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Heavy Metals in Water and Sediments and Their Impact on Water Quality in Andean Micro-watersheds: A Study of the Colorado and Alajua Rivers in the Ambato River Watershed, Tungurahua, Ecuador

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ABSTRACT

The present study aims to characterize the water and sediment quality of the Colorado and Alajua rivers within Ecuador's Ambato River watershed, with a specific focus on the presence of heavy metals. Measurements were conducted at five sampling points along the upper and lower zones of each river, where both physicochemical and microbiological parameters, as well as concentrations of heavy metals in water and sediments, were analyzed. Most parameters exhibited statistically significant differences, as determined by the analysis of variance (ANOVA), between the values observed in the upper and lower zones of the micro-watersheds. Water quality in the mentioned rivers was assessed using specific water quality indices, WQI, namely the NSF-WQI and Dinius WQI. Additionally, the impact of heavy metal presence in the water and sediments was evaluated using the Heavy Metal Evaluation Index (HEI). While most parameters met the Ecuadorian quality standards for water sources intended for human consumption, concerns emerged regarding elevated levels of total and fecal coliforms along both rivers, which could limit the suitability of these rivers as a water source for human use and consumption. At various sampling points, water quality criteria for the preservation of aquatic life were not met for several heavy metals. For example, the Colorado River exhibited elevated levels of zinc (59-76 $\mu g.L^{-1}$), copper (12-47 $\mu g.L^{-1}$), lead (1.2-3.9 $\mu g.L^{-1}$), iron (0.33-0.37 $mg.L^{-1}$), and manganese (0.37-0.47 $mg.L^{-1}$), while the Alajua River showed excess copper (11 $\mu g.L^{-1}$), iron (0.61-0.72 $mg.L^{-1}$), and manganese (0.62-0.98 $mg.L^{-1}$). Geological factors likely contribute to the concentration of heavy metals in the upper segments of the rivers, while agricultural runoff may contribute to concentrations in the lower segments. Sediments exhibited higher average values of the Heavy Metal Evaluation Index (HEI) (20.6-26.7) compared to water samples (13.9-15.4), indicating a potential accumulation of heavy metals in the river sediments. Overall, both rivers exhibited contamination levels ranging from regular to moderate, as indicated by the calculated average Water Quality Indices (WQI), with certain areas showing slight contamination or meeting acceptable standards. These results highlight the influence of anthropogenic activities on water quality, emphasizing the necessity of continuous monitoring to assess and control their impact.

INTRODUCTION

Water plays a crucial role in both human well-being and environmental integrity. The use of water is influenced by its condition, whether it is in its natural state or altered in its physical, chemical, or biological characteristics (WHO 2011). In this context, Ecuador has instituted a framework of standards and regulatory mechanisms intended to safeguard aquatic ecosystems, protect drinking water sources, and sustain agricultural irrigation (Ministerio del Ambiente del Ecuador, 2015). Nevertheless, the persistence of water pollutants and the economic and technological constraints in rural Andean communities turn water quality preservation into a lasting challenge for emerging economies.

Rivers located in the high-altitude Andean regions of Ecuador, such as the Colorado River (4048-3876 meters above sea level, a.s.l.) and the Alajua River (3236-2784 meters a.s.l.), which belong to the Ambato River watershed, predominantly constitute lotic ecosystems. These ecosystems are characterized by their rapid transport of the contained substances, including contaminants, such as heavy metals, persistent organic pollutants (POPs), nutrients, and pathogenic microorganisms. The conveyance of these pollutants poses potential detrimental impacts on human health and negative effects on the aquatic ecosystems (Timmerman 2011).

The quality of water in these rivers depends on both their intrinsic natural characteristics and the land use practices within their respective hydrographic watersheds. The concentration of various substances in these water bodies is influenced not only by the local geological and hydrogeological conditions but also by the introduction of compounds of anthropogenic origin (Fournier et al. 2019). Human-induced activities have negatively impacted the aquatic integrity of the main river systems within the Ambato River watershed. It is estimated that approximately 95% of the wastewater discharged into the water bodies of this watershed lacks proper treatment (Herrmann 2002). The presence of heavy metals in riverine systems can markedly influence their water quality. Metals such as lead, nickel, cadmium, chromium, and arsenic may enter water bodies via various routes. These include industrial operations, effluents and disposals, mining activities, and the mobilization of natural sedimentary deposits (Matta & Gjyli 2016).

The presence of metals in the rivers of Ecuador poses a significant environmental threat, particularly in the Cotopaxi and Tungurahua provinces, where the presence of heavy metals has been detected. Elevated concentrations of chromium have been documented at tannery wastewater discharge locations along the Ambato River, with recorded values between 8.2 and 30.2 mg.L^{-1} (Sánchez et al. 2020). With respect to cadmium, the highest concentration was observed in the Ambato-Huachi-Pelileo irrigation canal, reaching a level of 0.23 mg.L^{-1}. In the case of the Cutuchi and Pumacunchi rivers, arsenic emerges as the predominant contaminant, exhibiting maximum concentrations of 0.062 mg.L^{-1} and 0.067 mg.L^{-1}, respectively (Sánchez et al. 2020). On the other hand, lead (Pb), concentrations of 0.2 mg.L^{-1} were detected in the Ambato-Huachi-Pelileo irrigation canal and 0.18 mg.L^{-1} in the Ambato River.

Furthermore, in the study by Chiliquinga & Donoso in 2012, the presence of chromium was found with an average concentration of 0.0628 mg.L^{-1} in the Pachanlica River, located in the province of Tungurahua (Chiliquinga & Donoso 2012, Sánchez et al. 2020). The detrimental impacts of heavy metals are not confined to aquatic life forms. These metals can modify biogeochemical cycles and alter the composition of aquatic communities, consequently disrupting the natural balance of these ecosystems (Sonone et al. 2020, Vajargah 2021).

The Alajua River originates from the Casahuala volcano in Tungurahua Province, covering an area of influence spanning 123 km^2, accounting for 13% of the total watershed area. It plays an important role in providing water resources for agricultural purposes and human consumption within the Ambato canton. On the other hand, the Colorado River originates in the highlands of the Chimborazo volcano located in the Ecuadorian Andean region and serves as a significant tributary of the Pastaza River basin. It has an approximate length of 100 km, and its influence area within the basin encompasses approximately 164 km^2, constituting 18 % of the overall watershed area (Pérez 2015).

However, information regarding the presence of heavy metals in water and sediments in these Andean rivers is limited. Hence, the present study aims to characterize the water and sediment quality of these two rivers, which are the main ones in the Ambato River watershed in Ecuador. The study focuses on identifying the presence of heavy metals in both water and sediments and comparing the results with current environmental regulations in Ecuador. Additionally, water and sediment quality indices will be applied using the collected data, enabling the calculation of numerical values that reflect the environmental conditions of the Colorado and Alajua rivers, as well as the evaluation of the impact of heavy metals on the water quality of these rivers.

MATERIALS AND METHODS

Research Area

The study area, which encompasses the Ambato River watershed within Ecuador's Tungurahua province (Figs. 1 and 2), is located in the western Andes region of the country. It is geographically defined by neighboring catchment areas, with the Cutuchi River to the north, the Chambo River to the south, the Cutuchi and Patate Rivers to the east, and the Babahoyo and Yaguachi Rivers to the west. Covering an approximate land area of 130 173 hectares, this sub-basin constitutes 38% of the province's total territory (Pérez 2015). Serving as the primary water source for the Tungurahua province, it supports a wide range of uses in both urban and rural areas, including domestic consumption, agricultural activities, and industrial applications (Herrmann 2002).

The Ambato River watershed consists of 11 hydrological micro-catchments, with the Ambato, Pachanlica, Colorado, and Alajua rivers being the predominant ones (Fig. 3). The Colorado River is a significant tributary of the larger catchment area of the Pastaza River.

Field visits were conducted to identify pollution hotspots in the study areas, resulting in the determination of five sampling points in the upper and lower basins of each river. In the case of the Colorado River (Fig. 4), at point 1 (P1-AF) with an altitude of 4048 m, located near a meteorological station at coordinates 113.0'25°''S 78°52'37.1''W, vicuñas

Fig. 1: Location map of the Tungurahua Province, Ecuador.

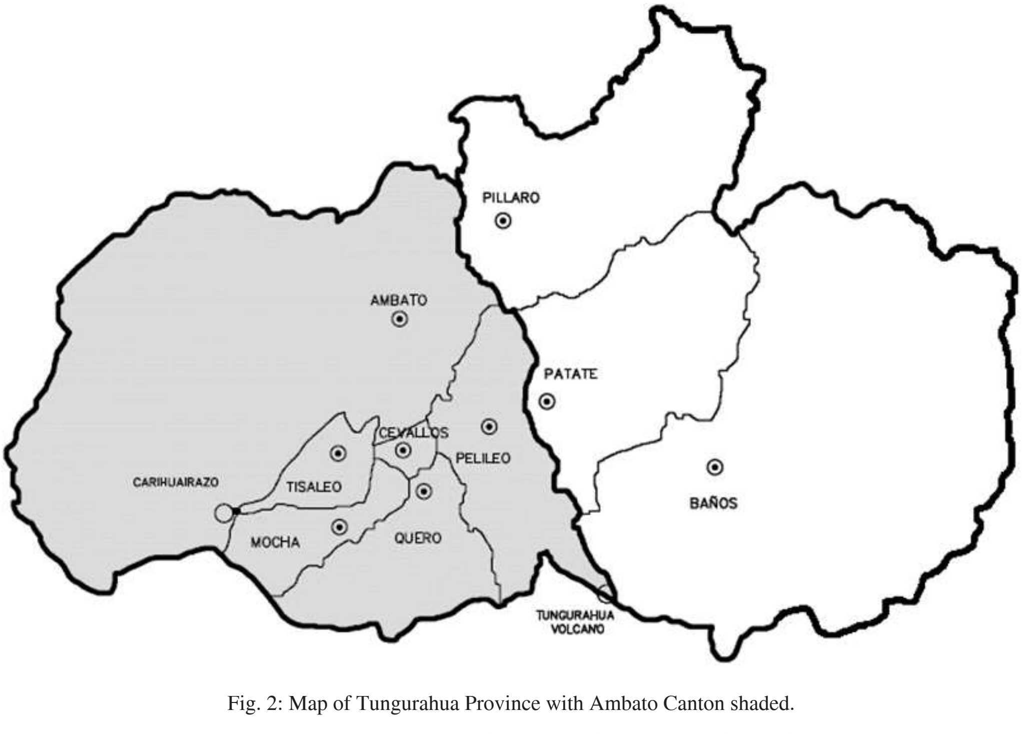

Fig. 2: Map of Tungurahua Province with Ambato Canton shaded.

were observed. At point 2, situated at an altitude of 3995 m at coordinates 1°24'55.5"S, 78°52'05.1"W, cows were seen along the river. On the other hand, at point 3, near the confluence of the middle tributary at 3994 m at coordinates 1°24'53.1"S, 78°51'49.5"W, no sources of contamination were identified. Additionally, residents testified that this site is used for human consumption without prior treatment. At point 4, located at 3881 m at coordinates 1°23’14.0’’S

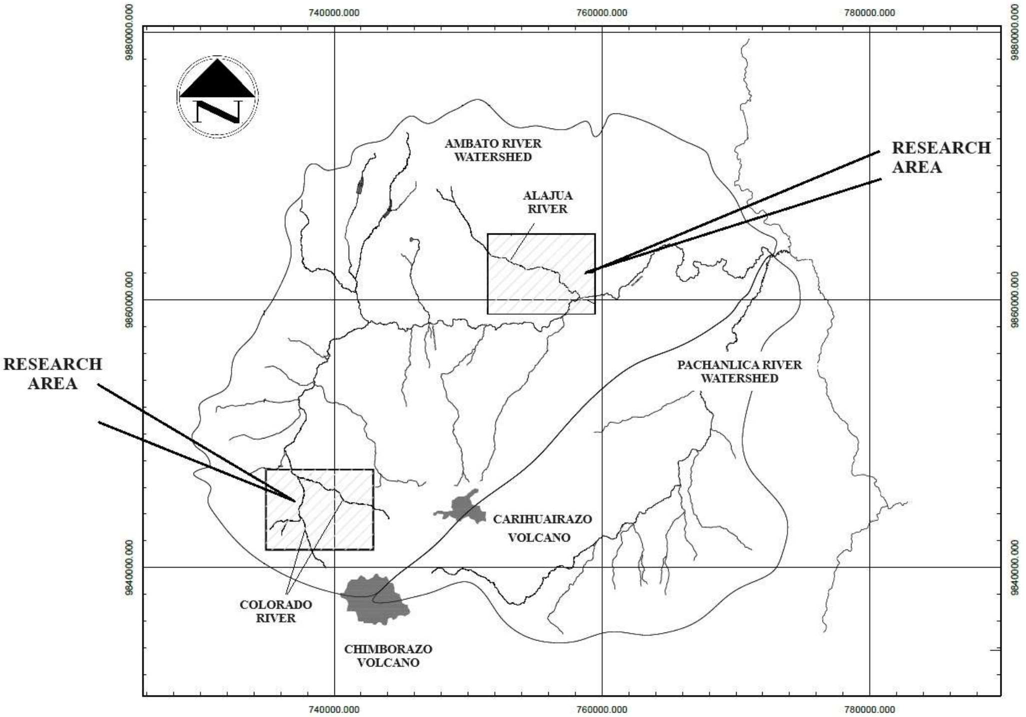

Fig. 3: Map of the Ambato River Watershed. Research Areas Colorado and Alajua Rivers.

78°51’59.1’’W, washing of containers used in dairies and laundry discharge was observed. Llamas and domestic wastewater discharges were witnessed at point 5, located near an underpass at 3876 m with coordinates 1°23'09.2"S and 78°51'57.7"W.

At point 1 of the Alajua River (Fig. 5), situated at 3236 m at coordinates 1°14'29.8" S 78°43'09.1"W, the waterway streamed amid forest vegetation. At point 2, on the Pumgoloma - Quisapincha road, located at 3191 m at coordinates 1°14'28.3" S 78°43'23.2"W, cultivated areas were observed. Point 3, positioned 200 m downstream from the road at an elevation of 3207 m and coordinates 1°14'29.6"S 78°43'15.7"W, had pastures for livestock, cultivated areas, and recreational spots for sport fishing. Point 4, located 200 m upstream of the EMAPA-Tilulum drinking water treatment plant, operated by the Municipal Water Company of Ambato (EMAPA) at 2788 m and coordinates 1°15'40.5"S 78°40'45.6"W, exhibited signs of deforestation in the surrounding area. Lastly, point 5 at the EMAPA Tilulum drinking water treatment plant, at an elevation of 2784 m and coordinates 1°15'48.3"S, 78°40'41.1"W, showed water discharges and areas used for fruit cultivation.

Water and Sediment Samples Collection

Simple sampling of water and sediments was conducted according to Ecuadorian standards (NTE-INEN 2176 2013), which took place during the dry season of the year (August) to minimize the impact of rainfall on the collected samples. All samples were collected in triplicate. The collection of surface water at each point was done using a Van Dorn bottle, which was submerged to a depth of 0.3 meters below the water surface. The collected water volume was poured into one-liter amber bottles and sterile 100 mL containers for microbiological analysis, avoiding the formation of air bubbles. On the other hand, along the riverbanks, 300 grams of sediment were collected using spatulas and placed in polyethylene plastic jars, which were then sealed in airtight plastic bags (Vega 2021). Samples for the analysis of heavy metals, sulfates, and chlorides were acidified with 0.1% concentrated 65% nitric acid. Subsequently, the samples were transported in containers with ice to prevent alteration until they reached the facilities of the Environmental Analysis Laboratory of the Faculty of Food Science and Biotechnology at the Technical University of Ambato, where they were characterized.

The detection of in-situ parameters is carried out using the HANNA HI 9829 multiparameter meter, as well as the LaMotte turbidimeter. At each station, in-situ measurements of temperature, pH, turbidity, conductivity, dissolved oxygen (DO), and total dissolved solids (TDS) were conducted by directly immersing the meter probe 25 cm below the water surface (Quiroz et al. 2017).

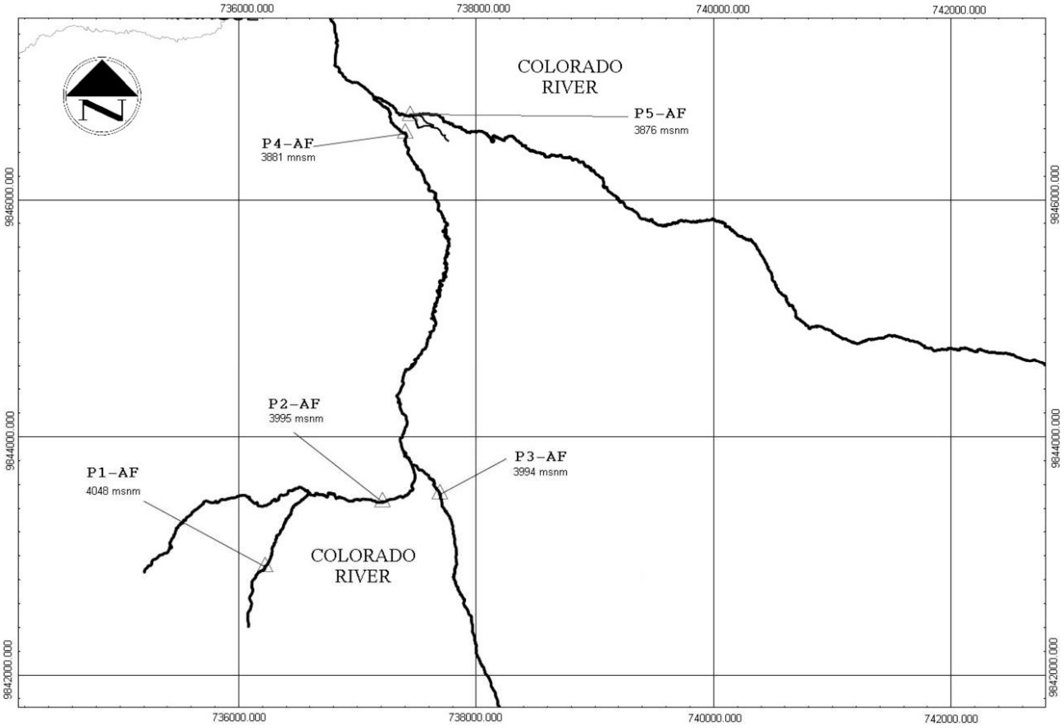

Fig. 4: Location of sampling points for the Colorado River.

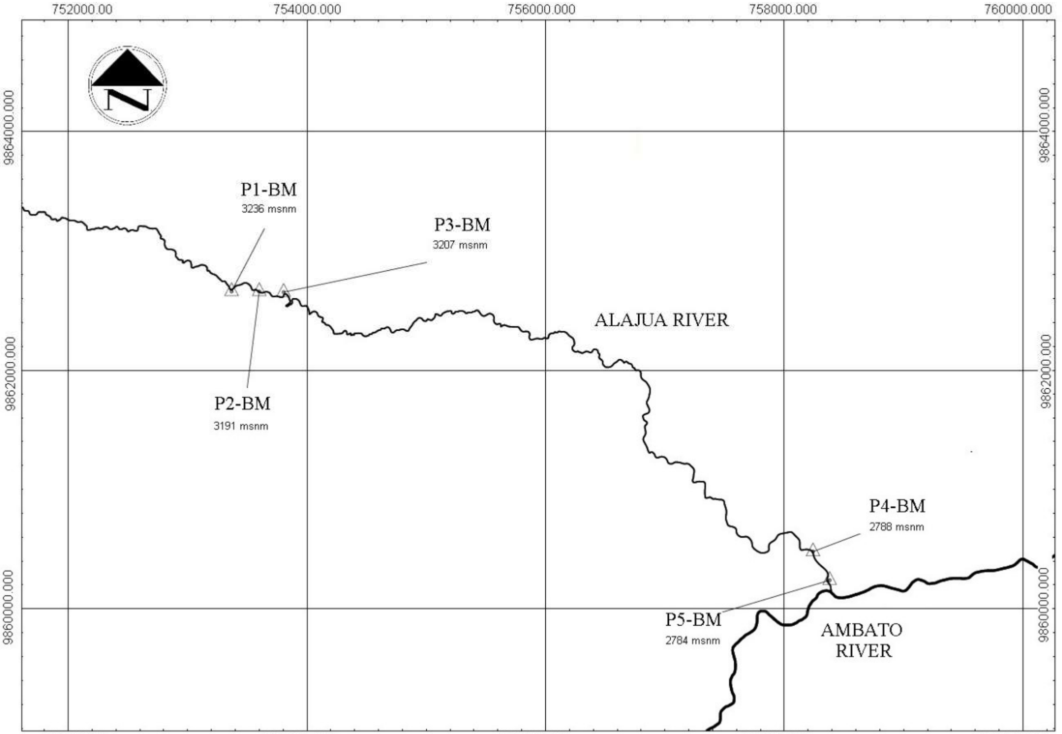

Fig. *5:* Location of sampling points for the Alajua River.

Analysis of Water and Sediment Samples

Total and fecal coliforms were determined using the membrane filtration (MF) technique. Samples were first agitated for 30 seconds, and then serial dilutions ranging from 10^{-1} to 10^{-3} were prepared using sterile buffered water (Plúas 2019). Next, sterile millipore membranes were placed in the funnels' receptacles, then the dilutions were transferred to the funnels of the vacuum equipment, filtration was initiated, and once completed, the membranes were removed and placed in Petri dishes with selective media, m-Endo for total coliform detection and rosolic acid for fecal coliforms. Finally, they were incubated at 37°C for 24 hours, and the colony-forming units (CFU.100.mL-1) were calculated (Larrea-Murrell et al. 2013).

The following ions were determined using the HI83399 Hanna photometer: nitrates, ammonia, phosphates, chlorides, sulfates, potassium, magnesium, calcium, hexavalent chromium, copper, zinc, and iron. The analyses were conducted following the Standard Methods for the Examination of Water and Wastewater (American Public Health Association, APHA, 2017). The total permanent hardness of the water, expressed as the mgL^{-1} $CaCO_3$ equivalent, was calculated in the water samples using the following formula (Pal et al. 2018): Hardness (mgL^{-1} $CaCO_3$) = 2.5(mgL^{-1} Ca) + 4.1(mgL^{-1} Mg).

The analysis of heavy metals, specifically arsenic, lead, nickel, and cadmium, was conducted using Graphite Furnace Atomic Absorption Spectrometry (GFAAS) with the PG Instruments AA500 spectrometer. Acidified surface water samples were filtered using 0.45 µm syringe filters (Econofilter). The measurements were carried out following the specifications recommended in the PGI AA500 Analytical Cookbook. For each specific metal analysis, predetermined calibration curves developed by the Environmental Analysis Laboratory at the Technical University of Ambato were utilized. These calibration curves exhibited Pearson Correlation Coefficients (R^2) above 0.98.

To determine the conductivity and pH in sediments, the procedure described by Romero et al. (2009) was employed. 200 grams of sediment were placed in a 1000 mL precipitation beaker along with 500 mL of distilled water. The mixture was stirred for 30 minutes to keep the particles suspended. Subsequently, conductivity and pH were measured using the portable photometer Hanna HI9829.

For the determination of heavy metals in sediments, prior digestion was conducted using the EPA 3051 method in a microwave oven (ETHOS UP). This involved weighing 5 grams of the sample into pre-labeled and pre-weighed crucibles, which were then dried at 105°C for 24 h. The dried samples were subsequently pulverized, and 0.5 grams were placed into digestion tubes. Next, 5 mL of concentrated HNO_3 and 1 mL of 30% (V/V) hydrogen peroxide were added. The tubes were then subjected to microwave digestion for 50 min (American Public Health Association 2017). Once the samples were digested and cooled, they were transferred to 100 mL volumetric flasks and topped up with distilled water. The samples were stored at 5°C until analysis (United States Environmental Protection Agency (EPA) 2013, Vega 2021). The digested samples were then analyzed using the atomic absorption equipment, with prior filtration using the WELCH vacuum filtration apparatus with 0.45 µm cellulose acetate filters. Finally, the results obtained from the GFAAS equipment are expressed in units of $mg.kg^{-1}$ dry sediment.

Water Quality Index (WQI) and Heavy Metal Evaluation Index (HEI)

Two different Water Quality Indices (WQI) were employed: the NSF-WQI (Water Quality Index according to the National Science Foundation), which primarily assesses water quality for human consumption, and the Dinius' WQI, which considers five water uses, including human consumption, industry and recreation, agriculture, fishing, and aquatic life (Torres et al. 2018). For the Water Quality Index (WQI), as outlined by Sierra (2011), the following parameters were considered: dissolved oxygen, pH, temperature, turbidity, total solids, total phosphate, nitrates, fecal coliforms, and Biochemical Oxygen Demand (BOD). This approach involves the utilization of a rating curve technique, linking the measured parameter concentrations (mg.L) to a quality sub-index value, S_i , ranging from 0 (lowest quality) to 100 (highest quality). Relative fractional weights are denoted as were assigned to each parameter, reflecting their respective importance and the specific aspects of water quality they assess. Utilizing the formula (1), the WQI value was then computed for each sampling zone, as elaborated by (Uddin et al. 2021).

$$\text{NSF-WQI} = \sum_{i}^{n} S_i \cdot W_i \quad \ldots(1)$$

The corresponds to the following water quality ranges: 91-100 (excellent), 71-90 (good), 51-70 (fair), 26-50 (poor), and 0-25 (very poor) (Méndez et al. 2020, Quiroz et al. 2017).

In addition, Dinius' Water Quality Index (WQI) was also employed, which encompasses 12 parameters, including dissolved oxygen (DO), Biochemical Oxygen Demand (BOD), total coliforms (CT), fecal coliforms (CF), nitrates, hardness, chlorides, alkalinity, pH, conductivity, temperature, and color (Flores 2022). Nine of these parameters were considered for the study, while three parameters—chlorides, which were undetectable (measuring below 0.5 $mg.L^{-1}$), as well as alkalinity and color, which were not measured—were excluded from the analysis. Consequently, weighting coefficients (W_i) were adjusted, and subindex values (Q_i) were determined using weighted geometric mean equations, with the results raised to the corresponding powers, n, (Dinius 1987). Finally, the DINIUS-WQI was calculated using the geometric mean with a multiplicative function:

$$\text{DINIUS-WQI}= \prod_{i=1}^{n} Q_i^{S_i} \qquad \dots(2)$$

The DINIUS-WQI is associated with the following water quality ranges: 90-100 (excellent), 80-89 (acceptable), 51-79 (slightly contaminated), 30-50 (contaminated), 20-29 (highly contaminated), and 0-19 (excessively contaminated) (Dinius 1987, Flores 2022, Guananga-Diaz et al. 2022).

There are several water quality indices developed to assess and analyze metal pollution, including the Heavy Metal Pollution Index (HPI), the Metal Pollution Index (MPI), the Heavy Metal Evaluation Index (HEI), and the Contamination Degree (Cd) (Boateng et al. 2015). However, it has been suggested that the use of HEI, due to its simplicity, is preferable for conducting heavy metal pollution monitoring (Edet & Offiong 2002). The Heavy Metals Assessment Index (HEI) was employed to gain a comprehensive understanding of water quality in the Colorado and Alajua rivers concerning heavy metal pollution (Moyel et al. 2015). This index is defined as follows:

$$\text{HEI} = \sum_{i=1}^{n} \frac{H_c}{H_{mac}} \qquad \dots(3)$$

Where H_c represents the measured value, while H_{mac} corresponds to the maximum allowable concentration of each trace metal (Rezaei et al. 2019). H_{mac} was determined based on the maximum permissible value specified according to the Ecuadorian environmental regulations, Annex 2 of Book VI of TULSMA (Ministerio del Ambiente del Ecuador 2015) in *"Water Quality criteria for the preservation of aquatic and wildlife in freshwater, marine, and estuarine waters."* However, for sediment samples, H_{mac} was chosen based on the maximum permissible value established in the "*Criteria for soil quality*," of the mentioned regulation. According to the HEI index value, three levels of pollution categories are proposed, described as follows: (i) HEI < 10 indicates a low level of contamination; (ii) HEI = 10-20 signifies a moderate level of contamination; and (iii) HEI > 20 represents a high degree of contamination (Boateng et al. 2015).

RESULTS AND DISCUSSION

Physicochemical and Microbiological Characterization of Water Samples

Water samples were collected during the dry season, and Table 1 presents their in-situ measurements. Both the Colorado River and the Alajua River exhibit dissolved oxygen (DO) concentrations approaching saturation due to the increased turbulence levels in these water bodies (Carvajal 2017).

The pH fell within the allowable range of 6.5 to 9, as stipulated in Tables 1, 2, and 3 of TULSMA. These tables outline the Ecuadorian environmental regulations of criteria for quality water, encompassing various uses, including human consumption and domestic use (Table 1), the preservation of freshwater aquatic and wildlife (Table 2), and agricultural irrigation (Table 3) (MAE 2015).

Electrical conductivity is directly linked to the presence of total dissolved solids (TDS) due to their ionic activity, which can originate from both organic and inorganic substances in solution (Cantera et al. 2009). In the Colorado and Alajua rivers, an increase in conductivity downstream was observed, rising from 196 to 484 $\mu S\ cm^{-1}$ and from 127

Table 1: Physicochemical parameters and on-site meteorological conditions at surface water sampling points.

	Sampling Points	pH	Temperature (°C)	ORP (mV)	OD (ppm)	TDS (ppm)	Turbidity (NTU)	Conductivity ($\mu S\ cm^{-1}$)	Height (m)	Pressure mmHg)
Colorado River	P1 – AF	8.2±0.1	8.7±0.2	20.7±0.5	7.4±1.5	98±1	1.2± 0.1	196± 1	4048	472
	P2 – AF	8.2±0.1	9.6±0.2	61.5±0.5	6.8±1.5	64±1	0.7±0.1	129±1	3995	469
	P3 – AF	7.0±0.1	8,6±0.2	79.0±0.5	6.8±1.5	114±1	0.3±0.1	228±1	3994	470
	P4 – AF	8.8±0.1	13,1±0.2	57.5±0.5	6.7±1.5	98±1	0.3±0.1	196±1	3881	483
	P5 – AF	7.4±0.1	13,5±0.2	-38.8±0.5	6.9±1.5	242±1	0.5±0.1	484±1	3876	482
Alajua River	P1 – BM	8.3±0.1	13.0±0.2	9.4±0.5	8.4±1.5	64±1	2.6±0.1	127±1	3236	526
	P2 – BM	8.3±0.1	12.6±0.2	67.0±0.5	8.4±1.5	64±1	2,3±0.1	128±1	3191	527
	P3 – BM	7.7±0.1	12.7±0.2	71.3±0.5	8.5±1.5	64±1	2.7±0.1	128±1	3207	526
	P4 – BM	8.6±0.1	9.3±0.2	88.8±0.5	9.7±1.5	76±1	2.1±0.1	152±1	2788	550
	P5 – BM	8.9±0.1	9.5±0.2	63.3±0.5	9.9±1.5	80±1	1.9±0.1	161±1	2784	552

to 161 µS cm^{-1}, respectively. This upward trend may be associated with increased agricultural and domestic activities since 2015. According to Vinueza et al. (2021), the average conductivity in surface waters of Andean rivers in Ecuador is approximately 137 µS cm^{-1}, which aligns with the figures obtained in this study. When comparing both rivers, the Colorado River exhibits higher conductivity than the Alajua River, with averages of 247 and 139 µS cm^{-1}, respectively. This difference could be attributed to a greater presence of salts discharged into the Colorado River, stemming from anthropogenic activities.

Regarding the Oxidation-Reduction Potential (ORP), Ecuador lacks specific regulatory standards for reference values concerning this parameter. Nevertheless, it is observed that samples from the Alajua River and the first four sampling points of the Colorado River exhibit oxidizing characteristics, indicated by their positive ORP values. Conversely, sampling point P5 displayed a negative ORP value. This anomaly could be linked to the elevated content of Total Dissolved Solids (TDS) at 242 mg.L^{-1}, high conductivity at 484 µS cm^{-1}, and a significant concentration of sulfates (35 mg.L^{-1}). These characteristics may result from agricultural runoff, the presence of farm animals, and native camelids in the area (Reichart et al. 2007)

Total Coliforms (TC) and Fecal Coliforms (FC) in Water Samples

The water quality criterion, as specified in Tables 2 and 3 of the TULSMA regulations, is 1000 CFU/100 mL of FC. Regarding this criterion, in both rivers, all values exceeded the limit, except at sampling points P1-AF and P3-AF of the Colorado River, where coliforms were not detected. The highest recorded figure was observed in the Colorado River, specifically at sampling point P4-AF, where the value reached 3.4×10^4 CFU mL^{-1} (see Table 3). This microbiological pollution can be attributed to anthropogenic contamination resulting from the improper disposal of organic animal waste and wastewater from human consumption.

The study conducted by Hong et al. (2010) demonstrated that TC is closely associated with physicochemical parameters of water, such as suspended solids, organic and inorganic content, pH, and temperature, as these factors influence the survival and growth of coliforms. In contrast, FC is linked to runoff, as it involves a greater transport of fecal matter into watercourses (Reitter et al. 2021).

Determination of Metals and Ions in Water Simples

Table 4 displays the concentrations of metals and ions in water samples collected from various points in both rivers. No chlorides were detected in the samples taken from the Colorado River. Furthermore, sampled areas showed low levels of nitrates, ammonia, phosphates, and sulfates, indicating a reduced degree of anthropogenic contamination (Strokal et al. 2020). Downstream points in the Colorado River (points 4 and 5) tend to exhibit higher concentrations of metals and ions, notably nitrates (377% higher), sulfates (129% higher), and magnesium (103% higher) compared to points in the upper zone (points 1, 2, and 3). This difference may be attributed to increased agricultural activity in the lower Colorado River watershed (Badrzadeh et al. 2022).

Regarding the Alajua River, the concentrations of all metals and ions analyzed comply with the permissible limits established by legislation for the preservation of aquatic and wildlife (MAE 2015). The concentration of ammonia at sampling point 3 is slightly elevated (0.90 mg.L^{-1}) compared to the other sampling points. According to the United States Environmental Protection Agency (EPA 2013), an ammonia concentration at pH 7.0 and 20°C of 17 mg.L^{-1} can lead to

Table 2: Determination of fecal and total coliforms.

	Sampling Points	Units	Fecal Coliforms	Total Coliforms	TULSMA Tables Annex 1 - Book VI		
					Table 1	Table 2	Table 3
Colorado River	P1 – AF	CFU.mL^{-1}	ND	ND	1000	-	1000
	P2 – AF		$3.7 \cdot 10^3 \pm 2.5 \cdot 10^2$	$4.0 \cdot 10^3 \pm 5.6 \cdot 10^2$			
	P3 – AF		ND	ND			
	P4 – AF		$3.4 \cdot 10^4 \pm 5.5 \cdot 10^2$	$3.2\ 10^4 \pm 8.0 \cdot 10^2$			
	P5 – AF		$1.6 \cdot 10^3 \pm 8.0 \cdot 10^2$	$9.0 \cdot 10^3 \pm 6.7 \cdot 10^2$			
Alajua River	P1 – BM		$3.7 \cdot 10^3 \pm 3.0 \cdot 10^2$	$7.7 \cdot 10^3 \pm 1.5 \cdot 10^2$			
	P2 – BM		$3.3 \cdot 10^3 \pm 2.5 \cdot 10^2$	$5.8 \cdot 10^3 \pm 5.2 \cdot 10^2$			
	P3 – BM		$1.3 \cdot 10^4 \pm 49.0 \cdot 10^2$	$1.9 \cdot 10^4 \pm 5.1 \cdot 10^2$			
	P4 – BM		$7.5 \cdot 10^3 \pm 4.0 \cdot 10^2$	$1.4 \cdot 10^4 \pm 7.0 \cdot 10^2$			
	P5 – BM		$3.4 \cdot 10^3 \pm 2.0 \cdot 10^2$	$6.1 \cdot 10^3 \pm 6.1 \cdot 10^2$			

Note: Values that were not detected are reported as (ND).

Table 3: Results of metal and anion concentrations in water samples.

Parameter	Units	Colorado River					Alajua River					Maximum permissible limit		
												Table		
		P1-AF	P2-AF	P3-AF	P4-AF	P5–AF	P1–BM	P2–BM	P3-BM	P4–BM	P5–BM	1	2	3
Calcium	mg.L^{-1}	19.5 ± 0.1	7.1 ± 0.1	20.6 ± 0.1	21.3 ± 0.1	33.2 ± 0.1	7.6 ± 2.8	18.1 ± 2.1	17.0 ± 2.8	15.2 ± 0.3	11.7 ± 1.1	-	-	-
Potassium	mg.L^{-1}	2.9 ± 0.1	2.7 ± 0.1	2.3 ±0.2	2.6 ± 0.2	5.0 ± 0.1	2.1 ± 0.06	2.0 ± 0.1	1.9 ± 0.1	1.8 ± 0.1	1.8 ± 0.1	-	-	-
Magnesium	mg.L^{-1}	1.3 ± 0.6	0.7 ± 0.2	1.7 ± 0.6	3.7 ± 0.6	1.3 ± 0.6	8.8 ± 0.7	10.1 ± 0.1	9.7 ± 2.2	10.7 ± 1.5	13.1 ± 1.4	-	-	-
Aluminum	mg.L^{-1}	1.0 ± 0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	-	0.1	5
Fluoride	mg.L^{-1}	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.5	-	$1^{fluorine}$
Ammonium	mg.L^{-1}	0.26 ± 0.20	0.09 ± 0.04	0.02 ± 0.01	0.08 ±0.05	0.07 ± 0.04	0.08 ± 0.01	0.08 ± 0.02	0.90 ± 0.04	0.12 ± 0.02	0.07 ± 0.03	-	-	-
Nitrate	mg.L^{-1}	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	1.8 ± 0.3	0.3 ± 0.2	0.9 ± 0.2	1.1 ± 0.2	1.2 ± 0.8	3.3 ± 0.2	3.2 ± 0.1	50	-	-
Phosphate	mg.L^{-1}	2.0 ± 0.2	1.4 ± 0.2	2.5 ± 0.1	2.4 ± 0.1	2.6 ± 0.1	0.3 ± 0.1	1.7 ± 0.2	2.0 ± 0,3	2.3 ± 0.1	3.0 ± 0.3	-	-	-
Chlorides	mg.L^{-1}	ND	ND	ND	ND	ND	1.6 ± 0.1	1.4 ± 0.2	0.9 ± 0.1	2.6 ± 0.3	2.2 ± 0.1	-	-	-
Sulfates	mg.L^{-1}	2.2 ± 0.8	15.1 ± 1.1	11.4 ± 0.9	8.7 ± 0.5	35.1 ± 0.6	0.8 ± 0.4	2.0 ± 0.7	2.1 ± 1.1	1.1 ± 0.8	5.6 ± 1.2	500	-	250

Note: Values that were not detected are reported as (ND). Table 1 indicates “Water Quality Criteria for Water Sources for human consumption and domestic use,” Table 2 indicates “Water Quality criteria for the preservation of aquatic and wildlife in freshwater, marine, and estuarine waters,” and Table 3 indicates “Water quality criteria for water intended for agricultural use” (MAE, 2015).

acute adverse effects on freshwater aquatic life, while chronic effects may occur at levels as low as 1.9 mg.L^{-1}. Furthermore, Ding et al. (2021) suggest that in Australia and New Zealand, the recommended limit for ammonium ions is 2.18 mg.L^{-1} at pH 7.0 to safeguard aquatic life. It can be concluded from the above that the levels of ammonia found in this study (ranging from 0.02 to 0.90 mg.L^{-1}) do not pose a threat to aquatic life as they are below the permissible limits of local regulations and are lower than the critical values established in different countries, indicating a limited impact from anthropogenic contamination.

Similar to the Colorado River, the lower zones of the Alajua River (points 4 and 5) exhibit higher concentrations of these pollutants: nitrates 207% higher, sulfates 105% higher, and phosphate 99% higher than at higher elevations (points 1, 2, and 3). Agriculture and communal wastewater discharges into the river are presumed sources of pollution (Mekuria et al. 2021). However, the presence of aluminum and fluoride was not detected in any of the samples taken in both rivers (except at point 1 in the Colorado River, with an aluminum concentration of 1 mg.L^{-1}).

Determination of Heavy Metals in Water Samples

Table 4 presents the results of heavy metal determination, including arsenic, lead, nickel, zinc, copper, cadmium, hexavalent chromium, iron, and manganese, in the water samples collected from various points in the Colorado and Alajua rivers. In the Colorado River, concentrations of zinc exceeding the established water quality criterion for aquatic life, which is 30 µg.L^{-1}, have been observed at points 2, 3, and 4. These elevated zinc concentrations are attributed to factors such as runoff from roads, agricultural areas, and the release of zinc-containing minerals due to weathering (Prasad Ahirvar et al. 2023). The presence of zinc and other metals in water can also be influenced by the geological and mineral characteristics of the soil (Tu et al. 2020). Zinc was not detected in the water samples from the Alajua River.

Regarding lead, the Colorado River exhibits levels exceeding the permissible limit (1 µg.L^{-1}) for the preservation of aquatic life at all sampling points (Table 4). This could be attributed to the atmospheric deposition of anthropogenic lead from sources like gasoline use, coal combustion, and vehicle emissions (González et al. 2020). The sampling areas of this river are influenced by the presence of roads and major routes connecting various cantons in the province, including the road to Guaranda. On the other hand, the Alajua River presented elevated lead concentrations (11.46-2.64-1.78 µg.L^{-1}) at sampling points 3, 4, and 5 (Table 4). The presence of this metal in the water of the Alajua River may be attributed to the fact that these areas are downstream of the Quisapincha-Pumgoloma route.

In sampling points 1, 3, and 5 of the Colorado River, iron (Fe) concentrations exceeding the established water quality standards for aquatic life (0.3 mg.L^{-1}) were detected. In contrast, at all 5 study points along the Alajua River, iron concentrations ranged from 0.612 to 0.722 mg.L^{-1}, surpassing the limits set by TULSMA for the preservation of aquatic life (Table 4). This is likely due to the presence of natural sources attributed to soil composition (Borja et al. 2020). The World Health Organization (WHO 2011) mentions that iron concentrations up to 0.7 mg.L^{-1} do not pose an immediate threat to public health. However, the accumulation of iron can lead to hemorrhagic necrosis and gastric mucosa disorders (WHO 2011). Furthermore, manganese levels in the Colorado River (0.433-0.467 mg.L^{-1}) and the Alajua River (0.621-0.983 mg.L^{-1}) exceeded the criteria for the preservation of aquatic and wildlife in freshwater (0.1 mg/L) and for agricultural use (0.2 mg.L^{-1}). Clearly, both rivers show an increase in manganese concentration downstream. The high levels of manganese in the river waters can be attributed to the natural presence of this element in the environment due to the erosion of manganese-containing rocks, volcanic activity, and plant decomposition (Bhuyan et al. 2019).

Determination of Metals in Sediment Samples

The concentrations of heavy metals in sediments serve as a key indicator of pollution within the aquatic ecosystem. In the sediment samples collected from the Colorado River, the following metals were detected: Cu, Cd, Ni, Cr, Pb, and Cr^{6+}. Similarly, sediment samples from the Alajua River revealed the presence of metals, including Fe, Cu, As, Pb, Ni, Cr^{6+}, and Cd.

Hexavalent chromium (Cr^{6+}) exceeded the soil quality criterion of 0.4 mg.kg^{-1} in all five sampling stations of both rivers (MAE 2015). Chromium concentrations ranged from 4.5 to 9.7 mg.kg^{-1} in the Colorado River and from 2.9 to 6.3 mg.kg^{-1} in the Alajua River (Table 5). This may be due to the geological accumulation of volcanic origin in the soil and processes of erosion and sedimentation in the sampled areas (González et al. 2020).

In terms of copper (Cu), the established limit of 25 mg.kg^{-1} has been exceeded at all sampling points in both rivers. Specifically, the highest levels of this metal were recorded at points 1 and 3 of the Colorado River, reaching 184 mg.kg^{-1} and 180 mg.kg^{-1}, respectively (Table 5). Furthermore, significant copper content was also detected at sampling stations 2, 3, 4, and 5 of the Alajua River, ranging from 194 mg.kg^{-1} to 228 mg.kg^{-1}. These findings indicate that the Alajua River exhibited a higher copper concentration compared to the Colorado River. The elevated

Table 4: Results of heavy metals in water samples.

Parameter	Units	Colorado River					Alajua River					Maximum permissible limit		
												Table		
		P1-AF	P2-AF	P3-AF	P4-AF	P5–AF	P1–BM	P2–BM	P3-BM	P4–BM	P5–BM	1	2	3
Arsenic	$\mu g.L^{-1}$	5.1 ± 0.5	4.9 ± 0.8	5.1 ± 0.3	5.1± 0.3	5.1 ± 0.5	5.0 ± 0.3	5.0 ± 0.1	4.9 ± 0.6	5.9 ± 0.7	5.8 ± 0.9	100	50	100
Lead	$\mu g.L^{-1}$	2.8 ± 0.1*	3.9 ± 0.1*	2.2 ± 0.3*	1.2 ± 0.1*	3.3 ± 0.2*	ND	ND	2.6 ± 0.5*	1.8 ± 0.1*	11.5 ± 1.2*	10	1	5000
Nickel	$\mu g.L^{-1}$	ND	ND	ND	ND	2.1 ± 0.1	ND	3.2 ± 0.1	ND	ND	2.4 ± 0.1	-	25	200
Zinc	$\mu g.L^{-1}$	3.0 ± 0.1	76 ± 0.1*	67 ± 0.1*	59 ± 0.2*	19 ± 0.2	ND	ND	ND	ND	ND	-	30	2000
Copper	$\mu g.L^{-1}$	47 ± 1	12 ± 1	4 ± 1	4 ± 1	23 ± 1	ND	4 ± 1	11 ± 1	2 ± 1	3 ± 1	2000	5	200
Cadmium	$\mu g.L^{-1}$	0.2 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	20	1	50
Hexavalent Chromium	$\mu g.L^{-1}$	19 ± 3	22 ± 3	20 ± 3	17 ± 2	17 ± 4	5 ± 1	26 ± 1	26 ± 1	26 ± 1	26 ± 1	50	32^{Cr}_{total}	100
Iron	$mg.L^{-1}$	0.37 ± 0.01*	0.17 ± 0.04	0.33 ± 0.01*	0.17 ± 0.02	0.36 ± 0.06*	0.61 ± 0.02*	0.65± 0.03*	0.65± 0.02*	0.72± 0.02*	0.72±0.04*	1	0.3	5
Manganese	$mg.L^{-1}$	0.43± 0.01**	0.43 ± 0,01**	0.47 ± 0.06**	0.37±0.01**	0.47± 0.05**	0.62±0.22**	0.79± 0.3**	0.81± 0.11**	0.98± 0.2**	0.90±0.2**	-	0.1	0.2

Note: Values that were not detected by the GFAAS were reported as (ND). Table 1 indicates “Water Quality Criteria for Water Sources for human consumption and domestic use,” Table 2 indicates “Water Quality criteria for the preservation of aquatic and wildlife in freshwater, marine, and estuarine waters,” and Table 3 indicates “Water quality criteria for water intended for agricultural use” (MAE, 2015). Values that exceed Table 2 are marked with (*), and those that exceed the limits for agricultural use (Table 3) are marked with (**).

Table 5: Results of heavy metals analyzed in sediment samples.

Parameter	Units	Colorado River					Alajua River					Soil Quality Criterion (TULSMA))
		P1-AF	P2-AF	P3-AF	P4-AF	P5-AF	P1-BM	P2-BM	P3-BM	P4-BM	P5-BM	
pH		7.4±0.1	7.5±0.1	6.7±0.1	7.2±0.1	7.5±0.1	8.0±0.1	7.2±0.1	7.7±0.1	7.0±0.1	6.8±0.1	6-8
	mg.kg^{-1}	*5.3±0.2	*4.5±0.2	*9.7±0.3	*5.3±0.5	*6.7±0.1	*4.4±0.6	*2.9±0.5	*6.3±0.3	*2.9±0.3	*5.0±0.4	0.4
Cu		*184±3	*170±1	*180±1	*173±1	*168±1	*179±2	*198±2	*199±3	*200±3	*233±1	25
Cd		*1.1±0.1	*3.4±0.1	*0.8±0.1	*1.4±0.1	*0.7±0.1	0.2±0.1	0.2±0.1	*1.8±0.3	2.0±0.1	0.6±0.1	0,5
Ni		11±2	12±1	12±1	16±2	4±2	0.9±0.1	13.8±1	3.7±0.7	4.1±0.7	8.5±4.6	19
Pb		16±5	16±7	3±1	6±4	2±1	2.2±0.5	2.7±1.0	9.0±2	10.5±1.5	2.1±0.4	19

Note: Results that exceeded the soil quality criteria established in Table 1, Annex 2 of Book VI of TULSMA (MAE, 2015) are indicated with (*).

copper levels in both rivers may result from runoff carrying copper-containing fertilizers and pesticides. Notably, the lower basin of the Alajua River, where more fruit crops are present, shows higher copper accumulation. This suggests that these chemicals are possibly used more frequently in this region, explaining the increased copper content in the river sediments (Shaw et al. 2020).

Cadmium (Cd) exceeded the permissible limit of 0.5 mg.kg^{-1} for soil quality in all samples from the 5 sampling zones of the Colorado River, with concentrations ranging from 0.7 to 3.4 mg.kg^{-1}. In the case of the Alajua River, it exceeded the regulations in sampling zones 3 and 5, with concentrations of 1.8 and 0.6 mg.kg^{-1}, respectively. The contamination of these rivers with cadmium is likely due to processes involving the deposition and release of sulfide minerals in sediments, as well as interactions with phosphate fertilizers used in agriculture or the presence of sedimentary rocks with high Cd levels (Hossain et al. 2019, Sarkar et al. 2021).

Statistical Analysis of Results

The water and sediment characterization results were analyzed using the ANOVA method. The majority of parameters between the upper and lower zones of the micro-watersheds of both rivers exhibited significant differences with p-values less than 0.05, except for arsenic and cadmium concentrations in water samples collected from the Colorado River.

The Determination of the Water Quality Index (WQI)

Table 6 displays the calculated values for the Water Quality Index (WQI) using the NSF and Dinius methods for the different sampling points in the Colorado and Alajua rivers.

The calculated NSF - WQI suggests that water quality in the Colorado River can be classified as moderate, as per Quiroz et al. (2017). Conversely, there was a decline in water quality in the sampling areas of the Alajua River, primarily due to elevated concentrations of fecal coliforms, as reported by Castro et al. (2022). This observation aligns with the findings of Pauta et al. (2019), who emphasize that fecal coliforms are the parameter with the most significant impact on water quality in Andean rivers. In some sampling areas of both rivers, signs of agricultural cultivation, livestock grazing, and domestic wastewater discharges were evident, and these activities intensified downstream in each river. Consequently, agricultural runoff can transport various contaminants into the rivers, including animal feces and organic fertilizers, leading to an overall increase in pollution levels, particularly in coliform counts (Pauta et al. 2019).

According to the Dinius Water Quality Index (Dinius 1987), water quality in the Colorado River was mostly classified as contaminated, except point 3, which was deemed acceptable. Consequently, agricultural use may not require treatment, but water treatment would be necessary for human consumption. Similarly, water quality at points 1, 2, and 3 in the Alajua River was deemed acceptable, suggesting that minimal purification may be necessary for agricultural uses. However, points 4 and 5 exhibited slight contamination, primarily due to anthropogenic activities in the area, such as fruit cultivation, domestic wastewater discharge, and mining. This contamination resulted in a decrease in the Water Quality Index (WQI) in the lower basin areas, as observed in Table 7 (Sierra 2011).

Additionally, it can be noted that the Colorado and Alajua Rivers have average NSF - WQI values of 59 and 67, respectively, indicating that the overall water quality is considered moderate for general use. However, the average DINIUS-WQI value for the Colorado River is 72, suggesting slight contamination, and thus, purification is necessary for crops requiring high-quality water. For human consumption, treatment is also required. In the case of the Alajua River, the average DINIUS-WQI value is 79, indicating acceptable water quality. Furthermore, for agricultural use, treatment is not necessary, but for human consumption, minimal purification will be required (Dinius 1987).

Heavy Metal Evaluation Index (HEI)

Table 7 presents the calculated values of the Heavy Metal Evaluation Index (HEI) for water and sediment samples collected in the Colorado and Alajua Rivers.

In terms of heavy metal presence in the water samples collected from different points along the Colorado River, points 1, 2, 3, and 5 exhibit Heavy Metal Evaluation Index (HEI) values ranging from 12.0 to 18.7, indicating a moderate level of contamination. Point 4 is the only sampling location with an HEI value below 10, registering 9.1, signifying a low level of contamination. The average HEI for the Colorado River stands at 13.9, placing it in the category of moderately contaminated with heavy metals (Boateng et al. 2015). The major contributors to the HEI in this river are manganese, copper, and lead. Furthermore, the HEI values in sediments exhibited a range between 24.1 and 33.8, signifying a higher degree of pollution in the sediments as compared to the water. This can be attributed to both the volcanic composition of the soil and the diminished transport of heavy metals in the sediments, resulting in their accumulation.

Conversely, the Alajua River displays a trend of increasing heavy metal contamination from its upper zones (points 1, 2, and 3, with low and moderate contamination levels) to the lower zones (points 4 and 5, with moderate and high contamination levels). The HEI value for the Alajua River reaches 15.4, surpassing the value recorded for the Colorado River. In the case of the Alajua River, the key metals contributing to HEI are manganese, lead, and iron. Ultimately, the HEI values within the sediment samples ranged from 16.4 to 28.0, with an average HEI of 20.6, signifying an increased level of pollution within the sediments when compared to the water. Similar to the situation observed in the Colorado River, this phenomenon could be attributed to the accumulation of heavy metals resulting from reduced mobility in the solid phase and the influence of the volcanic origin of the soil.

CONCLUSIONS

The water quality of the Colorado and Alajua rivers was assessed through the analysis of physicochemical parameters, microbiological tests, and the measurement of heavy metal concentrations in surface water and sediment samples using various methods. This comprehensive approach provided precise data on substances exceeding acceptable water quality standards for human consumption, aquatic ecosystem preservation, and agricultural irrigation. Additionally, investigations into potential factors contributing to the

Table 6: Values obtained according to NSF-WQI and Dinius-WQI.

Sampling points	NSF - WQI		DINIUS – WQI	
	General criteria		Agricultural & Human consumption criteria	
	Colorado	Alajua	Colorado	Alajua
1	67 (fair)	75 (good)	69 (slightly contaminated)	84 (acceptable)
2	53 (fair)	69 (fair)	75 (slightly contaminated)	83 (acceptable)
3	69 (fair)	69 (fair)	79 (slightly contaminated)	83 (acceptable)
4	53 (fair)	62 (fair)	67 (slightly contaminated)	73(slightly contaminated)
5	51 (fair)	60 (fair)	70 (slightly contaminated)	72(slightly contaminated)
Average	59 (fair)	67 (fair)	72 (slightly contaminated)	79 (slightly contaminated)

Table 7: Values obtained from the Heavy Metal Evaluation Index (HEI) for water and sediment samples from the Colorado and Alajua rivers.

Sampling Points	Heavy Metal Evaluation Index in Water (HEI)		Heavy Metal Evaluation Index in Sediments (HEI)	
	Colorado River	Alajua River	Colorado River	Alajua River
1	18.7 (moderate)	8.7 (low)	24.2 (high)	18.7 (moderate)
2	14.6 (moderate)	12.1 (moderate)	26.3 (high)	16.4 (moderate)
3	12.0 (moderate)	16.3 (moderate)	33.8 (high)	28.0 (high)
4	9.1 (low)	15.5 (moderate)	24.1 (high)	16.4 (moderate)
5	15.4 (moderate)	24.7 (moderate)	25.6 (high)	23.6 (high)
Average	13.9 (moderate)	15.4 (moderate)	26.7 (high)	20.6 (moderate)

decline in water quality in the sampling areas were carried out, considering environmental, geological, and human-related factors.

Most parameters across the upper and lower zones of both rivers' micro-watersheds show significant differences with p-values below 0.05. However, exceptions were observed in the arsenic and cadmium concentrations within water samples collected from the Colorado River. When comparing the results of water characterization with the Ecuadorian environmental legal requirements, most parameters met acceptable limits for human and domestic consumption. However, certain parameters in the Colorado River exceeded the criteria for the preservation of aquatic life. For instance, fecal coliform levels exceeded the limit. However, the more challenging issue lies in the presence of heavy metals. Zinc (Zn) levels in Colorado River water samples were elevated at points 2 (76 $\mu g.L^{-1}$), 3 (67 $\mu g.L^{-1}$), and 4 (59 $\mu g.L^{-1}$), surpassing the maximum permissible limit (MPL) of 30 $\mu g.L^{-1}$. Additionally, lead levels ranged from 1.2 $\mu g.L^{-1}$ to 3.9 $\mu g.L^{-1}$, exceeding the MPL of 1 $\mu g.L^{-1}$. In terms of iron (Fe) concentration, points 1, 3, and 5 slightly exceeded the 0.3 $mg.L^{-1}$ criteria, with values of 0.37 $mg.L^{-1}$, 0.33 $mg.L^{-1}$, and 0.36 $mg.L^{-1}$, respectively. Furthermore, manganese (Mn) concentrations ranged between 0.37 $mg.L^{-1}$ and 0.47 $mg.L^{-1}$, surpassing the irrigation water quality criterion for Mn, which has a maximum limit of 0.2 $mg.L^{-1}$.

Regarding the Alajua River, parameters that exceeded the permissible limit for the preservation of aquatic life included copper at point 3, measuring 11 $\mu g.L^{-1}$ (MPL of 5 $\mu g.L^{-1}$), iron, with concentrations ranging from 0.61 $mg.L^{-1}$ to 0.79 $mg.L^{-1}$ (MPL of 0.30 $mg.L^{-1}$), and manganese, with values ranging from 0.62 $mg.L^{-1}$ to 0.98 $mg.L^{-1}$ (MPL of 0.10 $mg.L^{-1}$).

The altered concentrations of heavy metals may originate from the volcanic geological conditions in both rivers. In most cases, sample points on the upper side of the micro-watershed (sampling points 1, 2, and 3) exhibited higher concentrations of heavy metals (lead, iron, zinc, copper, and manganese) than the maximum permissible limits (MPL). Additionally, river sediments displayed an accumulation of heavy metals, including hexavalent chromium, copper, and cadmium, exceeding the MPL for these metals in soil.

Furthermore, the Heavy Metal Evaluation Index (HEI) in sediment samples showed higher values, ranging from 16.4 to 33.8, in comparison to HEI values in water samples, which ranged from 8.7 to 24.7. These results emphasize the necessity for further investigation into the sources of heavy metals, their transport in water and sediments, and the potential direct exposure to metals through human consumption of water, as well as indirect exposure through agricultural feedstock and livestock farming.

Overall, the assessment of water quality using the NSF-WQI indicated that the Colorado and Alajua rivers in all five sampling zones exhibited regular to moderate levels of contamination. According to the Dinius index, a "slightly contaminated" level was observed in all sampling points, except at points 1, 2, and 3 (84, 83, and 83) of the Alajua River, which showed an "acceptable" level. In relation to heavy metal pollution, it is recommended to purify the water for human consumption due to the excessive presence of coliforms, Zn, Pb, Fe, and Mn.

Finally, it is advisable to implement specific actions, such as limiting intensive agriculture and livestock in certain areas of the watershed and defining water source protection zones. This will help preserve water resource quality and protect consumer health.

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