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Research article

Spatio-temporal evaluation of metals and metalloids in the water of high Andean livestock micro-watersheds, Amazonas, Peru

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ABSTRACT

Cattle ranching is a fundamental economic activity in northern Peru, where proper management of water resources is crucial. This study, a pioneer in the region, evaluated water quality and its suitability for human consumption, vegetable irrigation, and livestock production. It is also the first study to document the presence of metals and metalloids in vulnerable areas because they are located at the headwaters of river watersheds. The spatiotemporal evaluation of physicochemical parameters, metals, and metalloids was performed in five micro-watersheds (Cabildo, Timbambo, Pomacochas, Atuen, and Ventilla) from water samples collected in the dry season (October 2017) and wet season (March 2018). The parameters were analyzed using microwave plasma atomic emission spectrometry. The results were contrasted with international and Peruvian quality standards related to dairy cow production. The highest values of pH, total dissolved solids, and electrical conductivity were reported during the dry season, and the highest turbidity during the wet season. Of the metals evaluated, arsenic (As) was omnipresent in all the micro-watersheds, followed by lead (Pb).

In contrast to World Health Organization regulations, concentrations of As, cadmium (Cd), Pb, and iron represent a risk; according to Peruvian regulations, As and Pb exceed the concentrations established for use in animal drinking water and vegetable irrigation, and according to water guidelines for dairy cattle, concentrations of As, Pb, Cd, and Al exceed the permitted limits. The high concentrations of these metals in the study area are attributable to a synergy between natural factors, such as Andean geology and livestock activity. The data reported will allow for proper water resource management, pollution prevention, and the design and adoption of mitigation measures.

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1. Introduction

The availability of quality freshwater is one of the most critical environmental problems of the 21st century worldwide [1]. Anthropogenic activities such as industry, agriculture, livestock, mining, and urbanization introduce pollutants such as metals, agrochemicals, and various pharmaceutical elements into water bodies [2]; chemical contamination of water by these elements has caused various health problems worldwide [3], which have intensified since 1940 [4]. In livestock micro-watersheds, water is indispensable for breeding systems [5]; however, the intensification of agricultural, medical, domestic, industrial, and technological applications endangers water quality [6]. In particular, contamination by toxic metals such as cadmium (Cd), cobalt (Co), chromium (Cr), lead (Pb), iron (Fe), copper (Cu), zinc (Zn), nickel (Ni), and manganese (Mn) is of concern because of the associated risks to human health and aquatic ecosystems [7]. When these concentrations exceed established thresholds, they represent a risk because they contaminate food chains and cause different health problems [8], such as carcinogenic, teratogenic, and mutagenic problems [9]. In addition, human exposure to these elements at trace levels can occur through direct ingestion, inhalation, and dermal absorption, pathways related to water use [10]. Metals and metalloids are neither created nor destroyed, and many occur naturally in the earth's crust [11], as leaching, infiltration, and runoff move metals and metalloids into surface and groundwater. In the aquatic environment, they are often adsorbed on sediments and released by bioturbation [12].

In this context, globally, various investigations have been conducted to define the conditions of water bodies; for example, in the case of the Nile River, water quality was estimated by drinking water quality index (DWQI), metals index (MI), pollution index (PI), and turbidity (TRB) and total suspended solids (TSS), as well as twenty-three physicochemical parameters; 53 % of the samples ranged from excellent to good water, 43 % of the samples ranged from poor to very poor water, and 4 % of the samples were unfit for consumption [13]. Similar studies were developed in the northern Nile delta, where 33 % of the analyzed samples were classified as good water, and 67 % were classified as poor to unfit for drinking water according to the DWQI results [14]. At the same time, Ustaoğlu et al. [15] showed that the Turnasuyu stream (Turkey) presented good quality water, as the trace elements found did not pose a risk to public health; after calculating the water quality index (WQI), hazard quotient (HQ) and hazard index (HI).

The identification of point sources of contamination in water bodies serves to ensure their quality over time and to implement pollution prevention and mitigation activities [16], as is the case of the Pomacochas, Tambillo, Atuén, Cabildo, and Ventilla micro-watersheds located in the high Andean zone of Amazonas-Peru (headwaters of the watershed). These watersheds supply water for agriculture, livestock, and human consumption through drinking water treatment systems. Research on the exploration of metals and metalloids has been conducted in the middle and lower zones of the micro-watershed [17]; likewise, only biological indicators and studies on antibiotics have been reported [18]. This work constitutes the first exploration of components of this nature (metals and metalloids). In this sense, a spatial (Pomacochas, Tambillo, Atuén, Cabildo, and Ventilla micro-watersheds) and temporal (wet and dry seasons) evaluation of the metals and metalloids present in these high Andean livestock micro-watersheds was carried out. The specific objectives of the research were (i) to determine the concentration and distribution of physicochemical parameters, metals, and metalloids in the water of the micro-watersheds during the wet and dry seasons, (ii) to find the relationships between physicochemical parameters and metals and metalloids, and (iii) to compare the concentrations of metals and metalloids with national and international water quality standards. The results obtained from this research present the current conditions of the water resource to promote the adoption of appropriate measures to preserve its quality or mitigate its contamination.

2. Materials and methods

2.1. Study area

The study was conducted in the Amazon region in northern Peru, which covers an area of approximately 39,000.2 km^2 [19]. This area includes humid and dry forests, covering approximately 3,420,363 ha (86.1 %). The remaining territory comprises the Sierra or Amazonian Andes zone with 554,031 ha (13.9 %). It should be noted that the Amazon region has two distinct sectors: the first, the jungle sector, and the second, the inter-Andean sector. Consequently, precipitation volumes, temperature regimes, and other territory characteristics vary considerably [20].

According to the physiography, the Leymebamba and Monilopampa cattle-raising zones have warm to temperate climates characterized by high mountains with extremely steep slopes. These areas have temperatures ranging from 14.5 °C to 25 °C, annual rainfall between 500 and 4000 mm, and altitudes ranging from 500 to 3500 m asl [21].

In terms of geology, the Leymebamba cattle-raising zone has calcareous outcrops and lithologic materials composed of granodiorite to monzogranite, as well as dark gray carbonate shales with characteristic calcite veining and intrusive rock formations. In contrast, quartz sandstones and fine-grained silty sandstones have been recorded in the Molinopampa cattle ranching area [22].

The department of Amazonas's hydrographic network mainly consists of a sector of the Marañon River watershed, which belongs to the Amazon River watershed. On its right bank, the main tributaries of the Marañon River are the Nieva, Chiriaco, and Utcubamba rivers. The rivers studied in this work are tributaries of the Utcubamba River located at the watershed's headwaters [23].

Agriculture and livestock are the main economic activities of the population (65 %), as the province is an exceptionally suitable area for dairy and beef cattle [24]. In addition, there are four zones dedicated to cattle ranching in Amazonas: (1) Pomacochas-Jumbilla, (2) Molinopampa-Mendoza, (3) Leimebamba, and (4) Chiriaco. The first three zones are located in cold temperate climate areas, and dairy cattle predominate, while the last zone has a warm, humid climate and is mainly dedicated to raising zebu cattle [22]. Brown Swiss (11,640 individuals), Holstein (523 individuals), and Criollo (1778 individuals) cattle are raised in the study area. In proportion to agricultural production, the main crops are potato (125.93 ha), cornbeans (109.0 ha), olluco (4.73

ha), and cabbage (3.66 ha) [25]. A total of 13909.21 ha are reported to be occupied by pastures, meadows, and natural vegetation used for extensive cattle raising [26].

2.2. Establishment of sampling stations

The selected micro-watersheds located in extensive cattle ranching areas [27] were the Timbambo, Cabildo, Atuen, Pomacochas (Leymebamba) and Ventilla (Molinopampa) micro-watersheds (Fig. 1), which belong to the level 5 hydrographic unit of the Utcubamba River [28]. The delimitation of the micro-watersheds was developed following the protocol established by the ANA [29], and the sampling points were established based on the Freshwater Ecology and Management methodology used for the evaluation of green status in rivers; the selection of the main channel of the micro-watershed, its length and slope were taken into account. This research was punctual, and it was considered convenient that the distance between sampling stations was 1 km; this distance varied in some micro-watersheds due to accessibility [30]. The points were located below sectors with anthropic intervention and tributaries to the main channel [29].

2.3. Sampling and determination of physicochemical parameters

Sampling was developed in two seasons: the dry season (October 2017) and the wet season (March 2018), according to the seasonal patterns of the area [31]. Hydrogen potential (pH), electrical conductivity (EC), total dissolved solids (TDS), dissolved oxygen (DO), and temperature (T) were determined at each sampling point. All of these were determined with a portable multiparameter meter (brand: WTW; model: 363 IDS), with an accuracy of ±0.004 for pH, ±0.5 % for EC, ±0.5 % for TDS, ±1.5 % for DO and ±0.1 % for T. Turbidity (TRB) was also evaluated with a portable digital turbidity meter (brand: HACH; model: 2100Q), with an accuracy of ±2 %. Before the readings, the equipment was calibrated with calibration solutions, and its correct operation was verified.

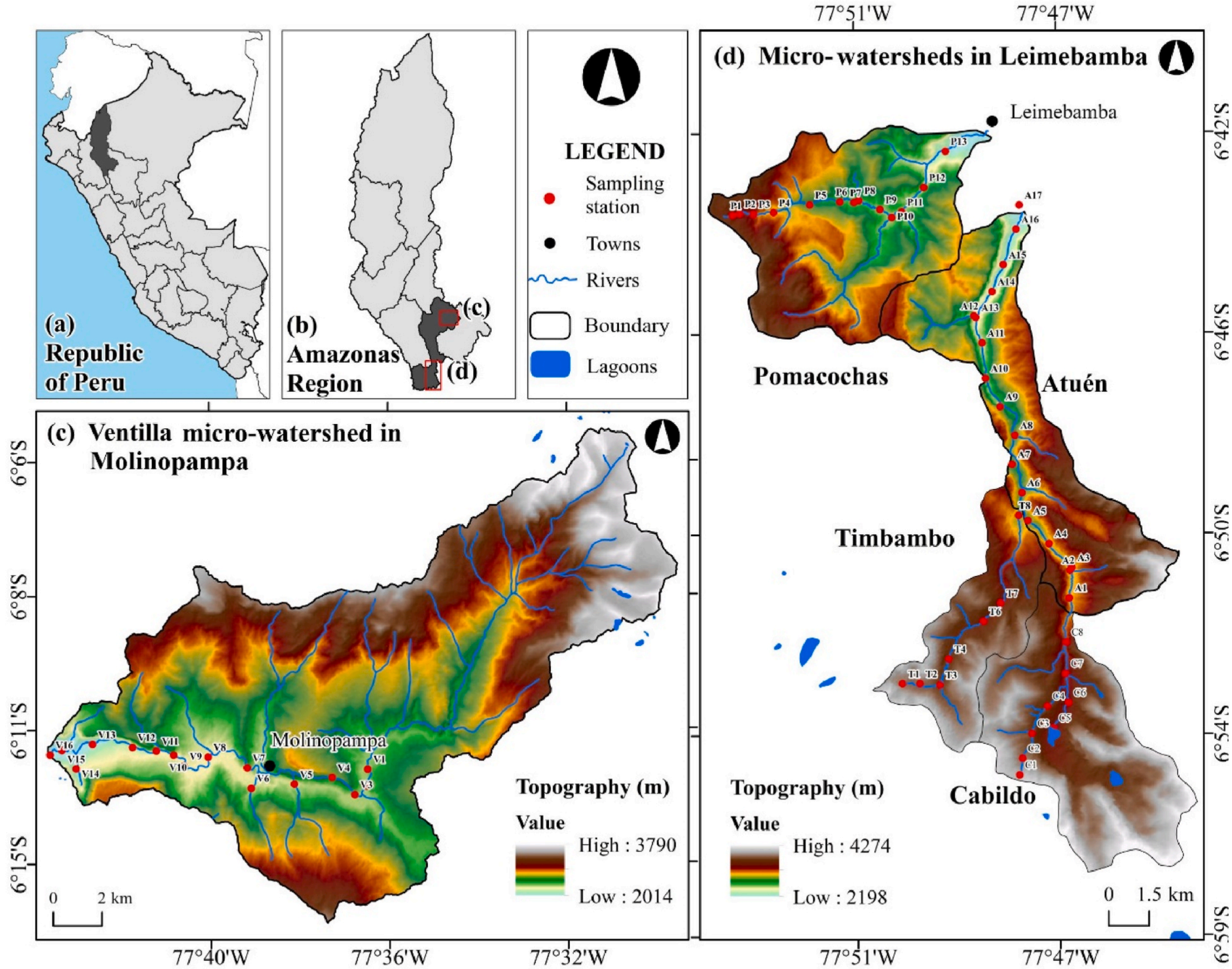


Fig. 1. Study area.

For the determination of metals, samples were collected in 100 mL polyethylene bottles, which were treated with a 10 % 1 M nitric acid solution at 10 % for 30 min and subsequently rinsed with distilled or deionized water [32]. Samples collected and refrigerated at 4 °C were immediately transferred to the Soil and Water Research Laboratory (LABISAG), a laboratory accredited under ISO 17025:2017, belonging to the Universidad Nacional Toribio Rodríguez de Mendoza de Amazonas, located in Chachapoyas, at a distance of approximately one and a half hours from the sampling site. Samples were stored at −20 °C in the laboratory until processing. Prior to storage, the water samples were filtered through cellulose filter paper (brand: CHMLab; qualitative grade: F1002; thickness: 190 μm), and the filtered product was acidified with HNO_3 (1 + 1) until reaching a pH below 2 [33].

2.4. Determination of metals and metalloids

The water samples were thawed at 4 °C in a refrigerator. Then, 10 mL of the sample was transferred to glass tubes previously cleaned with 0.1 M HCl. 0.5 mL of concentrated HNO_3 (brand: Fermont, purity: 65 %) was added to the tubes, which were capped and placed in a Hot Block (brand: Environmental Express, model: SC154). Digestion was carried out at 105 ± 5 °C for 2 h, following the APHA 3030-E method. After digestion, the tubes were cooled to room temperature before analysis by Microwave Plasma Atomic Emission Atomic Spectroscopy (MP-AES) using 3120-B methodology adapted for Inductively Coupled Plasma (ICP) [34].

The detection and quantification of metals and metalloids was performed using a microwave plasma spectrometer (brand: Agilent Technologies, model: 4100 MP-AES, accuracy: ±5 %). This instrument was equipped with a standard torch, an Inert OneNeb nebulizer, and a double-pass glass cyclonic spray chamber (brand: Agilent Technologies). The required nitrogen was obtained from the air using a nitrogen generator (brand: Agilent Technologies, model: Agilent 4107). The pump was set at a speed of 15 rpm. Before reading the samples, time intervals were set: 12 s for consumption time, 12 s for torch stabilization, and 30 s for rinsing time. The duration of the reading was 5 s. Before the reading, the equipment was calibrated with standard solutions of each element, which had different concentrations and were prepared from a 1000 ppm standard solution.

Agilent standard solutions, available in the spectrometry area of LABISAG, were used. After each reading, the equipment recovered both concentration and intensity, dispensing with the need to fortify the samples. The concentration analyses considered six physicochemical parameters, 20 metals, and two metalloids (Table 1) and the wavelengths in Table 2 were considered.

2.5. Data analysis

We began by checking the data's normality and the variances' homogeneity with the Shapiro-Wilk and Barlett tests, respectively. From these analyses, we determined the appropriate statistical tests for the treatment of the data. Subsequently, a principal component analysis (PCA) was performed to determine the behavior of the different parameters under study and simultaneously select the significant variables [35]. Once the PCA was calculated, a cumulative variance threshold was established to select the number of principal components between 70 % and 90 % of the cumulative variance. In addition, a biplot was performed, which was useful for interpreting the first two principal components [36]. To determine whether there were differences in physicochemical parameters, metals, and metalloids according to micro-watersheds and stations, an analysis of variance (ANOVA) was applied. In addition, Spearman's correlation coefficient was used to determine the degree of association between the parameters evaluated. The following degrees of correlation were considered: moderate correlation (between ±0.51 and ± 0.75), very strong correlation (between ±0.76 and ± 0.90), and perfect correlation for values between ±0.91 and ± 1.00 [37]. A significance level of 5 % was considered for all statistical analyses, and R software version 4.1.0 was used [38].

The results of the evaluated parameters were contrasted with the water quality guideline established by the World Health Organization [3], the Environmental Quality Standards for Peruvian Waters (ECA-Water) established by the Ministry of Environment through Supreme Decree N°004-2017-MINAM [39], and the water quality guidelines for dairy cows [40]. The contrast was developed from comparisons, using bar graphs, between the reference values of the standards and the concentrations of physicochemical parameters, metals, and metalloids evaluated in the micro-watersheds.

Table 1

Physicochemical parameters, metals, and metalloids were analyzed from the main livestock micro-watersheds, Amazonas.

Physicochemical Parameters	Metals		Metalloids
Hydrogen Potential (pH)	Cadmium (Cd)	Manganese (Mn)	Arsenic (As)
Temperature (T°)	Cobalt (Co)	Iron (Fe)	Antimony (Sb)
Turbidity (TRB)	Chromium (Cr)	Silver (Ag)	Boron (B)
Dissolved Oxygen (DO)	Copper (Cu)	Vanadium (V)	Silicon (Si)
Electrical Conductivity (CE)	Nickel (Ni)	Aluminum (Al)	
Total Dissolved Solids (TDS)	Lead (Pb)	Sodium (Na)	
	Zinc (Zn)	Potassium (K)	
	Magnesium (Mg)	Strontium (Sr)	
		Barium (Ba)	

Table 2
Wavelengths used to analyze the metals and metalloids analyzed from the main livestock micro-watersheds, Amazonas.

Parameter	Wavelength (nm)	Parameter	Wavelength (nm)
Metals			
Zn	213.857	Al	396.152
Cd	228.802	Mn	403.076
Mg	285.213	Pb	405.781
V	309.311	Sr	407.771
Cu	324.754	Cr	425.433
Ag	328.068	Ba	455.403
Co	340.512	Na	588.995
Ni	352.454	Li	670.784
Fe	371.993	K	766.491
Metalloids			
As	193.695	B	249.772
Sb	231.147	Si	251.611

3. Results

3.1. *Concentrations and distributions of physicochemical parameters, metals, and metalloids in water by micro-watershed and stations*

The PCA, with the first two principal components, was able to explain 33.01 % of the accumulated variance (Fig. 2), indicating that the grouping of metals such as Ni, Ag, Cr, Pb, Cd, Cu, Mn, Zn, and Al; metalloids such as B; and physicochemical parameters such as TRB had a more significant influence in the wet season (W). Metals such as As, Sb, Na, Li, K, and V and physicochemical parameters such as pH, EC, and TDS are influenced by the dry season. The overlapping area in Fig. 2 shows that cobalt (Co) and iron (Fe) are influenced by both seasons. In contrast, neither season influences metals such as Mg and Ba, metalloids such as Si, and physicochemical parameters such as DO.

3.1.1. *Physicochemical parameters*

Fig. 3 shows that in the dry season, the highest averages of pH (Atuen), TRB (Pomacochas), TDS (Atuen and Cabildo), T° (Ventilla), and EC (Atuen) were recorded; these values differ significantly from those reported in the other zones evaluated in the same season. In the wet season, Atuen and Ventilla had the highest temperature, Ventilla had the highest TRB, Pomacochas had the highest DO, and

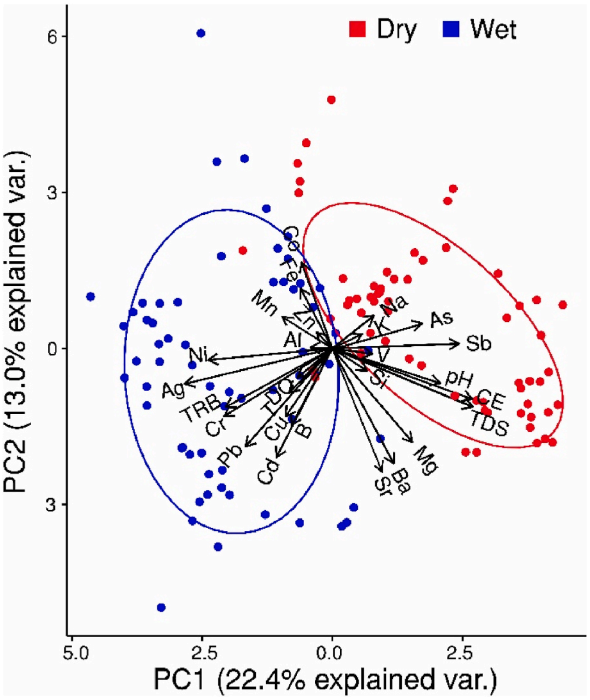


Fig. 2. Distribution of physicochemical parameters, metals and metalloids in dry (2017) and wet season (2018).

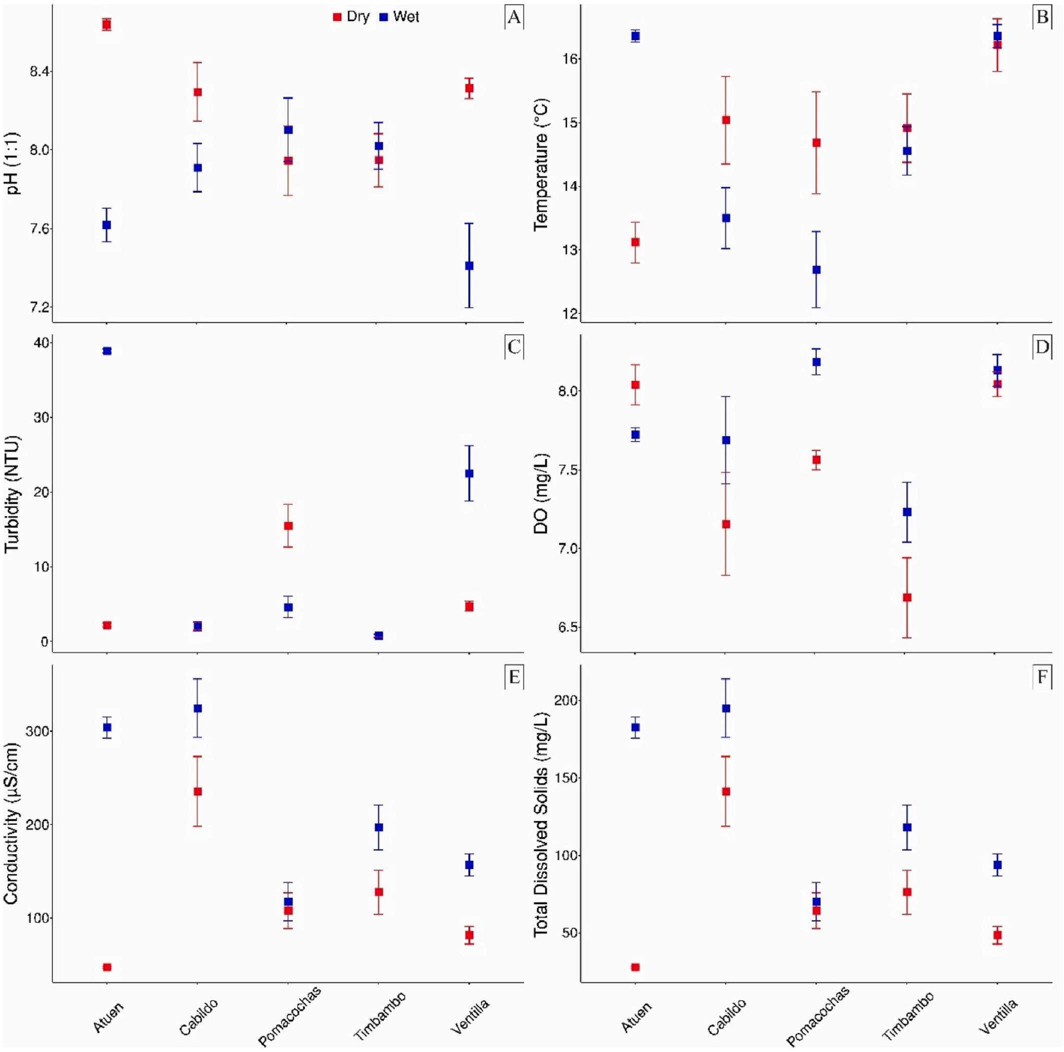


Fig. 3. Distribution of physicochemical parameters by micro-watersheds and seasonal period.

Cabildo had the highest EC. In the wet season, Cabildo, Pomacochas, and Timbambo had the lowest values for water GRR, and Atuen had the lowest values for TDS and EC.

3.1.2. *Metals*

Regarding the concentration of metals during the wet season, the highest amounts of Ba and Cd were observed in Cabildo, Co in Pomacochas, Cu in Ventilla, Cr in Cabildo and Timbambo, and St in Atuén. During the dry season, the most notable values were Ba in Atuén and Cabildo and Cu and Sr in Atuén (Fig. 4).

The highest concentrations of Ni, Ag, Pb, and Zn during the wet season were recorded in Ventilla, while V had higher concentrations in Pomacochas. During the dry season, the most representative values of Li, Ni, and Pb were observed in Ventilla, Ag in Pomacochas, V in Cabildo, and Zn in Timbambo (Fig. 5).

During the wet season, the elements with the highest concentrations were Al and Mn in Ventilla, Mg in Cabildo, and Fe in Pomacochas. In the dry season, Al and Na showed the highest concentrations in Ventilla, Mg in Cabildo, K in Atuén, and Mn in Timbambo (Fig. 6).

3.1.3. *Metalloids*

Fig. 7 shows the average concentration of metalloids by watershed and seasonal period, with a higher concentration of B in Cabildo (Fig. 7B) and As in Timbambo (Fig. 7A) during the wet season. During the dry season, Si concentrations were higher in Timbambo (Fig. 7D). However, there were no significant differences with the values reported for the other micro-watersheds, and the highest As values were reported for Timbambo and Atuen (Fig. 7A). Finally, Sb did not vary significantly during the two seasonal periods (Fig. 7C).

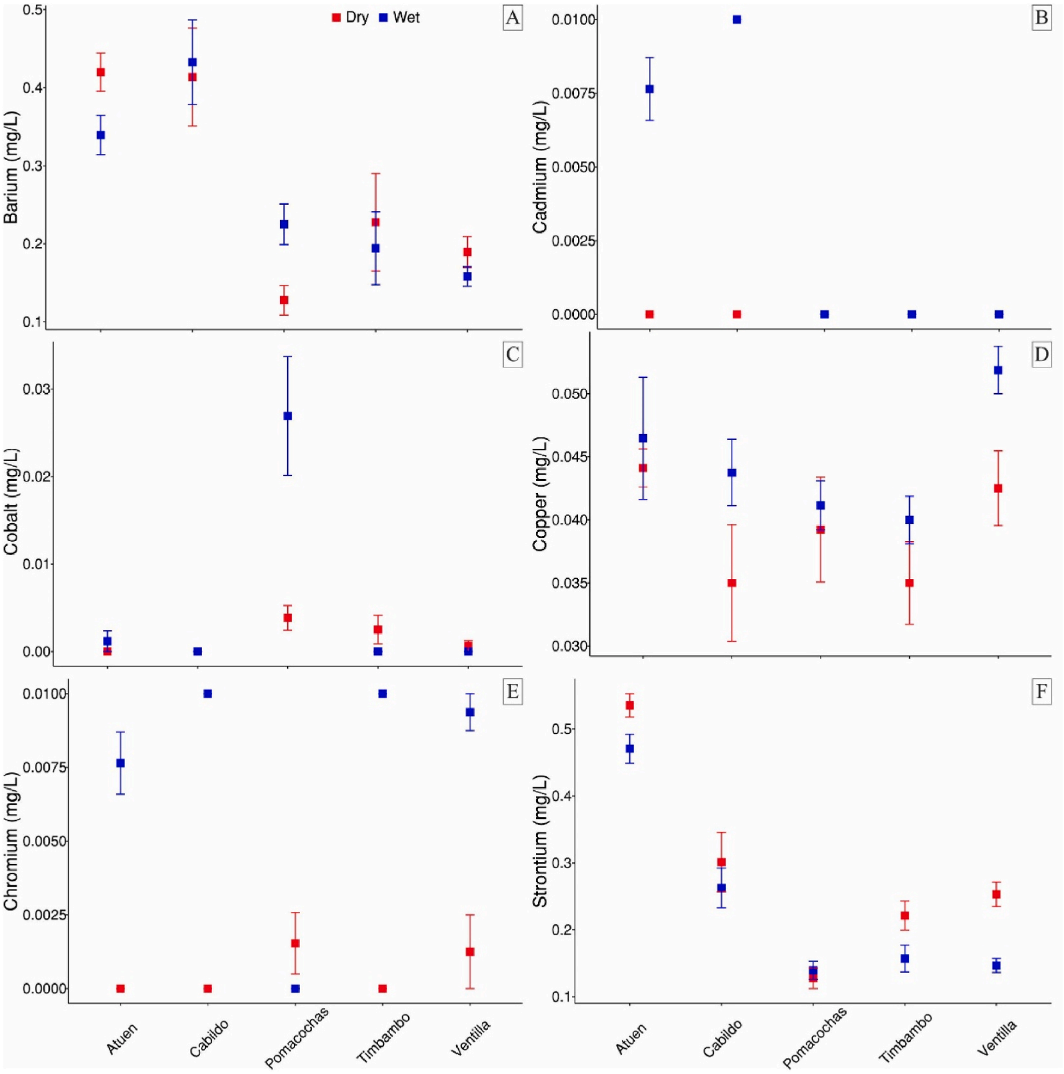


Fig. 4. Distribution of Ba, Co, Cr, Cd, Cu, and Sr by micro-watersheds and seasonal period.

3.2. Relationships between physicochemical parameters, metals, and metalloids

EC and TDS were the physicochemical parameters that showed a perfect positive correlation (0.91–1.00). Ag and Sb showed a very strong positive correlation (0.76–0.90). A considerable positive correlation (0.51–0.75) was shown between pH and Ag, TDS and Sb, Sb and Zn, Sb and Zn, Ag and Pb, Cr and Cd, Pb and Zn, Ag and Ni, and Ag and Cr. In addition to Sb and Zn, Ag and Pb, Cr and Cd, Pb and Zn, Ag and Ni, and Ag and Cr (Fig. 8).

3.3. Concentrations of metals and metalloids found in livestock watershed water and their contrasts with national and international standards and water quality guidelines for dairy cattle

In relation to the standards established by the World Health Organization (WHO), it was found that in all micro-watersheds and during both seasons, the arsenic (As) limits established at 0.010 mg/L were exceeded. The mean values for As were significant in Timbambo (D: 0.299; W: 0.793), Cabildo (D: 0.555; W: 0.398), Atuén (D: 0.771; W: 0.301), Pomacochas (D: 0.633; W: 0.335) and Ventilla (D: 0.796; W: 0.383). On the other hand, for lead (Pb), whose established limit is also 0.010 mg/L, it was observed that the micro-watersheds exceeded this value in both the dry and wet seasons, with mean concentrations for Timbambo (D: 0. 031; W: 0.050), Cabildo (D: 0.050; W: 0.069), Atuén (D: 0.051; W: 0.069), Pomacochas (D: 0.045; W: 0.055), and Ventilla (D: 0.055; W: 0.074). Regarding Cd limit values (0.003 mg/L), the micro-watershed that exceeded the limit value with average concentrations for the wet season was Atuén (0.008 mg/L). As for the Fe limit value (2000 mg/L), the micro-watersheds that exceeded the limit were Pomacochas (2.250) and Ventilla (0.498) during the wet season, and the Sb limit was exceeded in Timbambo (0.129), Cabildo (0.121) and Atuén

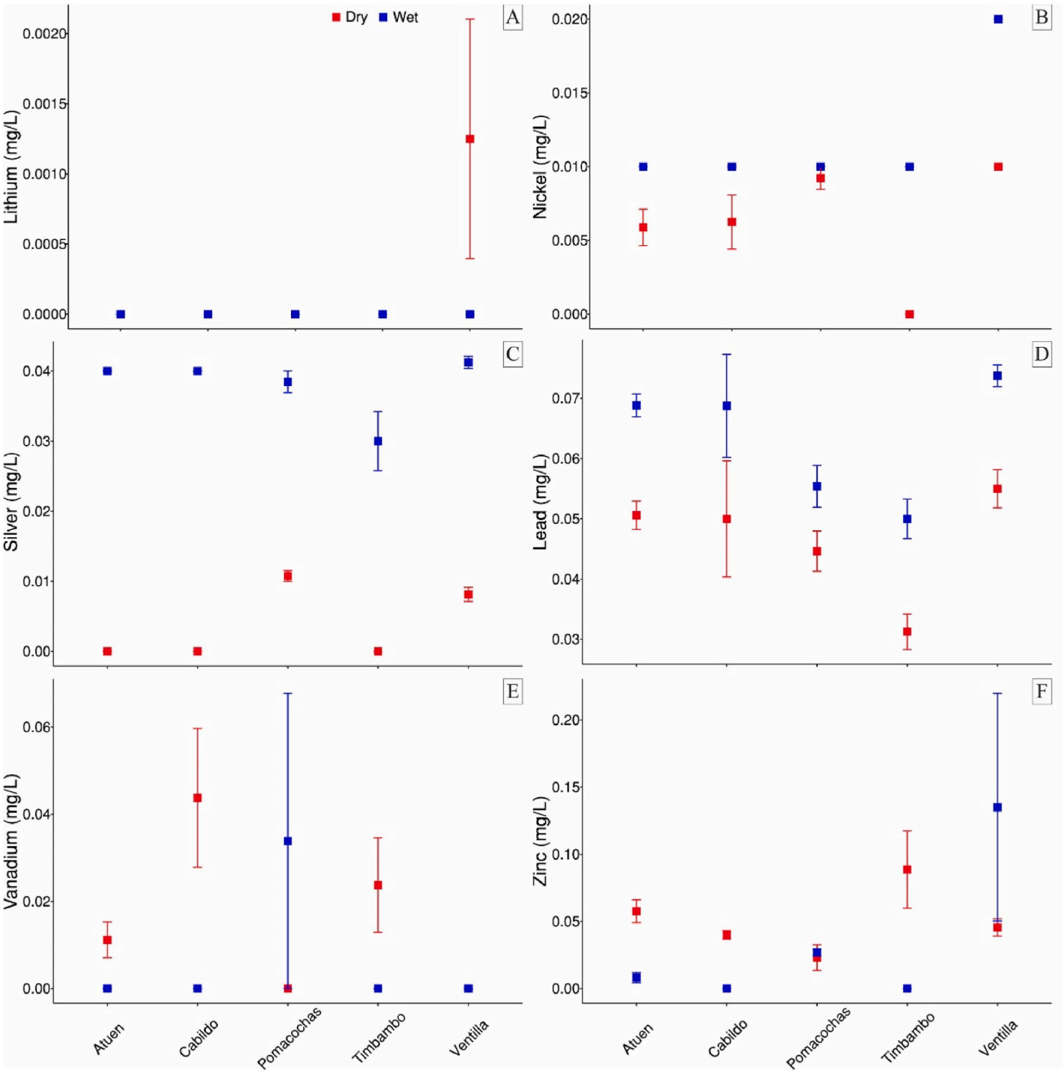


Fig. 5. Distributions of Li, Ag, V, Ni, Pb, and Zn by micro-watersheds and seasonal period.

(0.062) during the dry season.

According to the Water Quality Standards established by Peruvian regulations (D.S.004-2017-MINAM), As concentrations (0.11 mg/L) exceeded the limit in the Vegetable Irrigation category (AQL-C3.1), with the highest value occurring during the wet season in Timbambo (0.793) and during the dry season in Ventilla (0.796). In the Animal Drink category (AQL-C3.2) for As (0.2 mg/L), the reference value was exceeded in all micro-watersheds, with the same tendency in Ventilla for the dry season and Timbambo for the wet season. Pb limit values (D1: 0.050 mg/L-D2: 0.050 mg/L) exceeded the EQS-C3.2 category limits in the Cabildo (0.050), Atuén (0.051) and Pomacochas (0.045) micro-watersheds during the dry season, while Pb concentrations in Ventilla (D: 0.055; W: 0.074) exceeded the Animal Drink category limit in both seasons.

In relation to the Water Quality Guidelines for Dairy Cows, all micro-watersheds exceeded the limits for As (0.050 mg/L) and Pb (0.015 mg/L) in both the wet and dry seasons. During the wet season, Atuén (0.008) exceeded the limit for Cd (0.005 mg/L) and Ventilla (0.673) for Al (0.500 mg/L); in addition, Atuén (D: 0.281; W: 0.196), Pomacochas (D: 0.191; W: 0.209) and Ventilla (D: 0.453; W: 0.673) exceeded the limits for Cr in both seasons (Fig. 9).

4. Discussion

Research reports the presence and variation of concentrations of physicochemical parameters, metals, and metalloids in the high-Andean micro-watersheds of northern Peru. It is believed that the presence of these elements and some high concentration ranges are related to various factors, including the alteration of geomorphological conditions due to the settlement of populations [41]; in the study area, 5955 inhabitants are reported in Leymebamba and Molinopampa with a total of 105 populated centers [42], and the

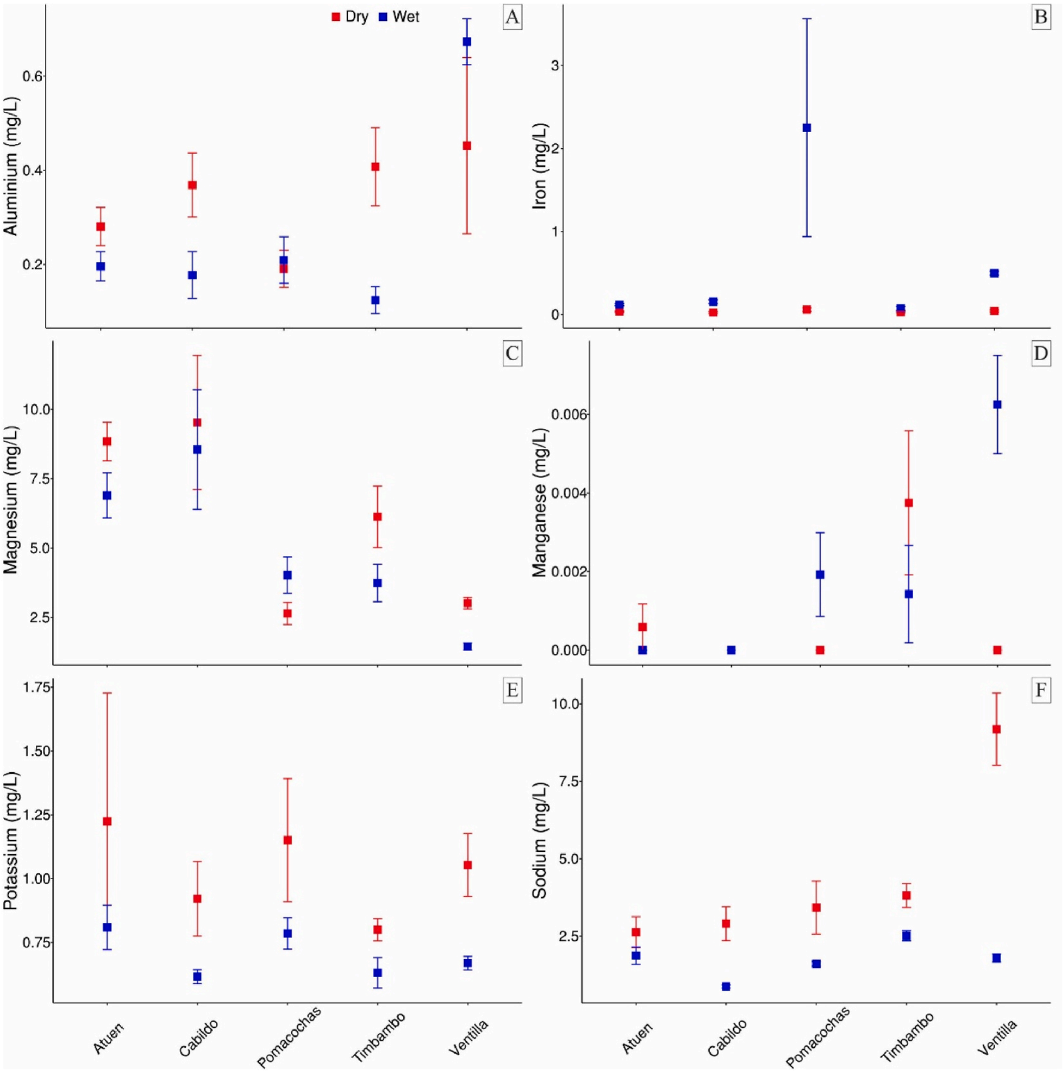


Fig. 6. Distribution of Al, Mg, K, Fe, Mn, and Na by micro-watersheds and seasonal period.

implementation of road infrastructure, which has a greater impact in the micro-watersheds of Atuén, Pomacochas, Cabildo and Ventilla. Ferreira et al. [43] found that road works in Coimbra, Portugal, altered water quality by increasing the concentrations of Cu (mg L^{-1}), Zn (5 mg/L), Pb (0.1 mg/L) and Cd (0. 01 mg/L), as well as pH, conductivity, turbidity and total solids, mainly during the summer season due to the accumulation of pollutants during drought periods and the amount of traffic that removes particles from the roads and is dragged into the water bodies during the wet season. Most metals, mainly Cr and Pb, are present in road dust, representing a risk due to their solubility in water [44].

Another factor that possibly produces alterations in water quality in the micro-watersheds is the expansion of cattle ranching and agriculture along the river margin [45]. In the study area, it is reported that there are approximately 212,371 ha intervened by agriculture and livestock [26]; livestock activity would be negatively affecting water quality due to extensive cattle grazing, trampling that produces soil compaction, acceleration of runoff, disturbance of the channels and dispersion of organic pollution by excreta [[46]. In relation to agriculture, the change in land use and land cover produces runoff rich in sediments and nutrients, as mentioned by Ni et al. [47], who, from their analysis in the Mississippi delta, showed that the concentration values of TDS, Nitrogen, and Phosphorus increased in the water (1–12 %), as the cultivation areas expanded. Similar results were reported by Ezzati et al. [48] in eight agriculturally dominated watersheds in Sweden, where the impacts of agriculture on water quality, together with factors such as precipitation and temperature, contributed to increased nitrogen and phosphorus loads, with this effect being accentuated during drought. Concentrations of certain metals in water may be due to soil movement, as reported by Bedoya-Perales et al. [49], who found high concentrations of As (70.9 mg/kg), Cd (7.1 mg/kg) and Pb (89.7 mg/kg) in agricultural soils in the Peruvian Andes, posing a risk of removal and insertion into nearby water sources.

Timbambo is one of the micro-watersheds less influenced by anthropic activity; it presents a little altered forest of good quality

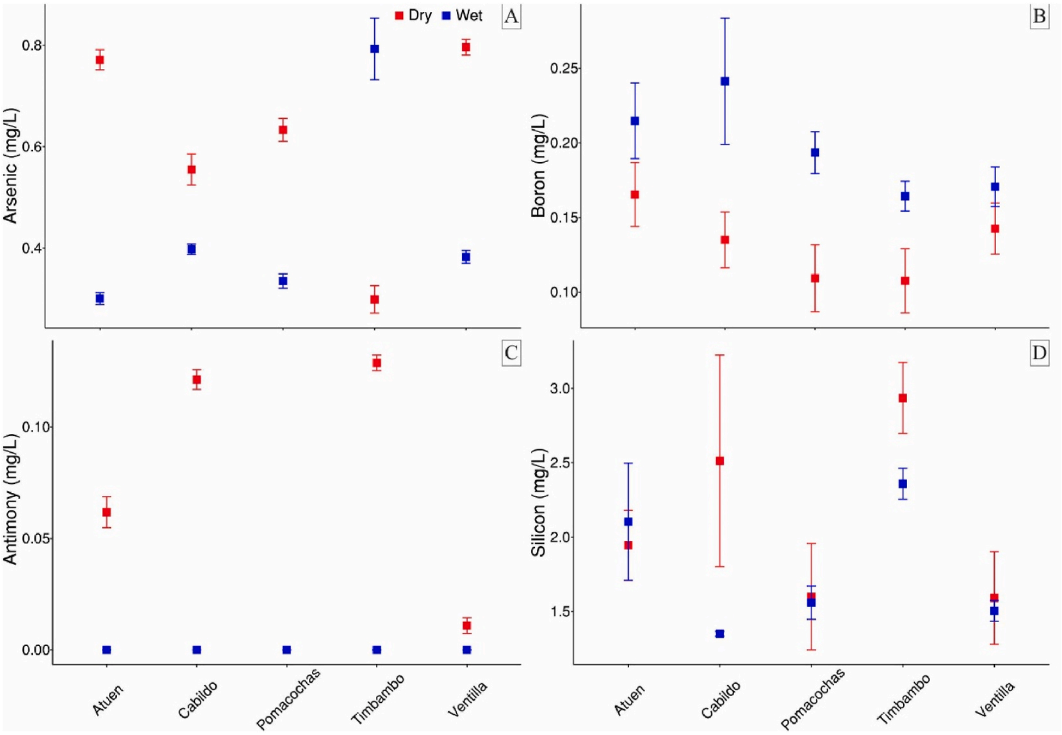
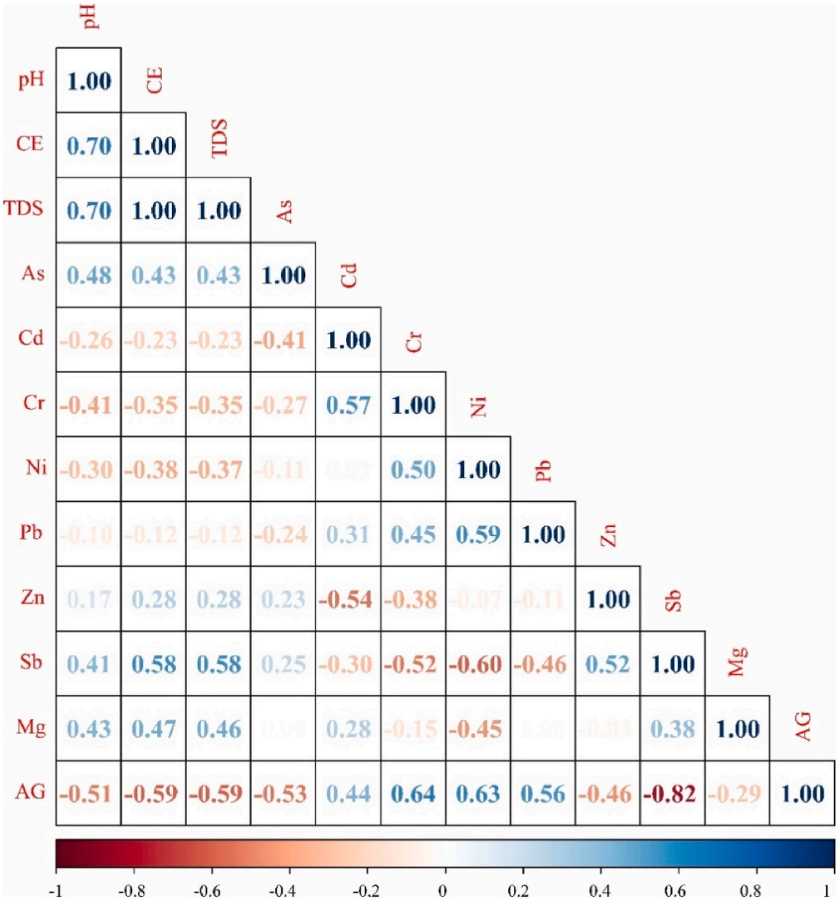


Fig. 7. Distribution of metalloids in the micro-watersheds during the seasonal period.

based on the quality indexes of riparian forest (QBR) and fluvial habitat (IHF); this is because it is the micro-watershed farthest from the main communication routes, thus presenting remnants of vegetation for restoration [50], strictly related to the water results reported in this study, due to the lower dragging of particles by land use.

Cattle ranching is the main economic activity in these micro-watersheds, followed on a smaller scale by agriculture [51]; livestock production and the implementation of grazing systems are carried out extensively and under similar conditions [52]. The high-Andean micro-watersheds were classified by Briceño et al. [45] using a Hydrogeomorphological Index (HGI) based on their land cover characteristics and according to their morphometric variables (linear, areal and morphological), being as follows: Ventilla (Poor), Cabildo (Moderate), Timbambo (Good) and Pomacochas (Very Good). The reported hydrogeomorphological quality is closely linked to the sociodemographic pressures caused by the increasing anthropogenic modifications of the watershed and floodplain [53], influencing the water quality we show in this study. Similar studies in headwatersheds were conducted by Pandey et al. [54], who evaluated metal contamination in water and sediments of major rivers in South Korea, where Ni concentrations in water were higher than recommended values, suggesting that metals contaminate rivers and could cause adverse effects on riparian ecosystems. Yakovlev et al. [55], meanwhile, report elevated concentrations of Al, Ni, As, Fe, Mn, Cr, Cd, and Ba as priority trace metal contaminants in the Pechora River in the headwaters of the Arctic Ocean watershed, whose concentrations may be due to dissolution processes of underlying rocks and mineral deposits. Another study prioritized in the headwaters of the watershed is the one conducted in the Ebonyi River, one of the most important in Nigeria since its watershed serves as the main source of drinking water, where high and risky concentrations of As, Cd, Mn, Cd, and Hg were found, and recycling of solid waste, wastewater treatment and the adoption of an organic farming system is suggested to improve its quality [56]. In Colombia, a country with environmental conditions similar to ours, an evaluation of the Sinú river was carried out; the results highlighted the human impact on the increase of certain metals such as Cu, Zn, Cd, and Pb in agricultural soils, attributing this increase to the application of fertilizers and chemical products such as pesticides and fungicides, which contain these metals [10].

In the central Andes of Peru, investigations were conducted in the Mantaro River to determine the concentrations of Cu, Fe, Pb, Zn, and As, and the risks to humans were assessed in terms of the dose of exposure to heavy metals and arsenic present in the water by ingestion and dermal route. Using standard methods established by the United States Environmental Protection Agency (USEPA), elevated doses of all elements were found due to areas influenced by mining activity [57]. Similar contributions have been made globally, such as those developed in the Nile River, where water samples were collected along the Rosetta and Damietta branches, and environmental quality indices were assessed at 51 different locations. To estimate water quality status, they assessed the drinking water quality index (DWQI), metals index (MI), pollution index (PI), turbidity (Turb.), and total suspended solids (TSS). Of the twenty-three elements evaluated, the mean values of ions and metals presented the following sequence: $Ca^{2+} > Na^{2+} > Mg^{2+} > K^{+}$, $HCO^{3}{}_{2-} > Cl- > SO_4^{2-} > NO^{3} - > CO^{-2}{}_{3}$ and Al > Fe > Mn > Ba > Ni > Zn > Mo > Cr > Cr [14]; notable differences are shown on the predominance of these elements since, in our case, Pb and As were representative. On the other hand, studies developed in the northern



	pH	CE	TDS	As	Cd	Cr	Ni	Pb	Zn	Sb	Mg	AG
pH	1.00											
CE	0.70	1.00										
TDS	0.70	1.00	1.00									
As	0.48	0.43	0.43	1.00								
Cd	-0.26	-0.23	-0.23	-0.41	1.00							
Cr	-0.41	-0.35	-0.35	-0.27	0.57	1.00						
Ni	-0.30	-0.38	-0.37	-0.11	0.02	0.50	1.00					
Pb	-0.10	-0.12	-0.12	-0.24	0.31	0.45	0.59	1.00				
Zn	0.17	0.28	0.28	0.23	-0.54	-0.38	-0.07	-0.11	1.00			
Sb	0.41	0.58	0.58	0.25	-0.30	-0.52	-0.60	-0.46	0.52	1.00		
Mg	0.43	0.47	0.46	0.04	0.28	-0.15	-0.45	0.00	-0.03	0.38	1.00	
AG	-0.51	-0.59	-0.59	-0.53	0.44	0.64	0.63	0.56	-0.46	-0.82	-0.29	1.00

Fig. 8. Spearman correlation of physicochemical parameters, metals, and metalloids.

delta of the Nile River used the drinking water quality index (DWQI) and indicated that 33 % of the analyzed samples represented good water and 67 % were poor to unfit for drinking water [14]. In the micro-watersheds evaluated in our research, the evaluation of the parameters established by WHO showed that As exceeded the values established for human consumption.

The highest mean concentrations for pH (7.8–8.2), TDS (71.0–132.0 mg/L), and EC (118.8–220. 0 S/cm) for all micro-watersheds were recorded in the dry season; similar results are reported by Chan Kujiek & Sahile [58] who from their evaluation in the Elgo River, show EC values ranging from 82 to 268 S/cm for both wet and dry seasons, while TDS (192.5–275.5 mg/L), like our data, shows the highest values in the dry season. These high TDS values for both studies may be due to a higher concentration of ions due to the effect of evaporation of the water masses [59]. On the other hand, in the Jialing River (China), similar results are reported for pH and EC parameters with higher concentration values in the dry season [60]. In the case of EC concentrations, the higher concentrations in the dry season are due to ion concentration due to increased river temperature and water evaporation [61]. On the other hand, the high values of TRB in the wet season in the Atuén and Ventilla micro-watersheds are due to particle entrainment, landslide and erosion [62]; this corresponds with what was supported by Lu et al. [63], who mention that the turbidity of rivers during wet periods, specifically in mountainous areas, varies dramatically; their study revealed that the increasing rates of turbidity values are closely related to rainfall intensity. This corresponds with data from the National Meteorology and Hydrology Service of Peru, which reports rainfall in Molinopampa of 520 mm and Leymebamba of 1017 mm [64]. Similar values to those reported in our study (5.045–13.757 NTU) are reported by Li et al. [65], who, in their evaluation of a mountainous river in southwestern China, report turbidity data from 0 to 9.935 NTU, revealing the impact of precipitation conditions on turbidity.

As for metals, the highest concentrations of Cd were found in the wet season in Cabildo, while the values were negligible in the dry season. Water hardness influences the concentration of this element, i.e., increasing hardness decreases the toxicity of cadmium in the environment due to competition between the element and Ca^{2+} and Mg^{2+} ions [66].

Co values in the dry season are still very low (0.001 mg/L). In contrast, in the wet season, the Pomacochas micro-watershed presents the highest values (0.029 mg/L), with similar results reported by Dunán Avila et al. [67], with concentrations ranging between 0.00 and 0. 03 mg/L in the 12 points sampled in the water of the Yamanigüey river, Cuba, finding as main source of origin the rocks present in the riverbed composed of the metal, which enables the water to dissolve them and incorporate them into its chemical composition as it passes through. On the other hand, Fernández-Rodríguez et al. [68] found cobalt values of 0.001–0.003 mg/L in the

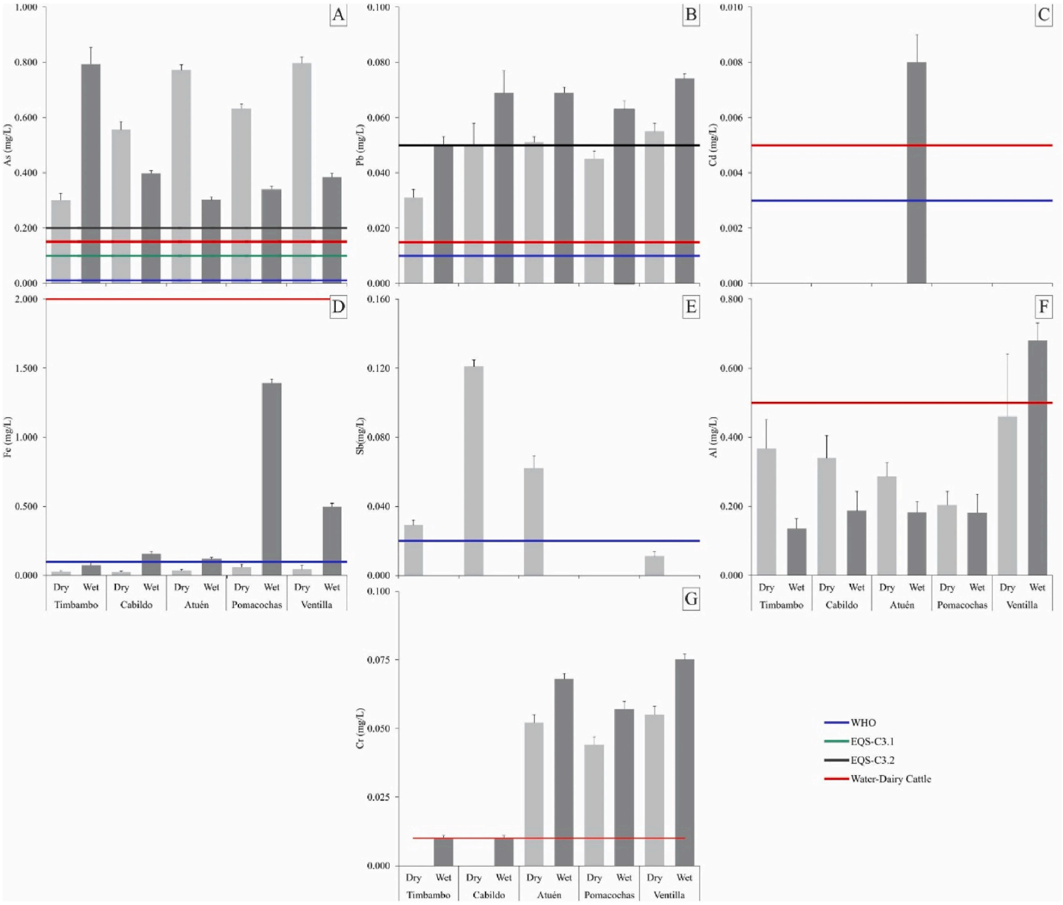


Fig. 9. Contrast the average concentration of metals and metalloids with Peruvian and international water quality guidelines.

Cayo Guam river, Cuba, being above the permissible standards for drinking water, justifying that its presence is mainly due to the lithology of the area and the mining development that facilitates its release. In the Portoviejo River, Ecuador, cobalt concentrations were found with values ranging from 0.01 to 0.34 mg/L as a result of wastewater discharges, anthropogenic activities (especially agriculture), and other contaminant sources such as lubrication plants and the population near the river meander [69].

On the other hand, the highest Cr values in the Atuén, Ventilla, Cabildo, and Timbambo micro-watersheds are due to bedrock weathering, with silicates being the predominant Cr-containing mineral [70]. Ni and Cu concentrations occur during the wet (rainy) season in the Ventilla micro-watershed; sediments are the main deposits of Ni and Cu, whose remobilization during the rainy season represents a risk for aquatic organisms due to their introduction into the trophic chain [71].

The high concentrations of Mn in Ventilla during the wet season are due to its presence in the interstitial waters of the sediments [72] and to its slow precipitation kinetics and solubility under reducing conditions [73], which cause a higher concentration in the water column. Direct exposure of mammals to Mn sources such as water causes neurotoxic problems [74]. The high Ba concentrations in Atuén and Cabildo during both seasonal periods are due to the availability of this element, which occurs naturally in all igneous, metamorphic, and sedimentary soils and rocks [75], suggesting its presence in water sources. The high values of Sr in Atuén during the dry and wet seasons occur because this element is highly distributed in air, soil, and water [76]. V concentrations do not show significant values, but their presence is suggested by natural sources such as rock leaching and soil erosion [77].

Fe concentrations are highest in Pomacochas during the wet season because DO has a direct relationship with Fe, causing it to decrease during thermal stratification from insoluble forms in the sediment to soluble forms in the water column [78]. Pb concentrations in the micro-watersheds are visibly high, with higher concentrations in the wet season and in the Ventilla, Atuén, and Cabildo micro-watersheds because lead in rivers is transported as particulate material in combination with Fe and Al [79]; additionally, the strong affinity of Pb for P related to its transport and presence at the sediment-water interface has also been demonstrated [80]. Zn variations were not significant; however, Zn is ubiquitous in the environment and is a micronutrient [81]; in turn, Zn is widely used in electroplating processes [71], which explains why its presence in one of the micro-watersheds is more influenced by anthropogenic activity.

Ag concentrations show elevated values for all micro-watersheds during the wet season. Peters et al. [82], from the evaluation of dissolved Ag in rivers in England and Wales, found that 100 % of the collected samples presented a mean value of 3 mg/L), lower than that reported in our study, clarifying that there is a scarcity of Ag monitoring data in freshwater environments due to the relatively low levels of Ag in the aquatic environment. On the other hand, a study developed by Sanchís et al. [83] justifies the presence of small concentrations of Ag in their study of Ag nanoparticles in the Besós and Ebro rivers whose mean dimensions evaluated were between 14 and 18 nm, this generally in river sections with notorious presence of industries or urban nuclei, which makes us suppose that the high concentrations of Ag in our study come from anthropic sources, which in wet season by runoff are concentrated in water bodies [84].

Al concentrations are more significant in the Ventilla micro-watershed during the wet season because, in surface waters, the main source of aluminum is leaching from soils [85]. Aluminum constitutes 7.91 % of the mass of the lithosphere and is present in all rocks [86]. High Al concentrations are related to extreme pH values because aluminum present in sediments is activated as the acidity of water increases [87]. This corresponds with the Al concentrations found in the Ventilla, considering that this micro-watershed presents the lowest pH value during the wet (rainy) season.

The higher concentrations of As in the Timbambo micro-watershed during the wet season and in Ventilla and Atuén during the dry season are consistent with the findings of Nicolli et al. [88], who reported the presence of this metal in the waters of countries such as Argentina and Chile; Tapia et al. [89] reported it in Bolivia; and George et al. [90] made the first report of high concentrations of As in drinking water in Puno, Peru. The presence of As in the micro-watersheds under study may be due to natural sources related to geology, mineral deposits, and anthropogenic sources such as industrial processes and often due to the use of pesticides and fertilizers [91], taking into account that the Ventilla micro-watershed presents a type of traditional livestock activity with one or another technological implementation in livestock management and pasture implementation. At the same time, Timbambo manages purely expansive livestock using natural pastures [92]. The contribution of As in the micro-watersheds can be attributed to natural sources [91] and is determined by the great lithological diversity generated in different geological epochs ranging from igneous, intrusive, and volcanic that end up manifesting in various sedimentation environments, basic, acidic, and volcanic intrusions within the micro-watersheds [93]. The marked seasonal variation of As occurs because this metalloid is mostly present in its oxidized form (As (V)), and its mobility in water bodies is influenced by dry and wet seasons, which allows the precipitation of secondary minerals [89].

Sb registered high concentrations in the dry season for the Cabildo and Timbambo micro-watersheds, which have the highest concentrations of dissolved solids. This is relevant to highlight since there is a strong correlation between these two variables, as indicated by Li et al. [94], who point out that Sb exists in union with dissolved matter.

Some processes, such as precipitation, aqueous complexation, and sorption on particles and colloids in the water column or sediments, determine the concentration of Sb in rivers [95]. One of the peculiarities of Sb is the low affinity for mineral surfaces, suggesting a higher presence in the aqueous medium [96]; a clearer picture of the behavior of Sb and As at the concentration level in water is provided by Hao et al. [97], who found that Sb and As concentrations were inversely proportional to the distance from the water flow, and that factors such as dissolution of silicate minerals from rocks such as silicified limestone increased the Sb concentration, while dissolution of carbonate minerals, ion exchange and competitive adsorption cause a rapid decrease in Sb concentration. However, we must recognize that the distributions of As and Sb in the environment are complex [96]. The results of this study are in agreement with the reports of Islam et al. [98] and Li et al. [94], who observed an increase in antimony (Sb) concentrations during the dry season in the marine sediments of the Bay of Bengal in Bangladesh and in the surface waters of the Taihu watershed in China, respectively. These studies suggest that the increase in Sb concentration can be attributed to several factors, such as reduced rainfall, frequent debris inputs, and wind intensity, which favor increased mobility and resuspension of sediments in surface waters. On the other hand, Fu et al. [99] argue that the determinants of the increase or decrease of Sb in a water body are sediment entrainment and depth since if there is no sediment entrainment and the river is shallow, no significant differences between dry and wet seasons will be appreciated.

On the other hand, B was present in all micro-watersheds during both seasons; however, higher concentrations were present in the wet season for Cabildo because B is an element of the earth's crust and is widely distributed in multiple environments, including volcanic, plutonic, sedimentary and metamorphic environments [100]. Moreover, its characteristics, such as volatility and solubility, cause it to diffuse significantly. The presence of B in rivers is widely distributed, and concentrations lower than 0.26 mg/L do not present a risk [101], which coincides with the concentrations found in Cabildo (0.25 mg/L); in addition, its presence in water is due to water-rock interactions and dilutions, absorption and precipitation in clay minerals [102]. The distribution and behavior of these elements require much more detailed analyses involving studies such as land use, meteorology, geology, and hydrology to determine the direct relationships between the variations in the concentration of these elements [103].

A strong negative correlation was observed between silver (Ag) and antimony (Sb). This may be because antimony is commonly found in nature as stibnite (Sb_2S_3), and its decomposition product, valentinite (Sb_2O_3), is often associated with copper, silver, and lead ores [104]. On the other hand, the remarkable positive correlation between lead (Pb) and silver (Ag) can be attributed to the co-presence of both metals in water, resulting from soil entrainment, where these elements frequently coexist.

Pb–Ag complexes in central and northern Peru present high As and Sb contents in flotation concentrates [105]. The strong positive correlation between silver (Ag) and chromium (Cr) may be due to the transport and fractionation of metals present in suspended solids. This process occurs in the flat zones of the interstitial water, where sediment resuspension and amalgamation occur [106]. The correlation of physicochemical parameters shows a perfect correlation between total dissolved solids (TDS) and electrical conductivity (EC) because TDS, as a consequence of soil entrainment, transports ions that directly influence EC concentrations [107]. In addition, there are considerable correlations between EC and pH because water transports ionic materials, whose movements produce electric current; conductivity increases as a function of ion concentration, which is perceived to influence pH [108].

World Health Organization (WHO) guidelines report the risk of As, Cd, Pb, and Fe due to their toxicity, persistence, and bioaccumulation [109]; these metals are considered essential to monitor because their presence in high concentrations affects all organs of the human body [110].

Research conducted in the La Plata watershed has shown high concentrations of As in the Andes Mountains and suggests that these sites are natural sources of contamination [111]. A study in the Carrizal River, Ecuador, reported that concentrations exceed the permissible limits (10 μg/L) established by the World Health Organization [112]. As exposure can cause serious damage to human health, such as skin lesions and cerebrovascular diseases [113]. In addition, exposure to Cd can cause lung cancer [114], and Pb directly affects the endocrine and immune systems [115]. The risk of high iron (Fe) concentration in water can cause serious health problems, such as liver disease, diabetes, and even infertility [116].

In contrast to the national standard, the Environmental Water Quality Standard (ECA-water) belonging to categories D1: Plant Irrigation and D2: Animal Drinking Water, a risk for As, Pb, and Se is reported. These results are similar to those reported in the Tambo River, Arequipa, where As exceeds the national standard in two monitoring stations evaluated [117]. In the Llaucano river, Cajamarca, As concentrations have also been reported to exceed the national standard in 3 of its five monitoring stations [118], while in the Ichu river, Huancavelica, As and Pb concentrations exceed the national standard, in the category of population and recreational use [119]. These metals can be contaminated through vegetable irrigation, as contaminated water used in vegetable production can accumulate on leaves [120]. In addition, there is a risk of ingesting vegetables and food contaminated with Pb, which causes direct entry into the bloodstream, causing disorders in the nervous, cardiovascular, renal, and reproductive systems [121].

Regarding water quality guidelines for dairy cows, the risk of As, Pb, Cd, and Al contamination in the five micro-watersheds is reported due to exposure pathways such as water sources and food crops irrigated with these metals [122]. The literature reports that ingestion of water contaminated by heavy metals (As, Pb, and Cd) contributes to a lower transfer rate in animals; for example, a level of less than 0.003 mg/L indicates a low toxicological and xenobiotic risk to the quality of dairy production [123]. High concentrations of these elements cause serious systemic problems and are undoubtedly transferred to milk [124]. Research conducted in dairy herds in the Oxapampa Valley, Pasco, reported Pb contamination in water and its transfer to milk [125]. The contributions of metals such as Pb and As are related to water, while the presence of Cr and Cd are related to soil contamination [122]. Frequent monitoring of heavy metals in livestock production areas is essential because high concentrations of heavy metals cause anemia, reproductive disorders, cancer, and animal teratogenesis, decreasing long-term production [126]. On the other hand, consuming food in a contaminated state is a risk factor for human health, as it alters the nervous system's and organs' functions, causing mutagenesis and carcinogenesis [127].

This research is one of the first studies developed in which the most significant livestock production comes from a region with multiple by-products. The findings on metal and metalloid concentrations highlight the importance of properly managing livestock activity to ensure quality over time. They also underscore the need to conserve the areas where this activity takes place by implementing measures to prevent and mitigate contamination.

It is recommended to continue monitoring the water bodies' monitoring activities, to report frequently the water conditions in these micro-watersheds and to allow immediate intervention as soon as contaminant concentrations increase. We hope that this research will serve as a baseline for the execution of research focused on implementing viable measures and technologies to counteract contamination by metals and metalloids in fragile ecosystems, such as the headwaters of watersheds, seeking to inform the population in a timely manner and socializing each of the innovations, thus closing the gap that exists between the academic field and the rural population.

5. Conclusions

This research presents the concentrations of metals and metalloids in the water of high Andean livestock watersheds in northern Peru for the first time. The distribution of several elements was revealed through the application of a temporal analysis using PCA during the wet and dry seasons. In the wet season, Co, Fe, Mn, Al, Zn, Ni, Ag, Cr, Cu, Cd, and B stood out, while in the dry season, Na, K, As, Sb, V, and Si predominated; on the other hand, elements such as Mg, B and Sr were not affected by either seasonal period. Regarding the spatial distribution of metals, the micro-watersheds with the highest concentrations were Ventilla (Cu, Li, Ni, Ag, Pb, Zn, Al, Mn, Na), Cabildo (Ba, Cd, Cr, V, Mg), Pomacochas (Co, Fe) and Atuen (K, Sr) and as for metalloids, the highest concentrations were recorded for Ventilla (As), Cabildo (B) and Timbambo (Sb and Si).

It is reported that the risk is due to the high concentrations of metals such as Pb and metalloids such as As present in the water of all the micro-watersheds evaluated in both wet and dry seasons, putting at risk the suitability of use of these water resources for human consumption and economic activities such as livestock and agriculture. Although the point sources of contamination and the dynamics of the concentrations of elements at the sediment level and their release into the water bodies have not been identified, further research is suggested to clarify the contamination panorama and determine whether the sources of contamination are of natural origin, as assumed, or anthropogenic sources. Despite this, the report of the concentrations of these elements is an opportunity for the pertinent implementation of pollution prevention and mitigation measures in vulnerable areas such as the watershed headwaters where our study area is located.

Data availability statement

The research data was deposited in a public institutional repository. The link to the repository is as follows: https://repositorio.untrm.edu.pe/bitstream/handle/20.500.14077/2819/Leiva%20Tafur%20Damaris.pdf?sequence=1&isAllowed=y.

CRediT authorship contribution statement

Damaris Leiva-Tafur: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Jesús Rascón:** Writing – review & editing, Supervision, Software, Conceptualization. **Fernando Corroto de la Fuente:** Writing – original draft, Methodology, Data curation, Conceptualization. **Malluri Goñas:** Writing – review & editing, Writing – original draft, Formal analysis. **Oscar Andrés Gamarra Torres:** Writing – review & editing, Resources, Conceptualization. **Manuel Oliva-Cruz:** Writing – original draft, Supervision, Resources, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e33013.

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