Water quality in the Tropical Andes Hotspot: the Yacuambi river (southeastern Ecuador)

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HIGHLIGHTS:

- Yacuambi river waters were good and medium according to Water Quality Index.
- Water is inadequate for drinking, preservation of aquatic life and irrigation.
- Color, As and fecal coliforms exceeded human consumption limits in all samples.
- All samples exceeded the threshold of preservation for aquatic life for Pb.
- Yacuambi river waters are unsuitable for irrigation due to As and fecal coliforms.

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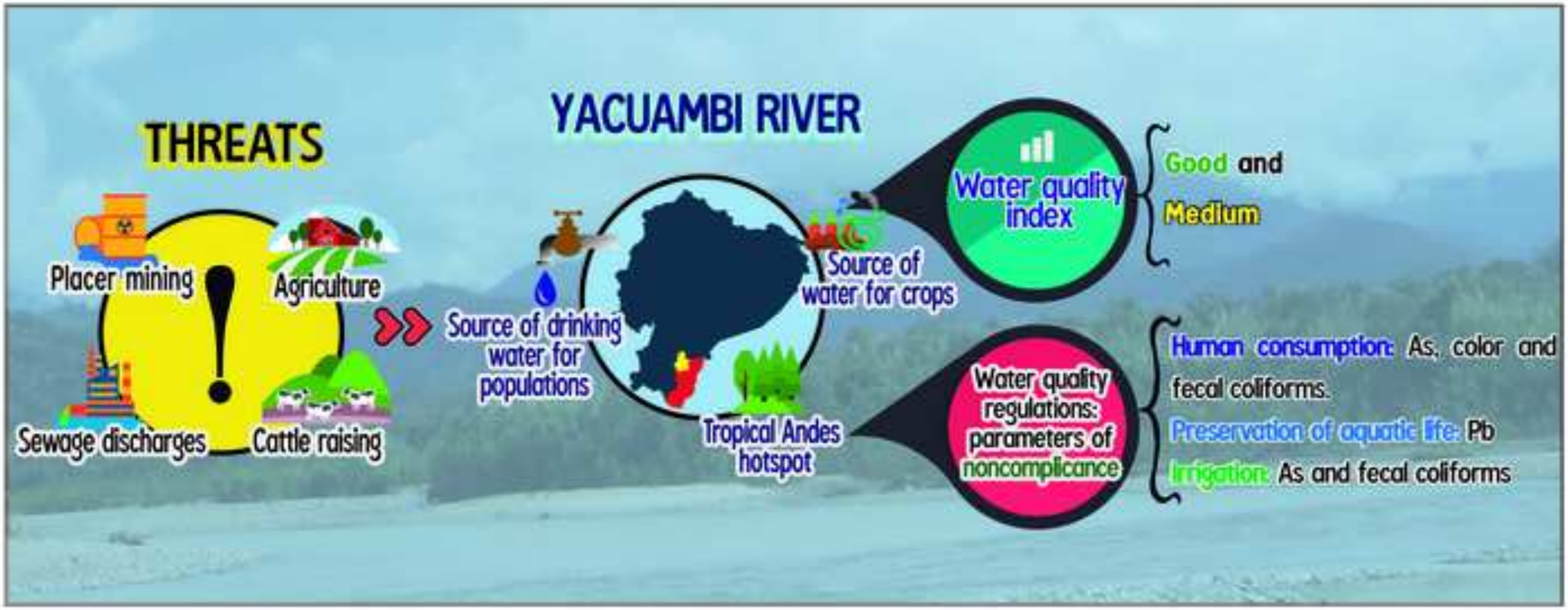
*Graphical Abstract



Abstract

Yacuambi river waters (southeast Ecuador, Amazonian region) were assessed to evaluate the potential risk to populations, who use it for drinking and irrigation, and ecosystems, which are part of Tropical Andes hotspot and considered some of the most biodiverse in the world. The water quality index was calculated and some quality parameters were checked to comply with Ecuadorian and North American standards for human consumption, preservation of aquatic life and irrigation.

Four samplings were carried out in six stations covering the entire length of the Yacuambi river. Several parameters were analyzed: pH, conductivity, dissolved oxygen, temperature, color, phosphates, nitrite, nitrate, biochemical oxygen demand, chemical oxygen demand, total solids, turbidity, metals (Ba, Cd, Cr, Pb, As and Hg), pesticides and fecal coliforms.

The water quality in the Yacuambi river was good and medium according to the classification of the Water Quality Index. However, it was unsuitable for human consumption, preservation of aquatic life and irrigation according to Ecuadorian and North American standards. Arsenic, color and fecal coliforms exceeded the limits for human consumption in all samples tested. Thresholds of preservation of aquatic life were exceeded in all samples in the case of Pb and in some samples for As, pH, nitrite and nitrate. Arsenic and fecal coliforms made Yacuambi river waters unsuitable for irrigation.

Keywords

Pollution; Metals; Trace elements; Pesticides; Zamora-Chinchipe; Environmental protection.

1 Introduction

Industrialization and economic growth in developing countries have led to an interest in pollution of aquatic ecosystems (Diop et al., 2015; Duong et al., 2014; Mwanamoki et al., 2014). Ecuador has made remarkable progress in recent years. However, a significant percentage of the population lives below the poverty line and lack access to safely managed drinking water (WHO/UNICEF, 2015). This problem is intensified in the Ecuadorian Andes, well known for its mining activities (Adler Miserendino et al., 2013; Velásquez-López et al., 2011, 2010; Zarroca et al., 2015).

Gold placer mining is the simplest way to extract gold (López-Blanco et al., 2015). This method consists in extracting the sediment located in the river bed and in the floodplain, until reaching the bedrock, at most 10 m deep (Stubblefield et al., 2005). Sediment extraction is usually carried out with pumps or excavators. The extracted material contains high purity gold nuggets, which are separated from the sediment around the river. The material is sieved using water from the river and introduced into small channels that have a textile in the bottom. The gold particles are denser, fall to the bottom and are retained in this material. All the sediment from the river bed and the floodplain are deposited back into the river (Byambaa and Todo, 2011).

When gold particles obtained are too small, amalgamation with Hg is used. In this process, a solution of Hg is added to these particles to form an Au-Hg amalgam, which is burnt with a blowtorch and bigger pure gold nuggets are produced (López-Blanco et al., 2015). In many cases, amalgamation is carried out on the river banks and releases Hg either dissolved in water or emitted into the atmosphere. Hg pollutes the environment, can be biomagnified through the food chain and can cause toxicity to humans and living beings (Kapia et al., 2016; Krupskaya et al., 2013). Artisanal scale mining releases 1,400 tonnes/year of Hg to land, water, and air (United Nations Environment Programme, 2013a). Approximately half of it (727 tonnes/year) is emitted to the air, making artisanal scale mining the largest source of anthropogenic Hg emissions (United Nations Environment Programme, 2013b).

Gold placer mining can also provoke other environmental problems (Batsaikhan et al., 2016). The turbidity of water may increase, because the bottom sediment is resuspended. The deep sediment could be moved to the top, suffering a change in redox potential from anaerobic to aerobic conditions, releasing part of the heavy metals contained therein, such as Zn, Cu, Cd, Mn, Pb, Ni, Fe, Cr, As, Hg and Se (Chakraborty et al., 2016). The movement of sediments can significantly alter the relief and landscape. In some cases, rivers have been diverted to facilitate sediment extraction and have disappeared.

Efforts to reduce the negative impacts of gold placer mining are taking place in Papua New Guinea (Kapia et al., 2016), China (Egidarev and Simonov, 2015), Malaysia (Eam et al., 2013), the Bering Sea (Jewett and Naidu, 2000), Russia (Krupskaya et al., 2014, 2013; Litvintsev, 2015; Panfilov et al., 2014) and South Africa (Tucker et al., 2016).

The Yacuambi river, located in the southeast of Ecuador, is exposed to the threats of gold placer mining in the area and other activities that could endanger the quality of its waters (López-Blanco et al., 2015). Agriculture uses pesticides that could end up in the river. In addition, agricultural fertilizers and manure from livestock could increase the content of organic matter and coliforms in the water. The nearby towns discharge sewage into the Yacuambi river without prior treatment. Much urban waste is deposited in the banks of the river due to the lack of municipal solid waste management systems (Gallardo et al., 2013).

The Yacuambi river is the main water source to populations within its catchment. Many of the inhabitants of the Yacuambi basin drink water directly from the river without any previous purification. It is also used for irrigation and fishes serve as a food source to local communities (Gallardo et al., 2013). Furthermore, Yacuambi catchment is located within the Northwestern Andean montane forests, considered one of the most biodiverse areas in the world by the WWF's Global 200 (Olson and Dinerstein, 2002) and the list of hotspots proposed by Myers et al. (2000). It is also a tributary of the Amazon river. Despite the risk for communities and the ecosystem, there are few previous studies on the quality of Yacuambi river.

This study aims to evaluate the risk of the Yacuambi river for populations who use it for drinking and irrigation and for the ecosystem, considered one of the most biodiverse in the world. For this purpose, the water quality index designed by Brown et al. (1970) was used. Moreover, compliance to Ecuadorian and North American standards for human consumption, preservation of aquatic life and irrigation was checked.

2 Materials and methods

2.1 Study area: Yacuambi river

The Yacuambi river (Figure 1) is located in the southeast of Ecuador, in the Yacuambi canton, Zamora-Chinchipe province, Amazonian region. It rises in the northern area of the canton, in the Andes mountains and runs from north to south along the 50 km long Yacuambi valley. It has many tributaries on both banks, among which are the rivers Tutupali, Yacuchingari, Shingata, Corral Huaycu, Garcelán, Negro and Quimi. Upon reaching the town of La Saquea, it flows into the river Zamora, part of the upper Amazon river basin.

Yacuambi river basin lies between longitudes 78° 05' and 78° 43' W and between latitudes 03° 31' and 03° 50' S. The area of the Yacuambi river basin is 126,580 ha, with a perimeter of 169.55 km. It is an elongated basin with a form factor of 0.241. The average height of the basin is 2,200 masl. The average slope is around 30% and, therefore, the relief is steep (Fundación Ecológica Arcoiris, 2007).

There are many settlements on the banks of Yacuambi river, among which are Tutupali, 28 de Mayo and La Paz. There is a relevant presence of indigenous communities, mainly Saraguros and Shuars. The Yacuambi canton is the main settlement of the ethnic group Saraguro in Zamora Chinchipe province. The populations' main source of water are nearby rivers and in many cases the water is not treated for consumption.

In the Yacuambi river basin, human activities threaten the quality of its waters, such as mining, agriculture, cattle raising and sewage discharges. In the Yacuambi canton, metal mining concessions account for 43,146 ha, i.e. 34% of the 126,000 ha estimated area with exploitable mineral resources. Both banks of the Yacuambi river have concessions to mining activities (Fundación Ecológica Arcoiris, 2007).

Agriculture and livestock occupy a significant area of the Yacuambi canton. These activities could lead to pesticide contamination and increased organic matter in the water by the use of fertilizers and animal manure spills. The main crops grown in the area are: cane, cassava, coffee, cocoa, annatto, bananas, baby bananas, yams, and citrus. Livestock typically consists of cows and, to a lesser extent pigs, horses and chickens. Cows occupy a significant part of the banks of the river, where they go to drink (Fundación Ecológica Arcoiris, 2007).

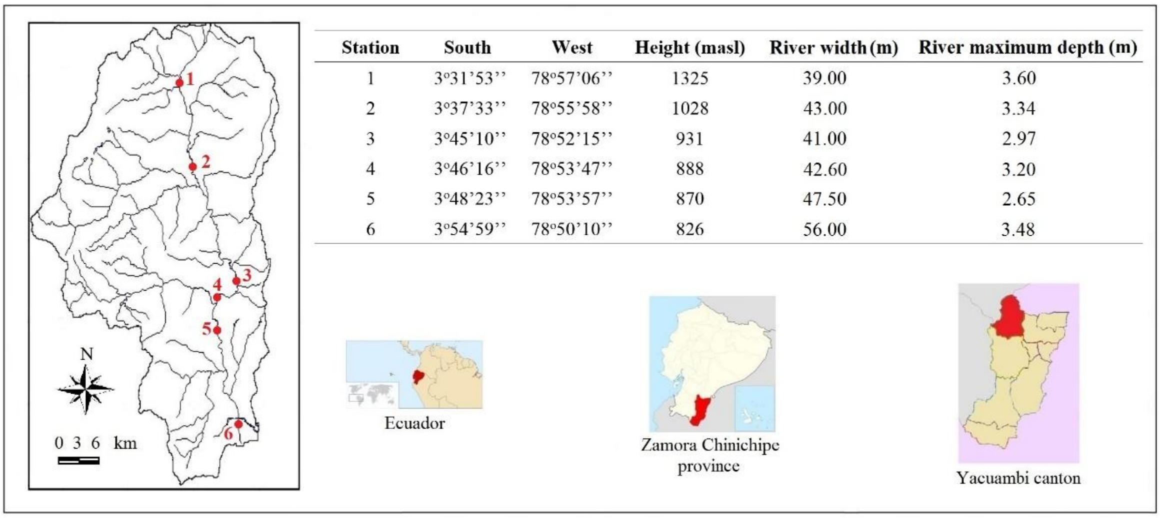
The nearby towns discharge into the Yacuambi river a large amount of raw sewage. In addition, many urban wastes are deposited in the banks of the river due to the lack of municipal solid waste management systems.

The area has a high ecological value. Around 60% of the Yacuambi basin is occupied by native forest and 57,000 ha of Yacuambi canton (44% of the total area) is a nature reserve called Yacuambi. Furthermore, the lagoons of el Condorcillo, a proposed Ramsar area, are located inside the nature reserve Yacuambi. Some endangered species have been recorded around these lagoons. This is the case for two mammals, the spectacled bear (*Tremarctos* *ornatus*) and the mountain tapir (*Tapirus pinchaque*), and a reptile, the Parker's Pholidobolus (*Macropholidus annectens*).

Considering a larger scale, Yacuambi basin is part of the Northwestern Andean montane forests, cataloged within the WWF's Global 200 project as an area of exceptional biodiversity and representative of its ecosystems (Olson and Dinerstein, 2002).

These forests are also part of the Tropical Andes Hotspot. A hotspot is one of the 25 most biodiverse areas globally, i.e. it comprises at least 0.5% or 1,500 species of vascular plants as endemics, and has lost at least 70% of its primary vegetation (Myers et al., 2000). The 25 hotspots include 133,149 plant species (44% of all plant species in the world) and 9,645 vertebrate species (35%) in only 2.1 million km^2 (1.4% of the Earth's land surface). They are endangered and seem likely to lose much of their remaining primary vegetation (Myers et al., 2000).

In addition, Tropical Andes is in the top five hotspots with most endemic species: over 20,000 plants (6.7% of all plant species in the world), and 5.7% of worldwide vertebrates. Thus, it should be considered as a hyper-hot candidate for conservation (Myers et al., 2000).



Station	South	West	Height (masl)	River width (m)	River maximum depth (m)
1	3°31’53’’	78°57’06’’	1325	39.00	3.60
2	3°37’33’’	78°55’58’’	1028	43.00	3.34
3	3°45’10’’	78°52’15’’	931	41.00	2.97
4	3°46’16’’	78°53’47’’	888	42.60	3.20
5	3°48’23’’	78°53’57’’	870	47.50	2.65
6	3°54’59’’	78°50’10’’	826	56.00	3.48

Figure 1. Yacuambi river basin and location, coordinates and height of stations.

2.2 In situ parameters, sampling and sample pre-treatment

Six stations were selected along the Yacuambi river. The stations were located close to communities settlements and in straight sections of the river with little turbulence.

Samples were taken in four different dates (09/08/11, 22/09/11, 29/09/11, 6/10/2011). These dates correspond to the dry season (López-Blanco et al., 2015; Zimmermann et al., 2007), when less water flows through the rivers, gold placer mining is more intense and higher concentrations of pollutants are expected. Dry season facilitates gold placer mining because more sediment is above the water level and the risk of sudden floods that endanger the lives of miners and machinery is reduced. Figure 1 details the location and height above sea level of the stations.

In-situ measurements of pH, dissolved oxygen concentration, electrical conductivity, and temperature were made with a Portable Multi-Parameter Meter HQ40d (Hach, United States) at 20-30 cm depth. The portable device was calibrated in situ with the standards provided by the manufacturer.

Water samples were taken in triplicate at each station following procedures described in standards ISO 5667-1:2006 (Water quality. Sampling. Part 1: Guidance on the design of sampling programmes and sampling techniques) and ISO 5667-3:2012 (Water quality. Sampling. Part 3: Preservating and handling of water samples).

Three different samples were taken in each station: general parameters samples, metals and pesticides samples and microbiological samples. For general parameters samples, 2 l polyethylene bottles were used. This bottles were previously washed in the laboratory with nonionic detergent free of metals, ammonia and phosphate, and Milli-Q water, i.e. type 1 water (Merck Millipore, Germany). For metals and pesticides samples 1 l topaz glass bottles were used to avoid the passage of light. These bottles were previously washed in the laboratory with 10% HNO_3 and Milli-Q water for metals samples and acetone and hexane for pesticide samples. In the case of microbiological samples, sterilized plastic vessels were used with a capacity of 300 ml with a tight lid and wide mouth. Before sampling, all bottles were rinsed 3 times with the river water. When taking the sample, bottles were placed in the opposite direction to the water flow.

Samples were placed in a portable refrigerator (4ºC) in the dark and transported within 8 h to Universidad Tecnica Particular de Loja’s laboratories (ISO 17025 certified), where chemical analyses were undertaken. Metals and pesticides samples were filtered through 0.45 µm pore Teflon filters. Metal samples were acidified with HNO_3 (at $pH<2$). All samples were stored at 4ºC until analysis.

2.3 Laboratory analysis

The parameters analyzed in the samples and the methods used are shown in Table 1. The quality of the results was guaranteed thanks to the rigorous procedures followed for the certification under ISO 17025, including interlaboratory tests.

Hereafter, the term metal includes metals and metalloids (i.e., As). Regarding metals, certified standards from Merck (Germany) were employed for the preparation of 4-point calibration curves. Multielemental standards and blanks were prepared and analyzed at the beginning and at the end of each sequence to ensure the consistency of the dataset. Metals assessed in the interlab comparisons showed differences with the average below 10%. Limits of detection of metals were as follows (mg/l): Ba, 0.5; Cd, 0.01; Cr, 0.5; Pb, 0.005; As, 0.005; Hg, 0.005.

In the case of organochlorine pesticides (α-HCH, Aldrin, 2-4 DDT and heptachlor) and organophosphate pesticides (quinalphos, fonofos and malathion), the GC/MS was calibrated using pesticide standards (Dr Ehrenstorfer GmbH, Germany). All the organic solvents were of analytical grade (Merck, Germany) and only Milli-Q water was used. For all the analyzed compounds, relative standard deviations (RSD) were less than 15% with recovery rates ranging from 91 to 106. These values are frequent in chromatographic methods (Lambropoulou and Albanis, 2005; León et al., 2006) and therefore the accuracy is acceptable. Limits of detection of pesticides were as follows (mg/l): α-HCH, 0.077; Aldrin, 0.068; 2-4 DDT, 0.068; heptachlor, 0.056; quinalphos, 0.001; fonofos, 0.0001; malathion, 0.0001.

The pesticides were selected following three criteria: their lack of use in the country according to the regulations and lists (with the exception of malathion), their toxicity for people and the environment and their widespread use at some time in the past or present.

Table 1. Methods of analysis of the parameters evaluated.

Parameter	**Laboratory equipment**	**Standard**
In situ parameters		
pH	Portable Hach Multi-Parameter Meter HQ40d	ISO 10523:2012
Dissolved oxygen	´´	ISO 5814:2012
Conductivity	´´	ISO 7888:1985
Temperature	´´	Standard Methods 2550 B
General paramenter samples		
Color	Hach DR2800 spectrophotometer	ISO 7887:2011 - method C
Phosphate	´´	Standard Methods 4500-P B
Nitrite	´´	Standard Methods 4500-NO_2 B
Nitrate	´´	Standard Methods 4500-NO_3 B
COD	Hach DR2800 spectrophotometer + Hach DRB 200 thermoreactor	Standard Method 5220 D
BOD_5	Espec-Nova-400	ISO 1899-1:1998
Total solids	-	Standard Methods 2540 B
Turbidity	Hach 2100N turbidimeter	Standard Method 2130 B
Metals and pesticides samples		
Ba, Cd, Cr	Perkin–Elmer 2380 AAS	Standard Method 3111 B
Pb	Perkin–Elmer 2380 AAS + HGA 900 Graphite furnace	Standard Method 3113 B
As	Perkin–Elmer 2380 AAS + hydride generator Perkin–Elmer MSH-10	ISO 17378-2:201

Hg	´´	ISO 12846:2012
Organochlorine pesticides (α-HCH, Aldrin, 2-4 DDT and heptachlor)	GC/MS Agilent 6890 gas chromatograph with a 5973 mass-selective detector	ISO 6468:1996
Organophosphate pesticides (quinalphos, fonofos and malathion)	´´	EN 12918:2000
Microbiological samples		
Fecal coliforms-		Standard Methods 9222 B

2.4 Water quality index (WQI)

The National Sanitation Foundation Water Quality Index (NSFWQI, or simply WQI) was calculated to summarize in a single figure the water quality at each station based on the various parameters analyzed in this study. This index was designed by Brown et al. (1970) and improved by the National Sanitation Foundation (Lumb et al., 2011; Stambuk-Giljanovic, 1999). The use of the WQI or its variants are popular not only in USA but in many other countries (Abbasi et al., 2012; Alexakis et al., 2016; Tyagi et al., 2013).

To calculate the WQI, nine parameters of water quality are used (Table 2). The water quality data are transferred to a weighting curve chart, where a value of quality of the parameter i (Qi) is obtained. Furthermore, a weight is assigned for each parameter (Table 2). The mathematical expression for the WQI is as follows

$$\mathrm{WQI} = \frac{\sum_{i=1}^{n} Q_i W_I}{\sum_{i=1}^{n} W_i}$$

where:

Q_i (0-100): quality of parameter i, function of value of parameter i in its original units.

W_i (0-1): weights assigned to parameter i. The sum of all W_i must be equal to 1.

WQI was calculated using the ICATest v1.0 software developed by Fernández et al. (2001).

Table 2. Parameters involved in WQI calculation and its weights (Brown et al., 1970).

Parameter	Unit	Weight
pH		0.11
Dissolved oxygen	Saturation %	0.17
Temperature change	ºC	0.10
Phosphate	PO_4^{3-} (mg/l)	0.10
Nitrate	NO_3^- (mg/l)	0.10
BOD_5	O_2 (mg/l)	0.11
Turbidity	NTU	0.08
Total solids	mg/l	0.07
Fecal coliforms	MPN/100 ml	0.16

WQI values allow interpreting water quality according to the classification proposed by Brown et al. (1970): 0-25, very bad; 26-50, bad; 51-70, medium; 71-90, good; 91-100, excellent.

2.5 Statistical analysis

Analysis of Variance (ANOVA) with Tukey's post hoc test were carried out using SPSS software version 20 to check the differences between parameters and indexes under different circumstances, such as fecal coliforms, WQI, etc. ANOVA's output is the p value, which indicates the probability that the difference between averages is due to chance and not to a real difference. It is assumed that a p value lower than 0.05, expressed as $p<0.05$, reflects a significant difference and, therefore, the random explanation is discarded. In case the p value is higher than 0.05 ($p>0.05$), there is no statistical evidence to reject randomness as responsible for the difference, therefore, it can not be assumed that there are real differences.

3 Results and discussion

3.1 Water quality index (WQI)

Figure 2 shows the results of the WQI. All samples analyzed had a good (16) or medium (8) water quality according to the classification proposed by Brown et al. (1970). Thus, they were in the second and third best categories of quality out of five categories, as mentioned in material and methods section. In the case of stations 4 and 5, all samplings obtained good quality. By contrast, in station 6 all samplings showed a medium quality. In the rest of the stations (1, 2 and 3) there were samplings in both categories. It is noteworthy that in the second sampling, 4 stations obtained a medium quality. In contrast, 5 stations in first and fourth samplings showed a good quality.

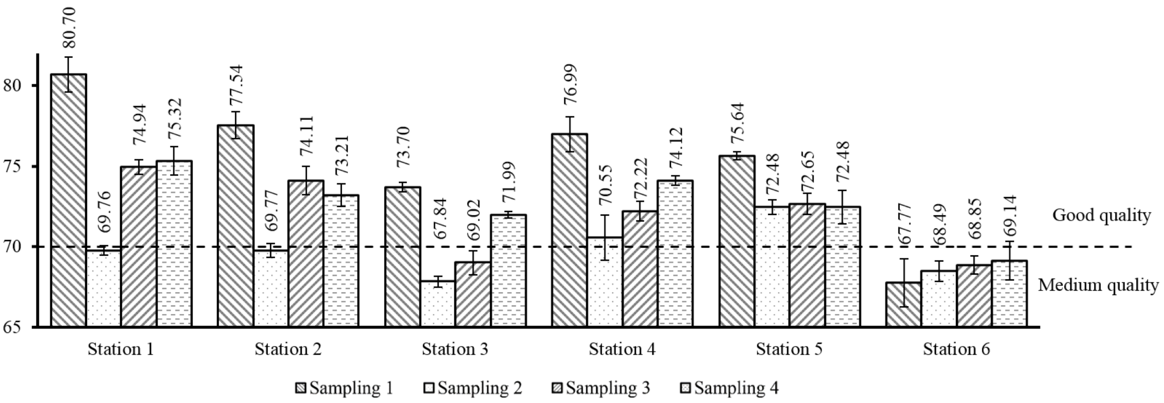


Figure 2. Water quality index (mean ± standard deviation) classified by sampling and station.

Figure 3 shows the mean of WQI at each station along the four samplings. Trends shown in Figure 2 are also noticeable in Figure 3. Station 6 scored medium quality, while the rest accounted for a good quality. Water quality of Yacuambi river decreased downstream from station 1 to station 3 ($p<0.05$). Station 3 represented a turning point. The average quality increased in stations 4 and 5 compared to station 3. However, averages of stations 3 and 5 could only be stated that are different for a confidence interval of 85% ($p=0.15$). In station 6, located downstream of station 5 and at the junction with the river Zamora, quality again decreased significantly ($p<0.05$). This suggests that the quality of Zamora river is lower and that negatively influences the final section of Yacuambi river.

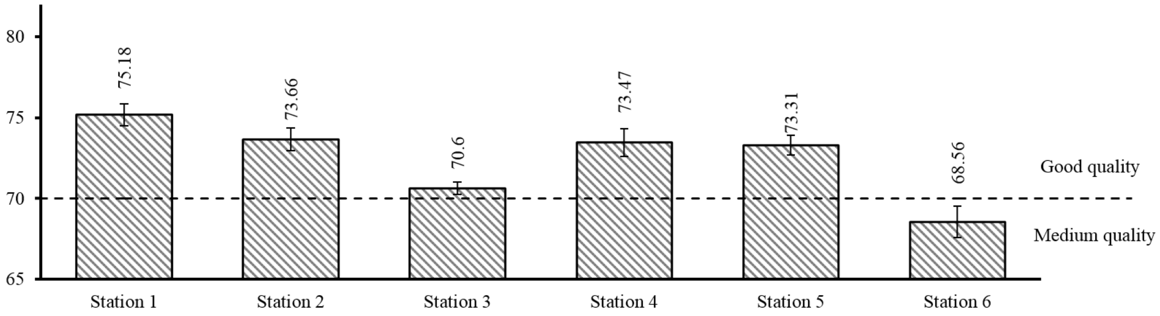


Figure 3. Water quality index (mean ± standard deviation) classified by station.

As shown in Figure 4, the averages varied across the samplings. Between sampling 1 and 2 there were significant differences in the values of WQI ($p<0.05$), in approximately 45 days. Between samplings 2 and 4 there were significant differences considering a confidence interval of 85% ($p=0.15$). In this case, the time lapse was 14 days. However, between samplings 2 and 3 there were no significant differences ($p>0.05$). These results demonstrate that water quality may change significantly in short periods of time. Therefore, it is recommended to carry out monitoring throughout the year at short time intervals.

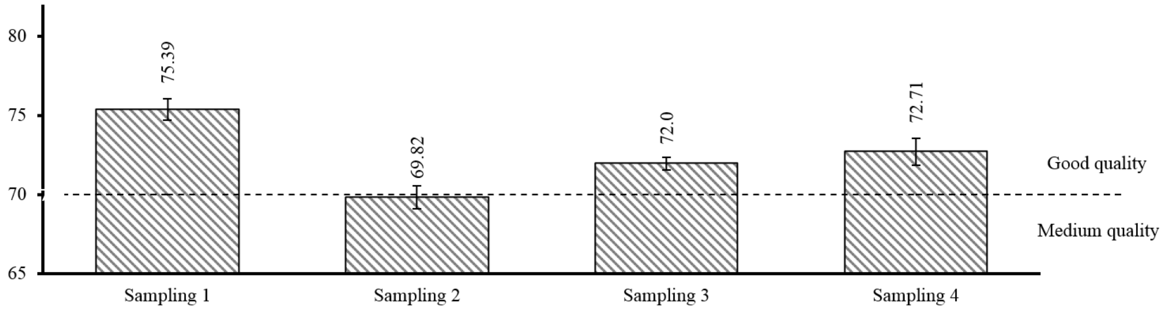


Figure 4. Water quality index (mean ± standard deviation) classified by sampling.

As explained in materials and method section, WQI calculation required assigning a quality value from 0 to 100 for each of the parameters analyzed (I_i). These quality values were interpreted with the same classification used for the WQI. Fecal coliforms showed the lowest quality ($p<0.05$), with an average close to 25 (bad-very bad). Quality of coliforms decreased downstream ($p<0.05$), i.e. the coliform concentration increased towards the Zamora river. The average decreased from 29.5 in station 1 (highest value) to 17.5 in station 6 (lowest value). The decline was accentuated from station 4 (26.5). The values in station 6 could be explained because the waters of the Yacuambi river merge with those of Zamora river, which receives discharges of wastewater from the city of Loja and Zamora.

BOD_5 had the second lower average ($p<0.05$), close to 57 (medium). The rest of quality parameters had an average higher than 70 (good and excellent). BOD_5 reached its minimum quality value at station 3 ($p<0.05$), influenced by the discharge of wastewater from the community Napurak in the La Paz canton.

The remaining parameters lacked a clear trend and differences were not significant. WQI values for dissolved oxygen found in all the stations were higher than 90 (excellent). Such high quality for dissolved oxygen favors the presence of any type of aquatic life and gives a high biological potential to Yacuambi river. As shown in Figure 1, heights vary from 1325 masl in station 1 to 826 masl in station 6. A higher altitude is related to a location closer to the source, a section of the river typically defined by steep slopes and frequent water jumps, which leads to a high degree of homogenisation and oxygenation and a lower organic pollution due to microbes activity.

Concerning the temporal variation, fecal coliforms presented values of lower quality (19) in the second sampling than in the rest (27). The differences were significant with sampling 3 ($p<0.05$) and significant when considering a confidence interval of 85% with the other two samplings ($p<0.15$). All other parameters showed no significant differences between samplings ($p>0.05$). Despite these results, further research with samplings distributed throughout a year is recommended to understand the temporal evolution.

Indexes, such as the WQI, give a general picture of the water quality at the expense of losing information, since not all parameters are included, and could mask the poor state of one parameter with the good state of others. Therefore, it is also necessary to discuss the quality of water through individual parameters, as is done in the next section.

3.2 Risk for populations and ecosystems

The results were compared with water quality guidelines for the uses of these waters from Ecuador and the United States (Table 3). If a parameter fails to comply with the threshold, it can be concluded that the water is not suitable for that use.

Considering the parameters analyzed, Table 3 shows that there are more parameters regulated in the Ecuadorian standards than in North Americans. In addition, Ecuadorian standards impose lower limits than North Americans in most cases. Regarding physicochemical parameters, Ecuadorian standards are more restrictive in 6 parameters, equal in 6 and less restrictive in 2. Referring to metals, the difference is greater. Ecuadorian standards are more restrictive in 10 metals, equal in 4 and less restrictive in 4. In respect of pesticides, Ecuadorians standards define levels for specific pesticide and groups of them, while Americans only do for each pesticide.

Table 3. Thresholds of analyzed parameters in standards of drinking water, preservation of aquatic life and irrigation in Ecuador (EC) and the United States (USA).

Parameter	Unit	Drinking water		Preservation of aquatic life		Irrigation water	
		EC[1]	USA[2]	EC[3]	USA[4]	EC[3]	USA[5]
pH		-	-	6.5-9	6.5–9	6-9	-
Color	Pt-Co	15	-	-	-	-	-
Turbidity	NTU	5	1	-	-	-	-
Nitrate	mg/l	50	10	13	-	-	-
Nitrite	mg/l	0.2	1	0.2	-	-	-
Fecal coliforms	MPN/100 ml	0	0	-	-	1,000	-
As	mg/l	0.01	0.006	0.05	0.15	0.1	0.1
Ba	mg/l	0.7	2	1	-	-	-
Cd	mg/l	0.003	0.005	0.001	0.00072	0.05	0.01
Cr	mg/l	0.05	0.1	0.032	0.085[6]	0.1	0.1
Pb	mg/l	0.01	0.015	0.001	0.0025	5	5
Hg	mg/l	0.006	0.002	0.0002	0.00077	0.001	-
Organochlorine pesticides	mg/l	-		10	-	-	-
Organophosphate pesticides	mg/l	-		10		-	-

[1] Ecuadorian quality standard for drinking water (NTE INEN 1 108:2011) (Ecuadorian Institute of Standardization, 2011).

[2] Table of Regulated Drinking Water Contaminants in the EPA's National Primary Drinking Water Regulations (NPDWR) (United States Environmental Protection Agency, 2015).

[3] Acuerdo Ministerial 28, de 13 de febrero de 2015, por el que se reforma el Texto Unificado de Legislación Ambiental Secundaria del Ministerio del Ambiente (TULSMA) (Ecuadorian Ministry of the Environment, 2015).

[4] Levels of chronic exposure for freshwaters registered in EPA's National Recommended Water Quality Criteria - Aquatic Life Criteria Table (United States Environmental Protection Agency, 2016).

[5] Recommended limits for constituents in reclaimed water for irrigation in long term use. EPA's Guidelines for water reuse (United States Environmental Protection Agency, 1992).

[6] This level of Cr is calculated as the sum of Cr (III) and Cr (VI) given in the original table.

None of the samples could be considered potable according to Ecuadorian and North American drinking water standards (Table 3 and Figure 5). All samples exceeded the thresholds of fecal coliforms and As of both standards, color (only Ecuadorian standard) and turbidity (only North American standard). 42% of the analyzed samples exceeded the Ecuadorian threshold for Pb, specifically all samples in station 1 and some in the stations

2, 3 and 4. Differences between samplings were appreciable. 67% samples of third sampling exceeded the Pb threshold, while only 18% of the second sampling. Most of those samples complied with North American standards. Regarding turbidity, 58% of the samples surpassed Ecuadorian threshold (5 NTU), i.e. all of the samples in stations 2, 4 and 6 and 50% of the samples of station 1.

Arsenic displayed a similar trend in all samplings. Station 1 showed the lowest concentration of As, followed by a significant increase on station 2 ($p<0.05$), where the highest concentrations are found. Station 2 represented a turning point and concentrations in stations 3 and 4 were lower again.

None of the samples were suitable to preserve aquatic life according to Ecuadorian standards and only station 5 in the sampling 1 is adequate according to North American standards (Table 3). The thresholds for Pb was exceeded in all samples (with the exception of station 5, sampling 1 for North American standard). The Ecuadorian threshold for As was exceeded at all stations in samplings 2, 3 and 4 (75% of samples). But at none of them in the North American standard due to higher threshold. The pH was lower than 6.5 in 75% of samples of station 1 and contravene both standards.

Half of the samples were not suitable to irrigate according to Ecuadorian standards (Table 3). Unsuitable samples were concentrated in stations 6 (100%) and 3 (75%). Fecal coliforms exceeded the threshold of 1,000 MPN/100 ml in all samples of sampling 2 and station 6. Arsenic also exceeded the threshold for Ecuador and North America (0.1 mg/l) in 21% of samples. Specifically, 75% of station 3 and 25% of stations 4 and 5.

The concentrations of the rest of the metals studied were below detection limits in all samples: Ba (<0.5 mg/l), Cd (<0.01 mg/l), Cr (<0.5 mg/l) and Hg (<0.005 mg/l), which can be considered low.

The concentrations of organochlorine and organophosphate pesticides in all samples tested were below the limit of detection (α-HCH: 0.077; Aldrin: 0.068; 2-4 DDT: 0.068; heptachlor: 0.056; quinalphos: 0.001; fonofos: 0.0001; malathion: 0.0001). These data can be considered low and meet with Ecuadorian standards described above (Table 3).

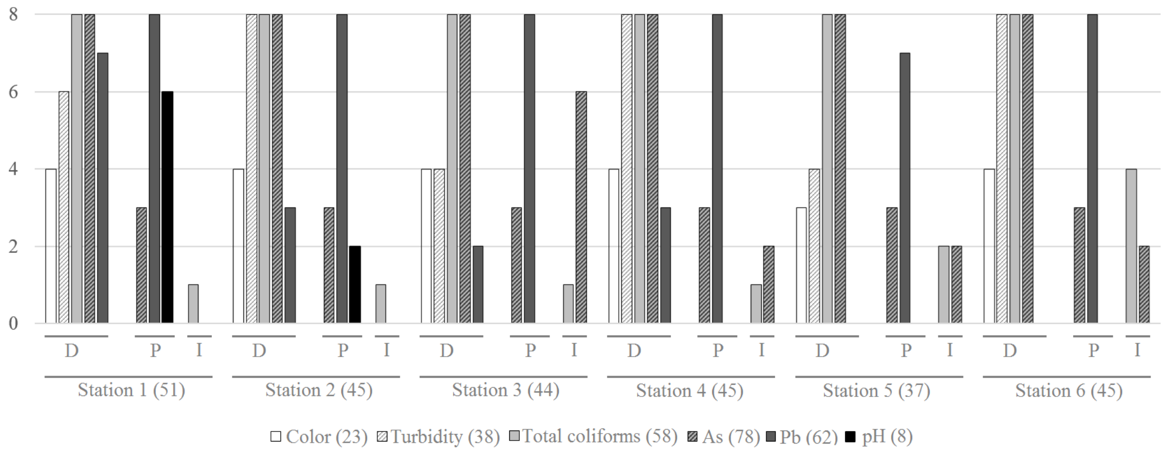


Figure 5. Number of times the thresholds of the drinking water (D), preservation of aquatic life (P) and irrigation (I) regulations are exceeded at each station in the 4 samplings. In brackets, the number of times thresholds are exceeded in a station or for a particular parameter.

Figure 5 describes that the thresholds of As, Pb and fecal coliforms for drinking, preservation of aquatic life and irrigation are those exceeded more times.

3.3 Potential sources of pollution

Several threats could affect water quality. Gold placer mining can cause several impacts on water, such as turbidity by resuspension of sediment. Turbidity values found (below 20 NTU) are sufficient to exceed the North American standard threshold (United States Environmental Protection Agency, 2015). However, this result suggests that mining had a low influence on turbidity. The large flow of Yacuambi river requires a significant amount of particulate material with a high proportion of fine sediment to affects turbidity significantly over long distances. During sampling, it was noted that turbidity of the water increased in some gold placer mining sites. However, turbidity decreased a few meters downstream due to the return of the material to the riverbed. This is confirmed by the data found in Mongolia, where the Tuul river turbidity reached up to 700 NTU due to effluents of gold placer mining (Batsaikhan et al., 2016).

Concentrations of Hg below 5 μg/l in all water samples can be considered low. These results suggest that the amalgamation of gold with Hg in Yacuambi is not intensive, probably because gold nuggets has a large size and high purity. It could also be explained due to the application of measures to prevent spills with high Hg content and Hg emissions into the atmosphere. These data are in agreement with those of López-Blanco et al. (2015), who found that Hg levels in soils along the Yacuambi river (below 0.5 mg/kg) are far below the Quality Guidelines for the Protection of Environmental and Human Health set on 6.6 mg/kg (Canadian Council of Ministers of the Environment, 2007). The levels of Hg in water are in agreement with those of the Nangaritza River, also affected by gold mining, where the concentration is below 1 μg/l (González-Merizalde et al., 2016).

However, López-Blanco et al. (2015) found that Hg concentrations in soils of the Yacuambi's river bank grow downstream, reaching higher values in the surroundings of the mouth than at the headwaters, free from the influence of mining. The absence of other potential sources of Hg in the Yacuambi basin suggests that gold placer mining is the main source of this slight increase. Furthermore, although concentrations of Hg in water are below drinking water thresholds, there may be a risk for humans since Hg is also present in the air. In a nearby area, the Nangaritza River Basin, concentrations of Hg in water were reported below 1 μg/l. However, Hg concentrations in children's urine were found above international guidelines (20 μg/g creatinine) for the production of adverse health effects (González-Merizalde et al., 2016).

What is more, considering the use of Hg in mining was banned in Ecuador in 2013 (Ecuadorian National Assembly, 2013), more control by the local authorities is needed to ensure the enforcement of the law. Further research on the risk of Hg in humans is recommended through the study of Hg in urine.

Arsenic values in Yacuambi river are higher than those (0.0002-0.0159 mg/l) found in the river Congüime, near the Yacuambi (León-Carrasco, 2014) although significant anthropogenic sources (artisanal scale gold mining and placer gold mining) take place in the Congüime river. The artisanal scale gold mining exploits a vein with arsenopyrite, which is accumulated in the streams, accelerating the chemical oxidation and release of As (León-Carrasco, 2014). Thorslund et al. (2016) found in Lake Baikal, Russia, exposed to gold placer mining, concentrations of up to 0.015 mg/l of As in water, whereas in Yacuambi were found concentrations up to almost 10 times that (0.135 mg/l) and concentrations of 0.09 mg/l were common. These results suggest that natural and anthropogenic sources, such as gold placer mining, could act combined to explain the concentrations of As observed in Yacuambi.

The sediment movement carried out by mining exposes deep sediments, predictably under anaerobic conditions, to aerobic conditions in which As has a tendency to solubilize (Bradl et al., 2005). According to López-Blanco et al. (2015), As concentrations in soils of the banks of the Yacuambi river are highly concentrated (over 30 mg/kg). Six of the seven samples exceeded the Quality Guidelines for the Protection of Environmental and Human Health set on 12 mg/kg (Canadian Council of Ministers of the Environment, 2007), in one case, more than 10 times. Thus, high concentrations of As could also occur in the sediment and this could lead to the high levels in water (Sanyal and Nasar, 2002). Under reducing conditions, As may be sequestered by co-precipitation with sulphide minerals (Brammer and Ravenscroft, 2009; Kumar et al., 2016; Sun et al., 2016).

Further research is needed to measure the concentration of As in the sediment and to characterize whether the As belongs mainly to the labile fractions that would facilitate its release.

In Yacuambi river, up to 0.113 mg/l of Pb in water have been found, and values of 0.005 to 0.010 mg/l are common. Thorslund et al. (2016) found in Lake Baikal, Russia, exposed to gold placer mining, Pb concentrations up to 0.006 mg/l in water and the most common values were between 0.001 and 0.0015 mg/l. Concentrations of Pb in the sediments of the Yacuambi river banks are lower compared to those of As (López-Blanco et al., 2015). Only one of the samples of López-Blanco et al. (2015) exceeded 30 mg/kg and none exceeded the values of the Quality Guidelines for the Protection of Environmental and Human Health set on 70 mg/kg (Canadian Council of Ministers of the Environment, 2007). Gold placer mining could lead to high Pb concentrations in water, but lower concentrations in soil helps to explain that the Pb concentrations in water are lower than those of As. Considering both elements have the same maximum value allowed in drinking water, the Pb exceeds the limit on fewer occasions.

Fecal coliforms can be considered high, reaching up to 8,200 MPN/100 ml, and values above 500 MPN/100 ml were common. These levels exceeded in several times those of a river near the area, the Congüime river, below 330 MPN/100 ml (León-Carrasco, 2014). Several reasons are possible, mainly urban wastewater discharges from untreated watershed populations, but also effluents of aquaculture of Tilapia, manure from livestock and cows that access the river to drink.

The results found in this study indicate a non-intensive use of organochlorine and organophosphorus pesticides in Yacuambi catchment. In fact, all pesticides were below the limit of detection. Many farmers only fumigate 1 or 3 times a year. In addition, many farmers use non-water soluble pesticides that would tend to be attached to soils and sediments. Further research is needed to confirm whether water-insoluble pesticides potentially used in agriculture are present in sediments, e.g. those belonging to the sulfonylurea group.

4 Conclusions

The waters of the Yacuambi river have a good and medium quality according to the classification of Water Quality Index (WQI) proposed by Brown et al. (1970). I.e., they are in the second and third best quality category out of five.

According to WQI, water quality is variable along the Yacuambi river. Water quality decreases from downstream of the head to the middle section, where it starts to increase again but then becomes significantly lower at the mouth. This fact suggests that the Zamora river negatively influences the Yacuambi river. Fecal coliforms and BOD_5 are the parameters with the lowest quality. All other parameters have an average quality corresponding to good and excellent categories.

Yacuambi river waters are unsuitable for human consumption and preservation of aquatic life according to the Ecuadorian and North American standards. For human consumption, color, As and fecal coliforms fail to comply with the standards in most cases. For preservation of aquatic life, the threshold for Pb is exceeded in all samples.

Yacuambi river waters are not always suitable for irrigation, especially in the end and medium sections. Arsenic and fecal coliforms exceeded the limits required by the standard for this use.

Further research is required on the river Yacuambi to identify and control sources of pollution in the basin and to ensure water quality for populations and ecosystems.

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