and dynamics of heavy metals and metalloids in the Mantaro River watershed is complicated by (1) the geology of the watershed contributing metals in the transported sediments, thus confusing identification of metals of anthropogenic origin, and (2) the temporal variability of the hydrological regime, characterized by heavy summer rainfall that is responsible for the transport of heavy metals linked to the sediments. Heavy metal transport processes depend on the presence and transport of fine-grained sediments (<2 mm) and on the physicochemical characteristics of the metals [53,54]. In addition, it is necessary to consider that factors such as pH, ionic strength, hardness, chemical oxygen demand, and others may limit the availability [55–58] and transfer of heavy metals and metalloids in aquatic systems [59].

Cu, Pb, Zn, Fe, and As revealed higher concentrations in the upper parts of the Mantaro River. This is in contrast to the other rivers in which higher concentrations of these metals were recorded in the lower parts of the rivers where there are concentrated human settlements. The higher concentrations of heavy metals and As observed in the upper Mantaro river (sector 1) could come mainly from its tributary rivers that run through areas with high mining activity and the metallurgical activity center of La Oroya [29]. The results of this study are consistent with those of Othman et al. [13], who found high concentrations of As in rivers receiving runoff from areas with tin mining in the Bestari Jaya basin in Malaysia.

The cluster analysis grouped the studied rivers into four well-defined groups according to the content of heavy metals and As, revealing that anthropogenic activity is a determinant of water quality. These results are supported by the principal component analysis that indicates that the waters of the Mantaro river have higher concentrations of Cu, Zn, and Pb. This is likely due to the proximity of the sampling sites to the metallurgical city of La Oroya, where one of the largest metallurgical centers in South America is located. The high concentrations of lead detected in the waters of the Mantaro river are of particular concern, as the waters of this river are widely used for irrigation of agricultural soils in the valley throughout the basin.

4.2. Human Health Risk Assessment

Humans are frequently exposed to heavy metals and metalloids through ingestion, inhalation, and dermal absorption. The HQ values for the exposure pathways reveal that water intake from the rivers assessed is the main route of exposure to heavy metals and metalloids. However, the hazard quotients varied according to daily intake, age, and the river assessed. In children, the hazard quotient for intake of water contaminated with heavy metals and metalloids was higher than the hazard quotient for intake of adults. Arsenic HQ_{ing} values in the Mantaro River revealed high chronic risk and probable adverse health effects on children, while, in adults, arsenic HQing values in the Mantaro River indicated probable adverse health effects. In addition, in the Chía and Cunas rivers, arsenic HQ_{ing} indicated probable adverse health effects. These results are supported by [55,56], who report that the chronic health impact of arsenic varies by source type. Many studies report that acute and sub-acute arsenic toxicity involves the gastrointestinal, dermal, nervous, renal, ophthalmic, and other systems [57,58,60–62]. The health effects will depend on the magnitude of the dose and the time of exposure [63,64].

This study reveals that ingestion of arsenic- and lead-contaminated water is a significant contributor to HQ. Pb HQ_{ing} values in the Mantaro river indicate likely adverse health effects and reveal that children have a relatively higher lead intake than adults. Several studies have reported that lead intake can cause significant changes in several biological processes, such as cell adhesion and signaling, protein folding, apoptosis, ion transport, enzyme regulation, neurotransmitter release, and encephalopathies [65,66]. During pregnancy, exposure to even low levels of Pb can cause miscarriages, premature births, low birth weight, and neonatal deaths [67,68], because of the ease with which lead can cross the placental barrier, concentrate in fetal blood, and move through soft tissue and across the blood-brain barrier [69,70]. In infants, increased absorption of heavy metals into the gastrointestinal tract has been shown to have negative effects on growth, kidney, and liver function during the first year of life [71]. In children, Pb intake has been documented to cause attention deficits, learning disorders, delayed psychomotor development, decreased intelligence quotient, and hearing disorders [72,73]. Furthermore, there is strong evidence that lead exposures are associated with the risk of diabetes, hypertension, and cardiovascular disease [74,75].

The HQ_{ing} values of Zn, Cu, and Fe obtained in this study indicate that adverse health effects on the inhabitants who consume water from the rivers evaluated are unlikely. However, in recent decades, attention has been focused on the possible consequences of excessive Zn intake, as it can affect the gastrointestinal tract, before it is distributed throughout the body [74]. Cu-induced toxicity is not common, and cases are generally limited to the individual's genetic susceptibility to copper overload [75]. Other studies also report that the imbalance of metal ions such as Zn and Cu play an important role in the pathogenesis of many neurodegenerative diseases [76,77]. Intake of high concentrations of Fe may cause a variety of disorders that can lead to pathological conditions, including diabetes mellitus [78,79], liver disease, and cardiovascular disease, as well as neurodegenerative disorders [80,81].

The health risk indexes for ingestion (HI_{ing}) in the water exposure of the Cunas, Chia, and Mantaro rivers are higher than the unit in children and adults. Except for exposure to Cunas River water in adults, which showed lower than unit HI_{ing} values. HI_{ing} values higher than unit indicate that there was a significant adverse risk [22]. The health risk indices for dermal contact (HI_{derm}) in the river water exposure studied are lower than unit in children and adults. These results indicate that there was no adverse health risk from dermal exposure to the water in the rivers studied. The carcinogenic risk (CR) from ingestion of As and Pb in the water of the rivers studied was greater than 1 in a million (10^{-6}), indicating a significant risk according to the US EPA [35]. Finally, other research related to the evaluated HQ, HI, and CR supports this study by revealing that ingestion of or contact with water contaminated with toxic metals is a risk to human health. Several studies document that consumption of vegetables from agricultural areas irrigated with water contaminated with these types of contaminants can increase the uptake since these metals can accumulate in the edible parts of the plant [82,83].

5. Conclusions

The rivers of the Mantaro river watershed in central Peru are exposed to contamination by heavy metals and metalloids from natural and anthropogenic sources; among the latter, the mining metallurgical industry, agricultural activity, and manufacturing industry are the main sources. The magnitude of contamination by heavy metals and arsenic in the studied rivers requires more frequent monitoring and supervision of the mining-metallurgical industries (which discharge their liquid waste into water bodies), as well as agricultural and other anthropogenic activities having an impact on water quality. Of the rivers evaluated, the Mantaro river has the highest concentrations of heavy metals and arsenic, which exceed the environmental water quality standards of Peru, the WHO, and US EPA.

The assessment of carcinogenic and non-carcinogenic risks due to exposure to heavy metals and arsenic through the routes of ingestion and dermal contact showed that, in both children and adults, the route of ingestion contributed most to the non-carcinogenic and carcinogenic risk. The mean Cu concentration varied from 0.99 to 14.60 µg/L, Pb from 0.73 to 9.50 µg/L, Zn from 6.30 to 58.30 µg/L, Fe from 14.40 to 1140.0 µg/L, and As from 0.70 to 21.10 µg/L. Pb and As showed the highest concentrations that exceeded Peru's water quality standards in 40% of the rivers evaluated. These findings demonstrate the urgent need for effective policies to control and reduce the pollution levels of the rivers, whose waters are destined for a variety of uses. Therefore, further studies of the dynamics of other heavy metals in the Mantaro River and tributary rivers, including in suspended sediment during seasonal periods of high flow, are recommended.

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