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Proposal of a Water-Quality Index for High Andean Basins: Application to the Chumbao River, Andahuaylas, Peru

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Abstract: The water from the high Andean rivers is peculiar due to its composition and the geomorphology of its sources, and naturally or anthropogenically contamination is not discarded along its course. This water is used for agriculture and human consumption, therefore knowing its quality is important. This research aimed to proposing and formulate a water-quality index for high Andean basins through the Delphi method, and its application in the Chumbao River located in Andahuaylas-Peru. Forty-three water-quality parameters were evaluated through the Delphi method, and the water-quality index (WQI_{HA}) was formulated with a weighted average of the weights of the selected parameters, it was compared with the WQI Dinius. For this purpose, ten sampling points were considered along the Chumbao River located between 4274 and 2572 m of altitude and the WQI_{HA} was applied. In addition, field and laboratory analyses were carried out in 2018, 2019, and 2021, in dry and rainy seasons. Twenty parameters were grouped in the physicochemical sub-index (SI_{PC}), heavy metals sub-index (SI_{HM}), and organic matter sub-index (SI_{OM}). Each group contributed with weights of 0.30, 0.30, and 0.40, respectively, for the WQI_{HA} formulation. The SI_{PC} and SI_{OM} showed that the areas near the head of the basin presented excellent and good quality, while the urbanized areas were qualified as marginal to poor; SI_{HM} reported good quality in all points and seasons. Regarding the WQI_{HA}, the index shows good quality in the zones above 3184 m of altitude, contrasting with poor quality downstream, decreasing notably in both seasons, suggesting continuous degradation of the water body.

Keywords: Delphi method; Chumbao River; heavy metals sub-index; high Andean water-quality index; organic matter sub-index; physicochemical sub-index

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1. Introduction

The headwaters from the High Andean Rivers are located in the Andes Mountains above 4000 m of altitude. Those are forming water bodies due to the melting of glacial ice caps [1–3]. The headwaters of the basin serve as a water pocket zone through wetlands and lagoons and these are rich in active and reserve metal mining deposits [4,5]. In addition, grazing activities are developed for auquenids such as the llama, alpaca, and vicuña; and the massive cultivation of potatoes and quinoa with the use of conventional and high-technological irrigation systems [6,7].

Rivers can become polluted on their way, transporting and accumulating pollutants. The problem can be aggravated when rivers pass through urbanized areas where contamination with organic matter stormwater runoff contributes further [8–11]. Additionally, rivers in urban areas are affected by untreated wastewater discharges from clandestine landfills, sanitary landfills, and industrial waste [12–16]. The anthropic activities surrounding a high Andean river basin, such as livestock, agriculture, and mining extraction, generate negative impacts on water quality and on surrounding soils [17–21], whose pollutant components, in many cases, are not biodegradable, or the self-purification capacity is very low [7,13,22], especially if they contain traces of dissolved metals and inorganic material [23,24].

Water quality is assessed by physical parameters such as turbidity, conductivity, and resistivity; chemical parameters such as pH, hardness, alkalinity, acidity, total solids, chlorides, nitrates, phosphates, fluorides, magnesium, iron, manganese, toxic metals, and dissolved gases; biological parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon; and further microbiological parameters [25–27], which might be associated with the incidence of anthropic activity in a region [8,15,28,29].

The High Andean Province of Andahuaylas is located in the Apurímac region, Peru, as a city, and the Chumbao river shares the same space in the basin. However, the city has not been able to establish a positive dynamic of coexistence with the river, restricting its natural tributaries and water outcrops, and predating its surrounding natural forests. The city treats the river as a dump, turning it into a dumping ground for domestic and industrial wastes and residues. Those waters are currently used for the irrigation of short-stemmed vegetables and roots for human consumption. Due to the pollution problems faced by the river and the city, the prioritization of environmental sanitation projects is necessary and mandatory in terms of water quality. So, it is useful to know the state of the water quality [30]. The state of water quality can be achieved through the implementation of a water-quality index (WQI) [24,27,31,32] for high Andean rivers.

One of the methods that allow quality criteria on ecosystem aspects to be established is the Delphi methodology [33–39], which allows categorizing quality indicators, by experts with scientific rigor [40–43]. Thus, the identification of parameters that allow a WQI to be determined for High Andean basins can be established through the application of this methodology. In comparison to multivariate methods, which allow the identification of water-quality parameters, which result just from the statistical decision [44–46]. However, the Delphi method collects the expert experience in water quality, for specific uses, who include within the selection criteria, the perception of the water body and its surroundings [38,43,47–49].

WQIs were developed for different water sources, taking into the consideration characteristic aspects of each basin such as rainfall, surrounding soils, topography, aquatic flora and fauna, and anthropic activities [30,50–55], which can be ranked and classified according to their importance through the Delphi method. Therefore, the research aimed in formulating a water-quality index for a high Andean River through the Delphi method, taking it as an application case the river of the Chumbao micro-basin, Andahuaylas, Apurímac, Peru, covering the seasons 2018 to 2021.

2. Materials and Methods

2.1. Study Area

The study is located in the Chumbao River, in the southern highlands from Peru, Apurímac region, Andahuaylas province. Hydrographically, it is a tributary of the Apurímac River that belongs to the Pampas River basin. Pampahuasi, Paccoccocha, Antaccocha, and Huachoccocha lagoons (Figure 1) are the highest tributaries. The influence area presents intense rainfall from October to March (between 500 and 1000 mm/year) and temperatures from 5 to 23 °C. it has an average relative humidity of 55%, with a Cwb climate according to Köppen climate classification.

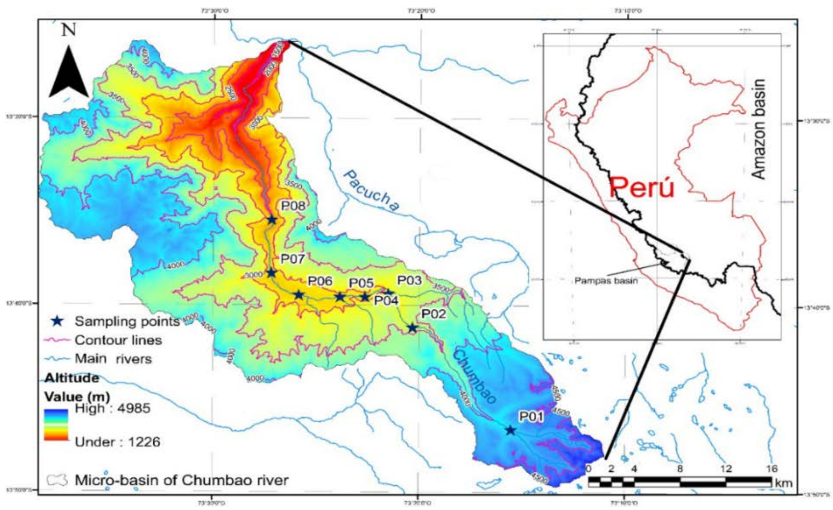

Figure 1. Study area, Chumbao micro-basin.

2.2. Sampling and Analysis

Eight sampling points along the river were considered, starting from the head of the basin (13°46′38.4″ S, 73°15′32.3″ W, and 4079 m of altitude), up to Sotoccmachay (13°35″26.4″ S, 73°27′00.8″ W, and 2572 m of altitude) (Table 1). The water was sampled in rainy and dry seasons in 2018, 2019, and 2021; and the criteria established by the National Protocol for Monitoring the Quality of Surface Water Resources [56] was considered for sampling.

Table 1. Location of sampling points.

Sampling Points	Coordinates		Altitude (m)	Characteristic of the Area
	S	W		
Paccoccocha lagoon	13°46′45.2″	73°13′50.0″	4274	Snowmelt and rainwater collector; native fish breeding
Pampahuasi lagoon	13°44′57.6″	73°14′35.7″	4212	Snowmelt and rainwater collector; native fish breeding
P1	13°46′38.4″	73°15′32.3″	4079	Water collecting basin/native flora and fauna
P2	13°41′10.9″	73°20′19.7″	3184	Water collection basin/limited agriculture, and grazing
P3	13°39′23.4″	73°21′30.7″	2981	Limited urbanization, agriculture, and intense grazing.
P4	13°39′33.2″	73°22′38.2″	2916	Increasing urbanization, limited agriculture, and grazing, limited urban industry
P5	13°39′37.0″	73°23′52.7″	2872	High urbanization and limited urban industry
P6	13°39′27.4″	73°25′50.8″	2807	High urbanization, limited agriculture, and grazing
P7	13°38′17.0″	73°27′10.6″	2767	Limited urbanization, agriculture, and intense grazing
P8	13°35′26.4″	73°27′008″	2572	Agriculture and intense grazing

The parameters analyzed were physical, chemical, and microbiological and these were determined in the field as much as the laboratory. Their methodologies are shown in Table 2. Some analyses were carried out in the Laboratory at José María Arguedas National University, Andahuaylas, Peru.

Table 2. Parameter analysis methods.

Parameter	Method	Unit	Reference	Place
Temperature	Selective electrode	°C	Hanna Multiparameter-HI 9828	On field
Turbidity	Selective electrode	NTU	Hanna Multiparameter-HI 9828	On field
TDS (Total dissolved solids)	Selective electrode	mg/L	Hanna Multiparameter-HI 9828	On field
Conductivity	Selective electrode	µS/cm	Hanna Multiparameter-HI 9828	On field
True color	Spectrometric-Pt-CO method	PCU	2120-C, Standard Methods [57]	In laboratory
pH	Selective electrode	-	Hanna Multiparameter-HI 9828	On field
Hardness	EDTA titration	mg CO_3^{2-}/L	2340-C, Standard Methods [57]	In laboratory
Nitrates	Selective electrode	mg NO_3^-/L	4500- NO_3^- D, Standard Methods [57]	In laboratory
Nitrites	Colorimetric	mg NO_2^-/L	4500- NO_2^- B, Standard Methods [57]	In laboratory
Ammonia	Selective electrode	mg NH_3-N/L	4500- NH3 D, Standard Methods [57]	In laboratory
Phosphates	Spectrometric, ascorbic acid method	mg P/L	4500- P B, Standard Methods [57]	In laboratory
Chemical Oxygen Demand (COD)	Closed Reflux, Colorimetric Method	mg O_2/L	5220 B, Standard Methods [57]	In laboratory
Dissolved oxygen (DO)	Selective electrode	mg O_2/L	Hanna Multiparameter-HI 9828	On field
Biochemical Oxygen Demand (BOD)	5-Day BOD Test	mg O_2/L	5210 D, Standard Methods [57]	In laboratory
Thermotolerant Coliforms, Total coliforms	Colorimetric	MPN/100 mL	Colilert-18/Quanti-Tray Method 9308-2:2014 [58]	In laboratory

The quantification of metals was analyzed in an Inductively Coupled Plasma–Optical Emission Spectrometer, ICP-OES 9820 Shimadzu, and the standard curves were prepared with standard solutions of chromium (Cr), iron (Fe), Zinc (Zn), and lead (Pb) (Calibration STD, SCP Science), with a regression coefficient, R^2, higher than 0.995. The water samples were analyzed in axial mode, in quadruplicate, rinse for 30 s at 60 rpm between samples, and gas flow of 10 L/min with plasma exposure of 30 s.

2.3. Delphi Method Application

We applied the Rand Corporation's Delphi methodology in order to construct the high Andean water-quality index (WQI_{HA}) [40], which consists of the application of questionnaires with controlled feedback that allows iteration within a panel of experts, in order to reach consensus through scientific and academic discourse, which is developed in stages or rounds [34,47–49,59].

2.3.1. Selection of Experts

In order to prioritize water-quality parameters and construct the WQI_{HA}, seven academic experts were selected [40,41,60], with expertise in water resources management, mainly in water quality in high Andean rivers.

2.3.2. Selection of Water-Quality Parameters

Forty-three water-quality parameters were considered, used for the quality indices proposed by the WQI-NSF, WQI-Dinius, UNEP-GEMS, UWQI-UE, ISQA-Spain, CCME-WQI, IAP-Brazil, ICAUCA-Colombia, ICA-Mexico, and MINAM-Peru [61–70]. The experts selected parameters for the construction of the WQI_{HA}, under the following criteria "Not included", "Undecided", "Included", considering applicable those parameters that reported coincidence in opinion $\geq$ 70% [40,71].

2.3.3. Assignment of Weights to Parameters

To the selected parameters weight were attributed on a scale from "1 = low" to "5 = high" according to the importance of its contribution to water quality for high Andean rivers. The mean of the results is considered as the weight of the parameter "Wi", which contributes to the WQI_{HA} [41].

2.3.4. Assignment of Nominal Value to Parameters

Nominal values were assigned for the selected parameters giving referential values (Table 3), considering a quality index "Qi" for each parameter on a scale from "0 = very bad" to "100 = excellent" [40,71,72], from which mathematical models are constructed and describe the quality of the selected parameter [40,73–75], using CurveExpert Professional V 2.7.1 software in demo mode.

Table 3. Selected parameters and reference values.

Parameters	Criteria Interval		Reference Value
	Min	Max	
Temperature (°C)	0	40	[61]
Turbidity (NTU)	0	300	[61,76–78]
TDS (mg/L)	0	600	[61,78]
pH	1	13	[61,76,77,79]
Conductivity (μS/cm)	20	3000	[61,78,80]
Hardness (mg/L)	5	1500	[61,78]
Color (PCU)	2	150	[61,76,77]
Nitrates (mg/L)	1	60	[61,76,78]
Nitrites (mg/L)	0	10	[46,61,78]
Ammonium (mg/L)	0	30	[61,76,79]
Phosphates (mg/L)	0	1.5	[61]
Lead (μg/L)	0	150	[61,76,78]
Chrome (μg/L)	0	150	[61,76,78]
Zinc (mg/L)	0	5	[61,76,78]
Iron (mg/L)	0	15	[61,76,78]
COD (mg/L)	0	300	[61]
DO (mg/L)	0	15	[61,76–78]
BOD (mg/L)	2	140	[61,76]
Thermotolerant Coliforms (MPN/100 mL)	10	50,000	[61,76–78]
Total Coliforms (MPN/100 mL)	100	150,000	[61,76,77]

2.4. Quality Index Construction

The parameters were grouped into physicochemical, heavy metals, and organic matter aspects and were called the quality sub-index, and assigned the weight "W_i" corresponding to their value "Q_i". The quality sub-index was obtained based on a weighted average, according to the equations shown in Table 4.

Table 4. Quality sub-index equations.

Subindex	Equation
Physicochemical—PC: Temperature, Turbidity, TDS, pH, Conductivity, Hardness, Color, Nitrates, Nitrites, Ammonium, Phosphates	$SI_{PC} = \sum_{i=1}^{11} W_i * Q_i$ (1)
Heavy metals—HM: Lead, Chrome, Zinc, Iron	$SI_{HM} = \sum_{i=1}^{4} W_i * Q_i$ (2)
Organic matter—OM: COD, DO, BOD, Thermotolerant Coliforms, Total Coliforms	$SI_{OM} = \sum_{i=1}^{5} W_i * Q_i$ (3)

In order to formulate the WQI_{HA} equation, the sum of SI_{PC}, SI_{HM}, and SI_{OM} with weights 0.3, 0.3, and 0.4, respectively were considered, taking as weight criteria the importance and the major source of pollution for high Andean rivers which are agricultural, livestock, and domestic activities [5–7,12].

The WQI_{HA} qualification was interpreted using the scale proposed by CCME [66] (Table 5), which is used for legal water-quality standards in many countries [27,62,67,81–84].

Table 5. WQI_{HA} qualification scale.

Quality Range	Scale	Description
95–100	Excellent	The water quality is not under any threat and it is not degraded and close to natural levels.
80–94	Good	The water quality is under a little threat and it is rarely seen under desired levels.
65–79	Fair	The overall water quality is protected; however, it is under threat in some cases and sometimes not in the desired conditions.
45–64	Marginal	1The water quality is frequently under threat and degradation and often not in the desired conditions
0–44	Poor	Water quality departs from its desirable level

Source: CCME [66].

3. Results and Discussion

3.1. Delphi Method Application

The results of the experts' evaluation through the Delphi method indicated that 20 of 43 parameters were selected, with a coincidence higher than 70%. It was observed that the parameters temperature, turbidity, pH, conductivity, hardness, nitrates, phosphates, zinc, DO, BOD_5, thermotolerant, and total coliforms had an appreciation of 100% (Table 6), whereas the parameters TDS, color, nitrites, ammonium, lead, and iron showed a coincidence of 85.7%, and the remaining with 71.4%.

In the total weighting score (maximum sum 35 and minimum 0), it was observed that the BOD_5 parameter obtained the highest weighting (35), followed by COD and thermotolerant coliforms (34); while pH, nitrates, phosphates, lead, and DO reported scores of 33. STD and temperature had lower scores: 25 and 20, respectively. The scores assigned by the experts had a variability ranging from 0.0% to 25%, whereas the BOD_5 reported 0.0% variability. This is an important indicator in surface and river water quality [10,12,14,17,29,40,51].

Likewise, it was observed that the W_i weights for SI_{PC} ranged from 0.073 to 0.105 (Table 6), with pH, nitrates, and phosphates being of a higher weight; while for SI_{HM} the weights ranged from 0.218 to 0.300, Pb being of higher interest; and SI_{OM}, reported weights between 0.181 to 0.211, with higher weight for BOD_5.

The importance of the parameter's weight is related to water use and source [85–89]. In the case of WQI applicable to surface waters, it would seem that the greatest weight should be given to the parameters DO, BOD_5, nitrates, suspended solids and total coliforms [5,12,17,25,43,64,68,88].

The pH is one of the parameters considered by all the WQI (Table 6), and this is a conditioning factor for the solubility and self-purification of solutes in the water in the same way, nitrates, DO, and BOD_5 are considered [43,64,68,90], which is related to the organic matter present in the water bodies [7,8,13,53]. In this sense, the proposed index takes into consideration these general aspects for rivers with anthropic influence.

The nominal valuation curves of the physicochemical parameters were adjusted to mathematical models with values $R^2 > 0.999$, and it was found that for values of temperature < 6.4 °C, turbidity < 3.0 NTU, TDS < 10 mg/L, 6.4 < pH < 7.4, conductivity < 81.4 µS/cm, hardness < 22 mg/L, color < 4.0 PCU, nitrate < 2.0 mg/L, nitrite < 0.1 mg/L, ammonium < 0.1 mg/L, and phosphate < 0.001 mg/L the individual Q_i quality index is 100% (Figure 2).

For the nominal valuation curves of the heavy metals parameters, it was observed that for values of Pb < 0.029 mg/L, Cr < 0.214 mg/L, Zn < 0.009 mg/L, and Fe < 0.009 mg/L, the individual quality Q_i is 100% (Figure 3). On the other hand, the nominal value curves for the parameters of the organic matter sub-index reported that values COD < 3.29 mg/L, 6.1 mg/L < OD < 7.1 mg/L, BOD_5 < 3.5 mg/L, thermotolerant bacteria < 50 MPN/100 mL, and total coliforms < 500 MPN/100 mL, the individual quality Q_i is 100% (Figure 4) obtained through mathematical models with values $R^2 > 0.999$.

Table 6. Selected parameter weights.

Parameters	**Proposal**				**WQI Reference Weights**				
	Inclusion Percentage	**Total Weighting Score**	**C.V. (%)**	**Weight (Wi)**	**UWQI [40]**	**Tigris River [43]**	**IAP–Brazil [64]**	**Dinius-NSF [68]**	**UWQI-UE [90]**
				Physicochemical					
Temperature	100.0	20	24.2	0.064			0.100	0.077	
Turbidity	100.0	32	11.7	0.102	0.0696	0.087	0.080		
TDS	85.7	23	14.9	0.073		0.091	0.080		
pH	100.0	33	10.4	0.105	0.0911	0.100	0.120	0.077	0.029
Conductivity	100.0	27	17.9	0.086	0.0692	0.116		0.079	
Hardness	100.0	24	15.6	0.076	0.0587	0.051		0.065	
Color	85.7	29	16.7	0.092				0.063	
Nitrates	100.0	33	10.4	0.105	0.0909	0.190		0.090	0.086
Nitrites	85.7	30	17.6	0.096		0.093			
Ammonium	85.7	30	17.6	0.096	0.1035				
Phosphates	100.0	33	10.4	0.105					
				Metals					
Lead	85.7	33	10.4	0.300					
Chrome	71.4	24	22.9	0.218					
Zinc	100.0	25	15.0	0.227					
Iron	85.7	28	25.0	0.255					
				Organic material					
COD	71.4	34	7.8	0.205		0.072			
OD	100.0	33	10.4	0.199		0.145	0.170	0.109	0.114
BOD_{55}	100.0	35	0.0	0.211		0.072	0.100	0.097	0.057
Thermotolerant Coliforms	100.0	34	7.8	0.205			0.150	0.116	
Total Coliforms	100.0	30	11.4	0.181				0.090	0.114
Calcium					0.0726				
Chloride					0.0742			0.074	
Chlorophyll a					0.0358				
Fluoride					0.0949				0.086
Magnesium					0.0710				
Manganese					0.0910				
Sulphate					0.0774				
Alkalinity								0.063	
Cadmium									0.086
Cyanide									0.086
Mercury									0.086
Selenium									0.086
Arsenic									0.113
Total phosphorus							0.100		0.057
Total nitrogen							0.100		
Sodium						0.058			

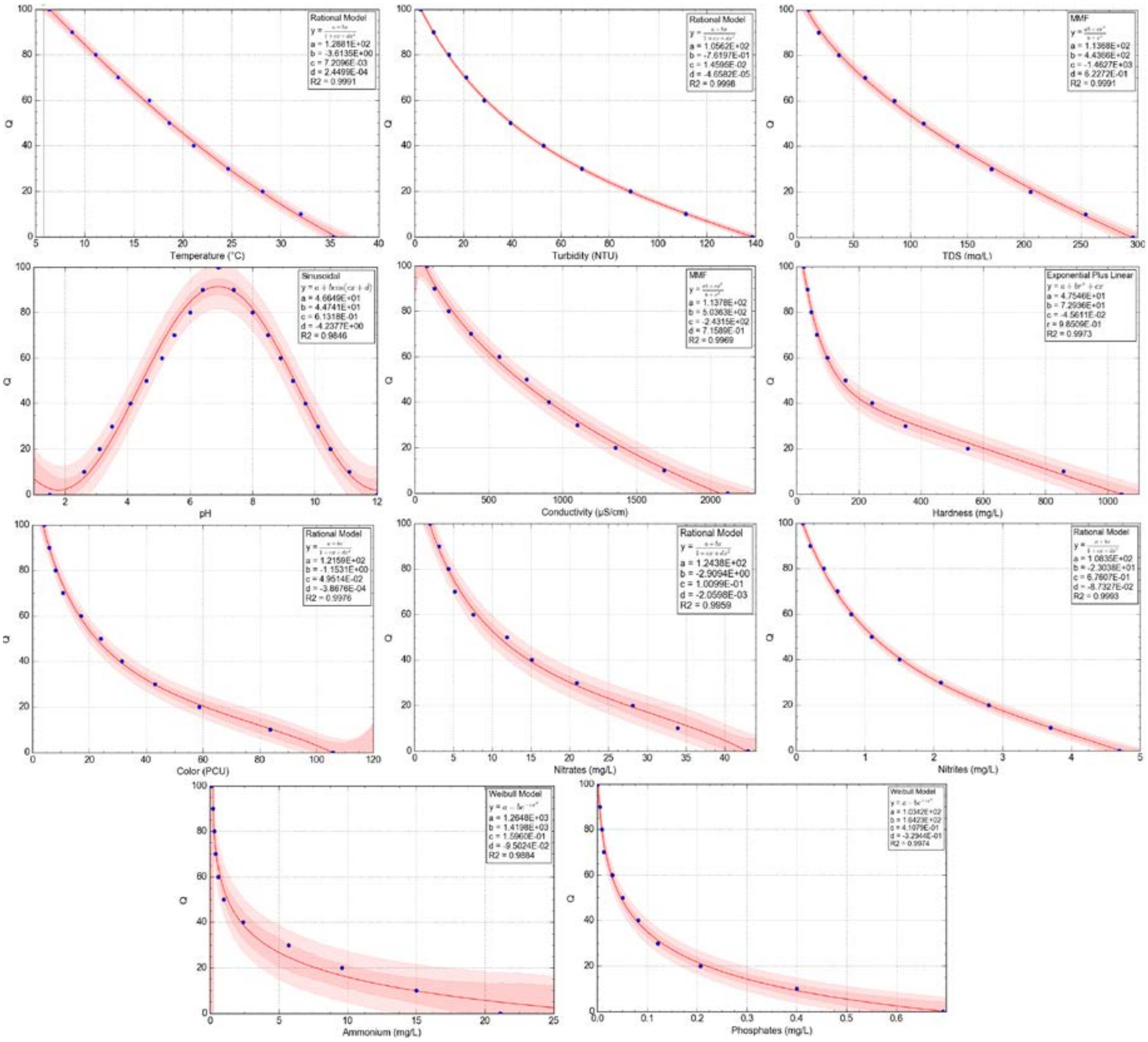

Figure 2. Nominal values curve for physicochemical parameters.

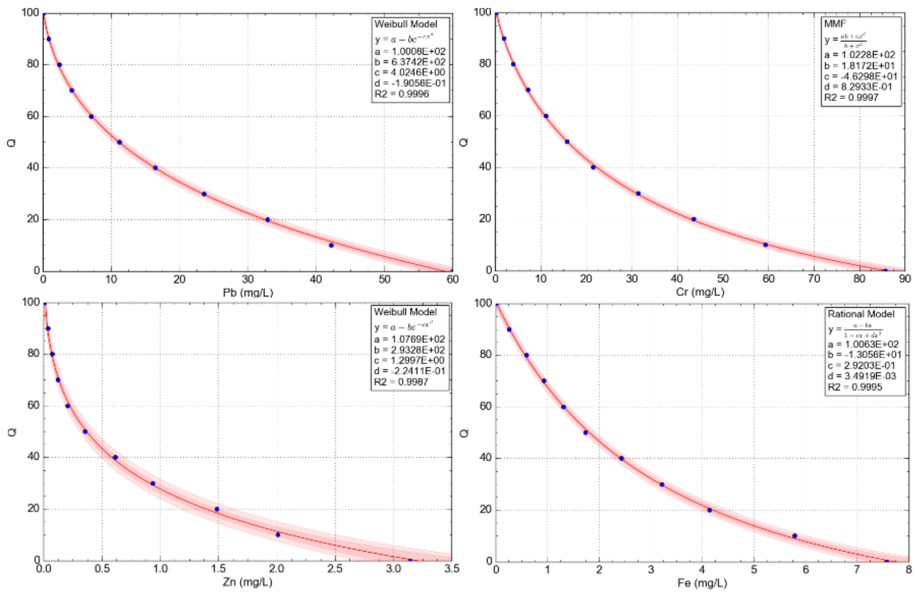

Figure 3. Nominal values curve for heavy metal parameters.

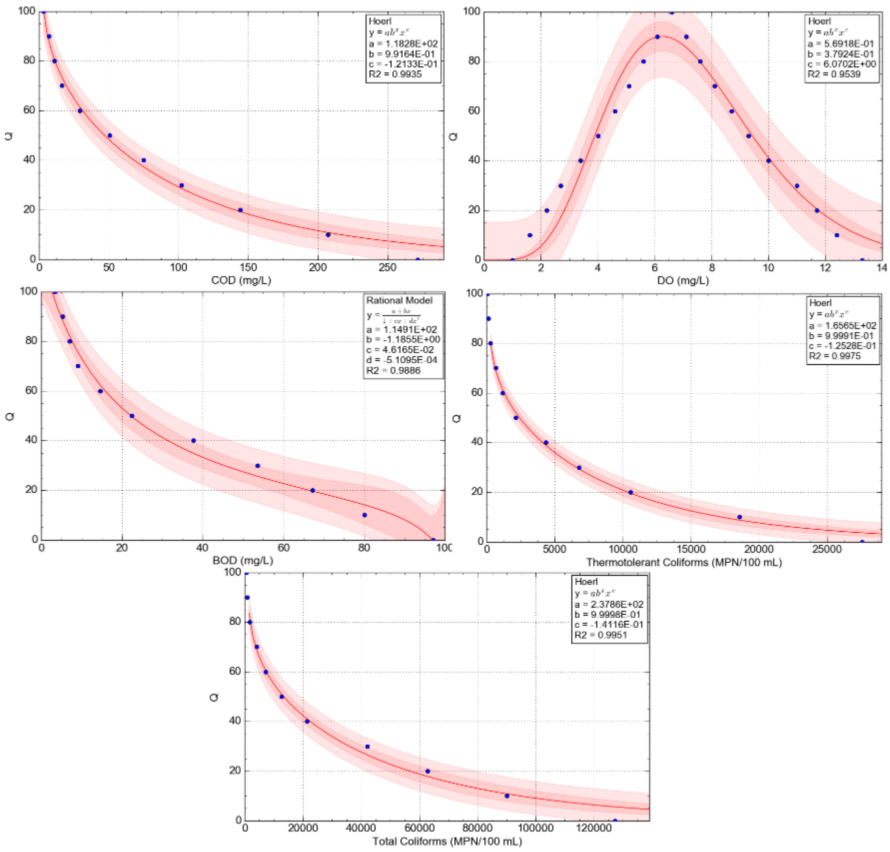

Figure 4. Nominal values curve for organic matter parameters.

3.2. Characteristics of the Quality Parameters of the Chumbao River

The mean values of temperature in the studied seasons oscillate between 11.85 and 17.61 °C (Table 7), increasing in the season 2019 and 2021, and in urban areas (Figure 5). Regarding turbidity, it was observed that in the high areas it is around 0.0 NTU and that it increased considerably downstream, ranging from 4.98 to 55.72 NTU (Table 7); with respect to TDS, conductivity, hardness, and color values, considerable increases were observed downstream, with higher values in dry seasons (Figure 5) (p-value < 0.05) and maximum values of 453.0 mg/L, 906.0 mg/L, 750 mg/L, and 172 PCU, respectively (Table 7).

Regarding the pH, the maximum value was 9.34 and a minimum of 6.91, with means between 7.53 and 8.10 (p-value < 0.05) (Figure 5), with significant variation observed in urbanized areas (between 2981 and 2767 m of altitude). This should be due to anthropic activities since the inhabitants of these areas discharge wastewater (household and agricultural) and solid waste into the riverbed [13,14,27,53,91].

Concerning the nitrogen series, levels of 0.0 mg/L for nitrates, nitrites, and ammonium, as well as phosphates (Table 7) were observed, especially in the high places of the high Andean basin of Chumbao (Figure 5). However, there is anthropic activity [10,26,92], mainly livestock activity (open field rearing of alpacas, sheep, and cattle) [6,12].

Concerning the level of selected heavy metals, maximum values of 1.50 ug/L, 83.0 ug/L, and 0.61 mg/L were observed for Pb, Cr, and Fe, with minimum values close to 0.0 mg/L (Table 8). In urban areas (below 4079 m of altitude) the level of these metals increased considerably. However, the values of Zn were not detectable in the study seasons (Figure 6).

Table 7. Maximum and minimum values of physicochemical parameters.

Parameters		Rainy 2018	Dry 2018	Rainy 2019	Dry 2019	Dry 2021	Parameters		Rainy 2018	Dry 2018	Rainy 2019	Dry 2019	Dry 2021
Temperature (°C)	Max	16.13	16.30	17.31	22.96	22.81	Color (PCU)	Max	41.00	40.00	97.00	172.0	94.00
	Min	9.67	4.99	8.86	10.86	10.42		Min	12.00	0.00	14.00	10.00	8.00
	Avg	13.14	11.85	12.64	17.61	17.55		Avg	26.73	11.47	42.80	56.50	41.41
	SD	2.05	3.81	2.87	4.31	4.45		SD	9.20	11.24	22.52	51.48	29.69
	CV (%)	15.63	32.12	22.69	24.47	25.38		CV (%)	34.41	98.02	52.62	91.11	71.71
	p-value	0.00	0.00	0.00	0.00	0.00		*p*-value	0.00	0.00	0.00	0.00	0.00
Turbidity (NTU)	Max	141.60	100.20	194.60	63.80	17.30	Nitrates (mg/L)	Max	1.10	0.00	0.00	0.00	1.70
	Min	0.00	0.40	0.30	0.60	0.30		Min	0.00	0.00	0.00	0.00	0.00
	Avg	55.72	35.22	47.97	20.11	4.98		Avg	0.21	0.00	0.00	0.00	0.18
	SD	43.99	33.88	65.55	18.93	5.21		SD	0.32	0.00	0.00	0.00	0.51
	CV(%)	78.94	96.20	136.64	94.13	104.64		CV(%)	151.13	-	-	-	289.49
	p-value	0.00	0.00	0.00	0.00	0.00		*p*-value	0.00	-	-	-	0.00
TDS (mg/L)	Max	155.00	471.00	178.00	453.00	356.80	Nitrites (mg/L)	Max	0.17	0.88	0.54	10.08	1.24
	Min	12.00	12.00	12.00	12.00	13.00		Min	0.00	0.00	0.00	0.00	0.00
	Avg	54.43	196.40	60.70	194.00	136.20		Avg	0.03	0.33	0.11	3.24	0.35
	SD	42.67	166.04	53.80	174.81	113.41		SD	0.05	0.37	0.17	3.82	0.40
	CV (%)	78.40	84.54	88.63	90.11	83.27		CV (%)	187.46	112.23	147.73	117.75	113.51
	p-value	0.00	0.00	0.00	0.00	0.00		*p*-value	0.00	0.00	0.00	0.00	0.00
pH	Max	8.15	8.67	8.73	9.34	8.59	Ammonium (mg/L)	Max	0.67	3.06	0.32	17.12	8.93
	Min	6.91	7.39	7.40	7.51	7.35		Min	0.00	0.00	0.00	0.02	0.01
	Avg	7.53	7.97	7.95	8.10	7.92		Avg	0.11	1.16	0.07	4.10	2.17
	SD	0.35	0.31	0.36	0.57	0.36		SD	0.18	1.19	0.10	6.18	3.16
	CV(%)	4.62	3.94	4.50	7.04	4.56		CV (%)	162.16	103.22	140.10	150.75	145.75
	p-value	0.00	0.00	0.00	0.00	0.00		*p*-value	0.00	0.00	0.00	0.00	0.00
Conductivity (µS/cm)	Max	311.00	917.00	340.00	906.00	714.10	Phosphates (mg/L)	Max	0.44	2.21	2.08	5.62	1.71
	Min	24.00	23.00	23.00	23.00	22.00		Min	0.00	0.11	0.03	0.04	0.21
	Avg	110.03	383.90	118.47	387.63	270.34		Avg	0.14	1.37	1.05	1.43	0.88
	SD	84.61	327.46	102.97	348.84	229.70		SD	0.13	0.63	0.78	1.67	0.54
	CV (%)	76.90	85.30	86.92	89.99	84.97		CV (%)	98.78	45.81	73.84	116.39	61.28
	p-value	0.00	0.00	0.00	0.00	0.00		*p*-value	0.00	0.00	0.00	0.00	0.00
Hardness (mg/L)	Max	68.40	256.60	201.80	171.10	750.00							
	Min	8.70	11.55	6.30	10.60	15.00							
	Avg	31.18	97.78	68.22	66.05	424.30							
	SD	19.23	78.02	60.30	51.29	295.60							
	CV (%)	61.67	79.79	88.40	77.66	69.67							
	p-value	0.00	0.00	0.00	0.00	0.00							

Data are presented as Average (Avg), ± Standard Error (SD), variance coefficient (CV) ($n = 3$). p-value < 0.05 indicates significant difference between sampling points.

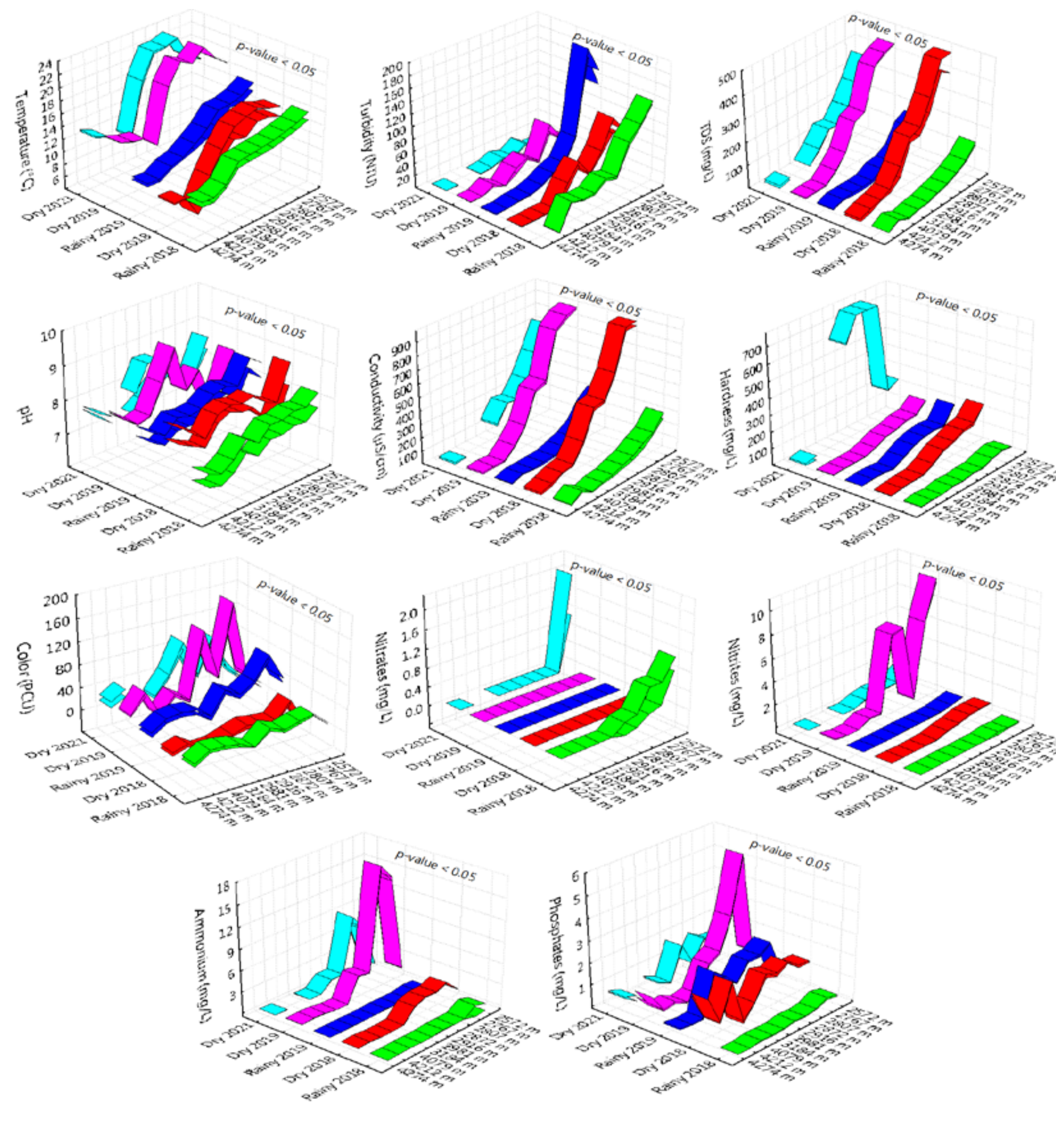

Figure 5. Physicochemical parameters values.

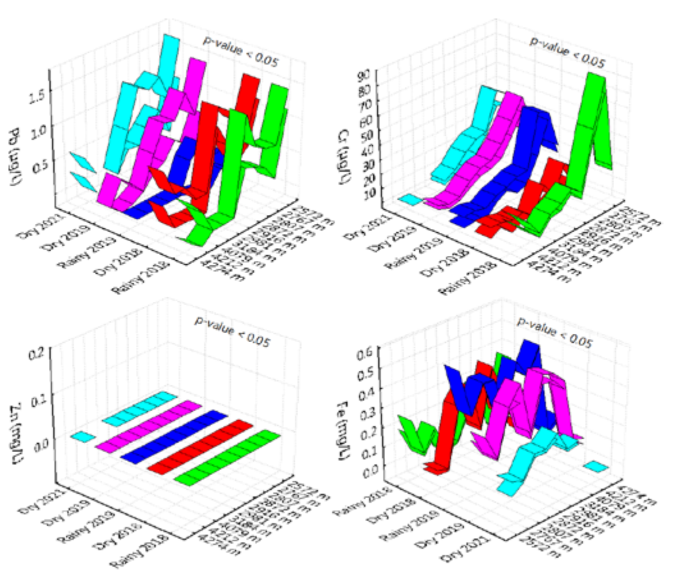

Figure 6. Heavy metals parameter values.

Table 8. Maximum and minimum values of heavy metals parameters.

Parameters		Rainy 2018	Dry 2018	Rainy 2019	Dry 2019	Dry 2021
Pb (ug/L)	Max	1.40	1.40	0.40	1.20	1.50
	Min	0.00	0.00	0.00	0.00	0.10
	Avg	0.46	0.62	0.08	0.40	0.64
	SD	0.46	0.46	0.12	0.37	0.40
	CV(%)	99.96	74.99	151.86	90.80	61.97
	p-value	0.00	0.00	0.00	0.00	0.00
Cr (ug/L)	Max	83.00	17.00	48.00	51.00	48.00
	Min	2.00	0.00	0.00	3.00	0.00
	Avg	25.10	5.67	15.77	19.50	17.67
	SD	22.69	5.42	14.91	14.24	16.62
	CV(%)	90.41	95.58	94.58	73.04	94.09
	p-value	0.00	0.00	0.00	0.00	0.00
Zn (mg/L)	Max	0.00	0.00	0.00	0.00	0.00
	Min	0.00	0.00	0.00	0.00	0.00
	Avg	0.00	0.00	0.00	0.00	0.00
	SD	0.00	0.00	0.00	0.00	0.00
	CV(%)	-	-	-	-	-
	p-value	-	-	-	-	-
Fe (mg/L)	Max	0.35	0.46	0.61	0.51	0.30
	Min	0.00	0.03	0.09	0.08	0.00
	Avg	0.15	0.21	0.41	0.33	0.17
	SD	0.11	0.14	0.17	0.15	0.10
	CV(%)	75.85	68.29	41.26	47.15	61.54
	p-value	0.00	0.00	0.00	0.00	0.00

Regarding the organic matter indicator parameters, maximum levels of 310 mg/L and 292 mg/L were observed and minimum levels were close to 0.0 mg/L for COD and BOD, respectively (Table 9). These increase considerably (p-value < 0.05) as the river flows through urbanized areas; although BOD_5 levels below 3000 m altitude were low (Figure 7). This was due to the river's own self-purification [53], especially in rivers with steep slopes [12], which is demonstrated by the opposite behavior of DO.

Table 9. Maximum and minimum values of organic matter parameters.

Parameters		Rainy 2018	Dry 2018	Rainy 2019	Dry 2019	Dry 2021
COD (mg/L)	Max	225.00	310.0	330.00	66.00	55.00
	Min	0.00	0.00	0.00	13.00	8.00
	Avg	45.73	51.33	59.43	32.43	25.00
	SD	63.13	87.60	95.98	16.85	16.29
	CV(%)	138.03	170.65	161.49	51.95	65.16
	p-value	0.00	0.00	0.00	0.00	0.00
DO (mg/L)	Max	7.94	8.53	7.12	8.72	5.81
	Min	5.86	3.50	4.56	2.18	1.80
	Avg	7.09	6.20	5.29	6.24	4.06
	SD	0.60	1.47	0.77	1.84	1.43
	CV(%)	8.48	23.75	14.59	29.48	35.17
	p-value	0.00	0.00	0.00	0.00	0.00
BOD_5 (mg/L)	Max	0.90	29.00	124.00	292.00	105.00
	Min	0.00	0.00	0.00	0.00	0.00
	Avg	0.17	5.94	30.88	66.27	31.51
	SD	0.30	11.40	41.66	93.22	35.46
	CV(%)	182.62	191.88	134.92	140.67	112.53
	p-value	0.00	0.00	0.00	0.00	0.00
Thermotolerant Coliforms (MPN/100 mL)	Ma×	2.7×10^5	6.9×10^5	4.0×10^5	1.5×10^6	1.4×10^6
	Min	0.00	0.00	0.00	0.00	0.00
	Avg	7.1×10^4	1.2×10^5	8.6×10^4	2.9×10^5	2.7×10^5
	SD	9.6×10^4	2.2×10^5	1.2×10^5	4.5×10^5	4.4×10^5
	CV(%)	133.95	176.03	134.50	154.02	165.27
	p-value	0.00	0.00	0.00	0.00	0.00
Total Coliforms (MPN/100 mL)	Ma×	3.3×10^5	2.2×10^6	1.4×10^6	4.1×10^6	5.1×10^6
	Min	1570.00	0.00	0.00	900.00	1100.00
	Avg	1.1×10^5	3.4×10^5	2.6×10^5	1.3×10^6	1.7×10^6
	SD	1.2×10^5	6.6×10^5	3.8×10^5	1.4×10^6	2.0×10^6
	CV(%)	110.46	192.83	148.67	109.76	118.31
	p-value	0.00	0.00	0.00	0.00	0.00

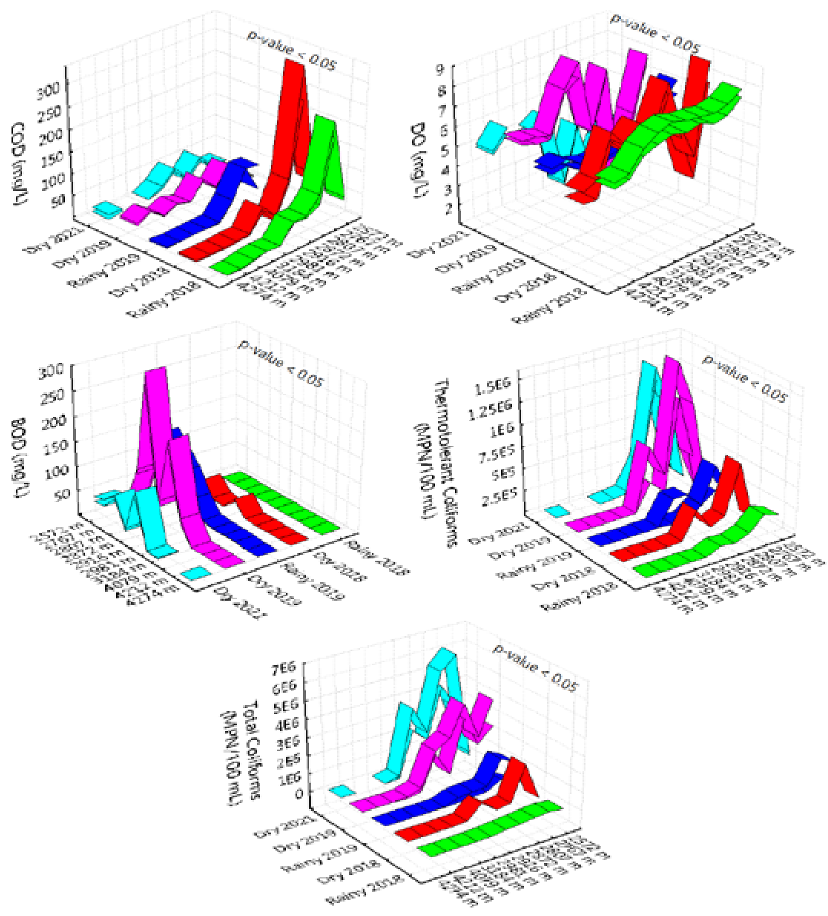

Figure 7. Organic matter parameter values.

The high level of coliforms (Table 9) is mainly due to domestic activity, although these values are relatively low in the areas near the headwaters of the basin (Figure 7). In most cases, this increase is due to the discharge of domestic water into the watercourse and the existence of domestic solid waste in the riverbed.

3.3. High Andean Water-Quality Index

There are numerous WQI for rivers based on physical, chemical, microbiological, and biological parameters [9,15,19,23,53,93], with criteria in national or international standards or norms [94–97]. However, aspects such as heavy metals are often not considered [54,93,98,99]. In this sense, a WQI was formulated considering physicochemical, heavy metals, and organic matter aspects, as shown in Equation (4), taking into account the high Andean basin of the Chumbao River (WQI_{HA}), where it circumscribes different large-scale mining deposits which could provide inorganic material to the water.

$$WQI_{HA} = 0.3xSI_{PC} + 0.3xSI_{HM} + 0.4xSI_{OM} \quad (4)$$

The water quality in the Chumbao River, regarding SI_{PC} and SI_{OM} (Figure 8a,c), are in "good" range for the high areas above 3184 m of altitude, and that it decreases considerably to "marginal" and "poor" levels due to the fact that domestic wastewater and residues from agricultural activities are dumped directly into the riverbed. Regarding SI_{HM}, they are in the "good" and "excellent" range, although with a slight decrease, especially in urbanized areas below 2872 m of altitude (Figure 8b).

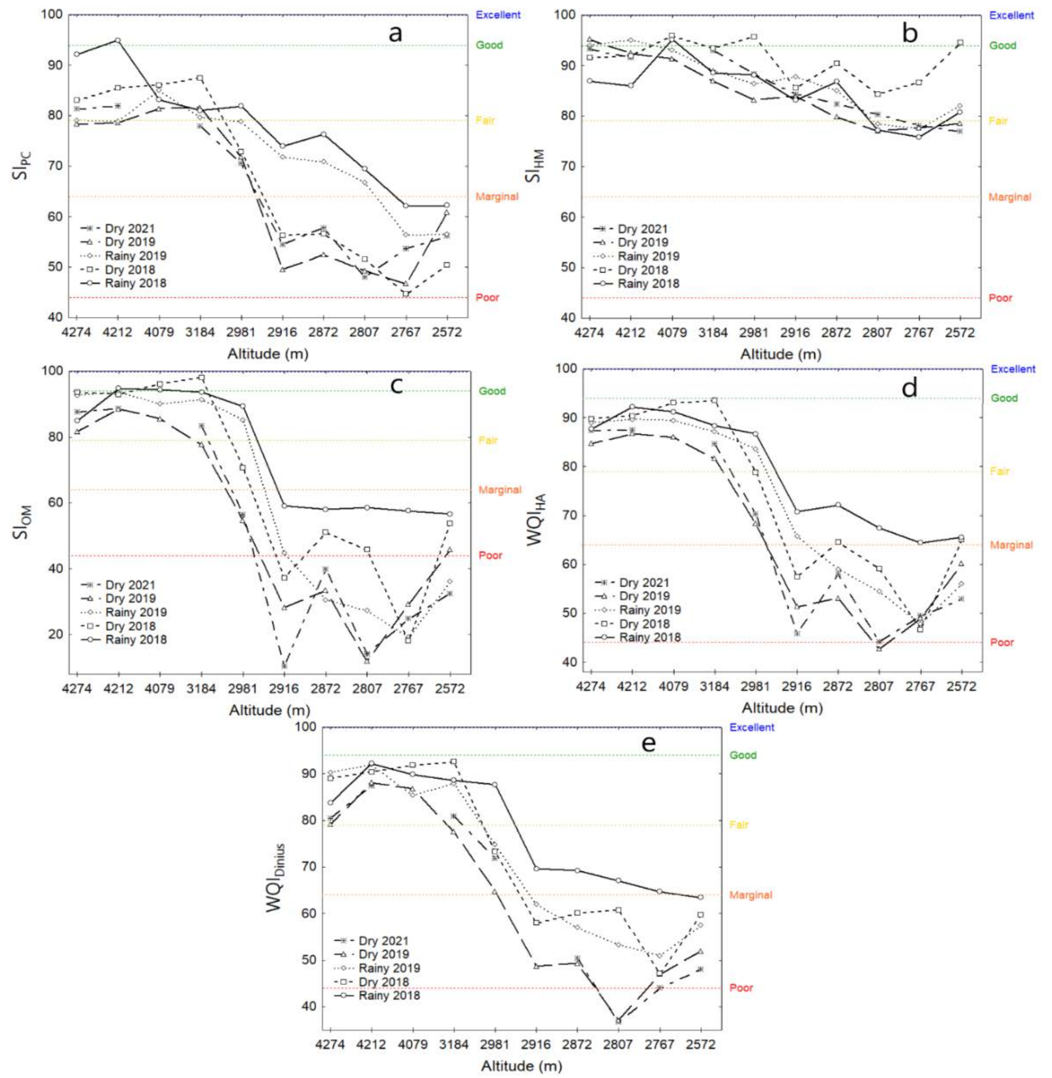

Figure 8. (**a**) Physicochemical subindex—SI_{PC}; (**b**) heavy metals subindex—SI_{HM}; (**c**) organic matter subindex—SI_{OM}; (**d**) high Andean water-quality index—WQI_{HA}; (**e**) Dinius WQI.

In regard to the WQI_{HA}, it reported a rating of "good" in the points near the headwaters, and in urbanized areas, the quality is between "marginal" and "poor" (Figure 8d). This behavior is characteristic of this type of river [86,99,100]. However, water-quality indexes are reported up to limits of bad or very bad [81,88]. In that sense, the water of the Chumbao River could be considered to be in medium-quality conditions in comparison to other rivers with the same characteristics.

Unlike the quality index according to Dinius, the WQI_{HA} is more robust because it considers physicochemical, heavy metals, and organic matter parameters, compared to Dinius, which does not take heavy metals into account. However, it reports similar behavior for the high-altitude zones (Figure 8e).

It has been observed that the quality subindexes, as well as WQI_{HA}, have decreased over time (Figure 8), especially in urbanized areas, which suggests that quality could be even more affected by anthropic activities and the growing population, especially in the high Andean zones of Peru, where the lack of basic sanitation, wastewater collectors, as well as wastewater treatment plants is evidenced. In addition, most of the population lacks environmental education and does not care about the environment. A tool that would allow measuring water quality over time for rivers with characteristics of high Andean zones is the proposed $WAQI_{AH}$.

4. Conclusions

The proposal of a water-quality index for high Andean rivers, based on the physicochemical subindex (SI_{PC}), heavy metals subindex (SI_{HM}), organic matter subindex (SI_{OM}), allows evaluating the behavior of the quality by grouped pollutants, with a real approximation on the natural and anthropic characteristics of this type of basins.

The application of WQI_{HA} in the water from the high Andean basin of the Chumbao river showed that the areas surrounding the head of the basin present good quality, and they are not threatened, showing levels close to the natural state, and that it is rarely seen. However, urbanized areas are frequently threatened and degraded, due to anthropic practices; and that degradation has been increasing over time.

This WQI_{HA} will allow the evaluation of water quality in high Andean areas influenced by anthropic domestic, agricultural, livestock, and mining and metallurgical activities, such as the Andes in South America.

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