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Evaluation of the impact of domestic and semi-industrial wastewater on the physical-chemical quality of the Chiquito River, León from May 2016 - January 2017.

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SUMMARY

The present study evaluated the impact of wastewater on the physical-chemical quality of two sampling sites, upstream and downstream, in a selected transect of the Chiquito River in the city of León. Samples were taken during four sampling campaigns, two in the rainy season and two in the dry season. Fifteen physical-chemical parameters and twelve metals, metalloids and nonmetals were compared with national (NTON) and international guidelines (U.S. EPA, CCME, NOM, INEN, and FAO). Canadian Software WQI 1.2 was used to comprehensively assess water quality based on a quality index (CWQI), for different uses of water: protection for aquatic life, and irrigation. High levels of contamination excelled by suspended solids, organic matter (oils and fats, BOD and COD, turbidity), nutrients (ammonium, iron) and metals such as Al, Cr^{3+}, Cu, Mn, Se, V, and Zn. The water quality index categorized the site upstream as marginal to regular and poor for downstream, which implies that it was almost always threatened and in most cases departed from desirable levels for the specific uses to which it was submitted. According to CONAGUA, water quality was deteriorated by classifying it from Contaminated to Heavily Contaminated for both sites, with organic matter prevailing implying contamination by discharges of municipal wastewater and tanneries. Hexavalent chromium was detected in May at the upstream site which makes the water in this area more toxic, and the majority of chromium present is in a reduced state.

1. INTRODUCTION

Rivers are natural continuous water currents that are currently affected by climate change, and therefore the physical-chemical quality of the river's water over time and throughout its course. However, human activities cause loss of water quality in an uncontrolled way, causing the elimination of the species' habitat, leading to immense damage to the dynamics of a body of water (Castañé, et al., 1998). Among the human activities that cause the most damage to the environment worldwide is that of leather tanning, whose severity increases in medium or semi-industrial tanneries that generally do not treat their potentially toxic effluents before dumping them into receiving bodies (Roig Orts et al., 2003). Pollution in the last 50 years of the Chiquito River in the city of León has been the object of study by government agencies, environmental agencies, universities, and various organizations, since along its banks' tannery industries are located, mainly (Mayor of León, 2016). Obtaining data through monitoring in an investigation is a very complex job; since it will depend on the multidimensional nature of the river's water quality, which constantly changes at all points throughout its course, making it difficult to understand due to the chemical nature of the substances present (Samboni, Carvajal and Escobar, 2007).

Nicaragua is the Central American country with the greatest privilege in terms of water resources. The available water resource is 38 668 m^3/capita/year, which places it above the Central American average (Jiménez and Galizia, 2012). The city of León is located in the northwest of the national territory. León is the second most important city in the country. The Chiquito River crosses the perimeter of the urban helmet of the city, measures 21 kilometers in length, of which seventeen km is a rural area and 4.5 km within the urban center. The fall of wastewater represents a very severe source of pollution, in addition to solid waste and the remains of dead animals, which are thrown daily into the river bed by the population, which has generated losses of springs, biodiversity, visual pollution, loss of landscape and recreation sites (Lezama, 2013).

On the shore are tanneries, soap stores, the municipal dump, among others, which have been deteriorating the quality of the water through their direct dumping of toxic waste (Palacios and Zapata, 2011). Around 30 tanneries have been counted in the lower part of the river, which generates a high load of organic matter contaminating the water resource, the air and the soil, which is why León represents 60% of the tannery activity nationwide (MIFIC, 2008). Tannery workers are exposed to contact with chemicals throughout the leather tanning process. Cr^{6+} is the pollutant that carries greater risks to the population's health and is used by tanneries due to rudimentary methods and procedures (Chávez, 2010). Almost entirely, the tanneries dump their wastewater directly into the river bed without prior treatment, so there is no removal of the suspended material (Henríquez de Guidos, 2003).

This research contributes to an evaluation of the impact of wastewater from domestic activities and semi-industrial and artisan tanneries on the physical-chemical quality of the Chiquito River water, with an emphasis on chromium. The estimation of water quality was made comparing physical-chemical parameters with emphasis on potentially toxic metals in the two selected sites of interest. The results were compared with the national regulation NTON 05-007 98 for the use of water in agricultural and international applications associated with the use of water for the protection of aquatic life and use in agriculture (irrigation): Canadian Council of Ministers of the Environmental (CCME), the North American Environmental Agency (USEPA), the Mexican standard NOM-001-semarnat-1996 and the Ecuadorian INEN for the protection of aquatic and wildlife, the United Nations Organization for food and livestock (FAO). This investigation is an input for local authorities (MARENA-León, Mayor's Office) and tannery representatives and workers in the decision-making process in the definition and execution of corrective measures to lessen the impact of semi-industrial and artisanal activities on the quality of water resources.

2. METHODOLOGY

Study area

The study was carried out from May 2016 to January 2107 in a 3.5 km transect selected from the Chiquito River, located in the urban area of the city of León. Two representative sites named upstream and downstream were selected. Four sampling campaigns were established to collect the surface water samples from the river, two in the rainy season (May to September) and two in the dry season (November to January). The sampling points are represented in Table 1.

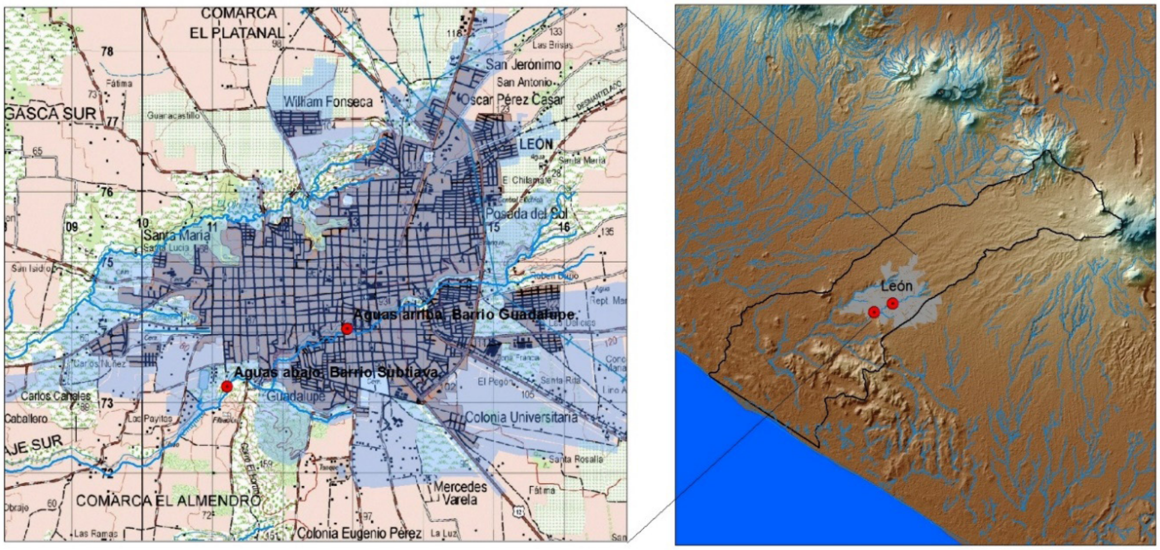


Figure 1. Study area and selected sites in the Río Chiquito sub-basin, León

Table 1. Geographical coordinates of the sampling sites in the Chiquito River.

Place	Coordinates	
	N	E
Upstream	1374152	512938
Downstream	1373352	511234

Source: self-made

Selection of variables and toxic substances

Variables were selected as a priority for the development of aquatic life and existing biodiversity, as well as other physical-chemical parameters of risk to human health according to the use of water. From these criteria, the following field and laboratory parameters were selected, shown in Table 2.

Sampling

Spot samples of surface water were taken at each site. The collection, preservation, transport and laboratory analysis were carried out following the recommendations and procedures of standardized methods (APHA, 2012).

For the determination of recoverable total metals, the samples were preserved with concentrated HNO_3 and stored under refrigeration at 4 °C. For the analysis of dissolved metals, the sample was filtered, brought to pH <2, preserved and stored under the same conditions. The samples were injected by the analytical technique Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Hexavalent chromium was quantified through Visible Ultraviolet spectrophotometry. The analysis of physical-chemical parameters such as pH, conductivity, redox potential, alkalinity, chlorides, turbidity, oils and fats, sulfates, sulfides, ammonia, suspended solids, settleable solids, BOD and COD, are detailed in Table 2.

Table 2. Physical-chemical parameters of interest, methodology and analytical technique used.

Parameters	**Analytical Method**	**Analytic technique**
Hydrogen potential (pH) SMWW	SMWW 4500.H^+B	Potentiometry
Redox Potential (ORP)	U.S.EPA 9045 + SMWW 2580.B	Potentiometry
Electrical conductivity	SMWW 2510.B	Potentiometry
Total alkalinity	SMWW 2320.B	Titrationmetry
Chlorides	SMWW 4500-Cl^-.B	Titrationmetry
Turbidity	SMWW 2130.B	Turbidity
Oils and greases	SMWW 5520.B	Gravimetry
Sulfates	SMWW 4500-SO_4^{2-}.E	Spectrophotometry
Sulfides	SMWW 4500.S^{2-}.D	Colorimetry
Ammonium	HACH 8038	Spectrophotometry
Total Suspended Solids	SMWW 2540.D	Gravimetry
Settable solids	SMWW 2540.F	Gravimetry
Biochemical Oxygen Demand	SMWW 5210.B	Incubation
Chemical Oxygen Demand	SMWW 5220.C	Reflux closed
Hexavalent chromium	SMWW 3500-Cr.B	Ultraviolet / visible spectrophotometry
Total recoverable metals: Aluminum, Barium, Boron, Zinc, Copper, Chromium, Phosphorus, Iron, Manganese, Potassium, Selenium, Vanadium	SMWW 3030.F+3120.B U.S.EPA 200.7 Rev.4.4, 1994/ ICP-OES	Emission Spectrometry / Colorimetry
Dissolved metals: Calcium, Magnesium, Sodium	SMWW 3030.B+3120.B	Emission Spectrometry

Parameters	Analytical Method	Analytic technique
U.S.EPA: U.S. Environmental Protection Agency; SMWW: Standard Methods for the Examination of Water and Wastewater; ICP-OES: Inductively Coupled Plasma Optical Emission Spectrometry. HACH Company/Hach Lange GmbH, 2007-2017. Nitrogen. Ammonia-U.S.EPA Nessler Method. DOC316.53.01078, Edition 9.		

Source: Self-made

Water quality estimation using CWQI software

CWQI 1.2 software is a program developed by the Canadian Council of Ministers of the Environment (CCME). It calculates complex physical, chemical and biological data into an indicator that simplifies water quality and makes it easy to interpret. The Index is based on a) Scope: number of variables that do not meet the water quality objectives; b) Frequency: number of times the objectives are not met; and c) Amplitude: the amount by which they are not met. The software was developed in an Excel spreadsheet where the results obtained in the analyzes were compared with the quality objectives. The result is a number between 0 (*lower* quality water) and 100 (*higher* quality water), so the quality of the water is classified into different ranges to which a qualitative description of the degree of contamination is assigned (Samboni, Carvajal, & Escobar, 2007) (CCME, 2001), see table 3.

Table 3. Categorization and classification of the CCME index.

CWQI Value	Category	Description
95 - 100	Excellent	Water quality is protected with a practical absence of threat or deterioration; conditions are very close to natural levels. Those index values can only be obtained if all measurements are within targets virtually all the time.
80 - 94	Good	80 - 94 Good Water quality is protected with a lesser degree of threat or deterioration; conditions rarely deviate from natural or desirable levels, and usually by a small margin.
65 - 79	Fair	Water quality is usually protected but sometimes exceeds natural levels or set value and possibly by a small margin.
45 - 64	Marginal	Water quality is frequently threatened or deteriorated; conditions typically deviate from natural or desirable levels by a considerable margin.
0 - 44	Poor	Water quality is almost always threatened or impaired; usually deviates from natural or desirable levels by a considerable margin.

Source: (CCME, 2001)

3. RESULTS

The table below shows the summary of the results obtained from the research:

Table 4. Results of Physical Chemical Parameters and Heavy Metal Content

Sampling date	**27/05/ 2016**	**05/09/ 2016**	**11/11/ 2016**	**18/01/ 2017**	**27/05/ 2016**	**05/09/ 2016**	**11/11/ 2016**	**18/01/ 2017**
Time	12h00	11h55	10h56	11h14	10h20	10h35	09h45	09h15
Sampling site	Upstream (Guadalupe neighborhood)				Downstream (Sutiaba neighborhood)			
FQ parameters								
pH (units)	6,250	7,367	7,450	7,112	7,120	7,504	8,679	7,092
C.E. (µS/cm)	553,0	559,0	583,0	548,0	742,5	770,5	807,5	1 283,0
E_h* (mV)	165,7	262,7	290,8	177,4	284,4	268,0	286,6	301,0
S. Thirst. (ml/l)	<0,1	<0,1	0,1	1,7	<0,1	<0,1	0,4	1,6
S.S.T. (mg/l)	51,6	85,2	92,0	176,4	63,7	76,0	180,7	186,6
Alkalinity (mg/l)	89,0	204,0	221,2	222,0	103,8	214,0	227,5	228,0
Dissolved organic matter								
Oils and Fats (mg/l)	41,4	8,2	52,3	53,1	18,85	8,75	15,35	17,10
DBO_5 (mg/l)	168,00	141,12	94,96	172,15	80,00	49,00	122,95	91,14
DQO (mg/l)	255,00	216,03	174,72	296,46	165,00	137,48	221,32	148,23
Turbidity (UNT)	31,75	103,2	79,2	127,2	94,0	85,6	106,0	133,0
Anions and cations								
Cl^- (mg/l)	33,51	27,86	27,64	28,23	70,42	73,69	86,93	192,29
SO_4^{2-} (mg/l)	85,193	41,723	42,113	54,751	65,817	15,263	64,140	188,387
Ca_{dis} (mg/l)	16,659	24,040	19,225	75,446	24,647	29,888	41,942	41,613
Mg_{dis} (mg/l)	7,512	9,013	10,169	9,056	10,575	9,550	10,631	11,747
K (mg/l)	14,775	14,166	15,854	14,512	14,686	13,939	17,034	14,709
Na_{dis} (mg/l)	56,095	39,641	43,541	107,384	56,550	57,675	79,114	134,192
Nutrients								
NH_3-N (mg/l)	17,555	16,644	18,956	22,035	20,388	18,240	20,731	23,046
B (mg/l)	0,122	0,063	0,084	0,121	0,039	0,260	0,304	0,311

Sampling date	**27/05/ 2016**	**05/09/ 2016**	**11/11/ 2016**	**18/01/ 2017**	**27/05/ 2016**	**05/09/ 2016**	**11/11/ 2016**	**18/01/ 2017**
Fe (mg/l)	0,903	0,777	0,652	2,600	0,740	0,644	1,045	1,389
P (mg/l)	2,302	2,312	3,243	3,434	2,359	2,354	2,922	2,970
Other elements / compounds								
S^{2-} (mg/l)	0,705	0,259	0,416	7,900	0,338	0,361	0,860	1,057
Cr^{6+} (mg/l)	0,022	<0,016	<0,016	<0,016	<0,016	<0,016	<0,016	<0,016
Metals, metalloids and non-metals								
Al (mg/l)	0,532	0,486	0,435	3,002	0,340	0,365	0,736	1,334
Ba (mg/l)	<0,001	0,176	0,096	0,115	0,137	0,135	0,136	0,116
Cr (mg/l)	<0,002	nd	<0,002	<0,002	0,626	1,047	0,605	39,719
Cu (mg/l)	<0,005	<0,005	<0,005	<0,005	<0,005	<0,005	<0,005	0,022
Mn (mg/l)	0,131	0,192	0,094	0,084	0,169	0,231	0,207	0,141
Se (mg/l)	nd	nd	nd	nd	<0,010	<0,010	nd	0,949
V (mg/l)	0,015	0,021	0,061	0,039	0,014	0,016	0,065	0,019
Zn (mg/l)	0,111	0,038	0,051	0,135	0,041	0,031	0,053	0,065
*: by calculation; NA: Not Detected; Source: self-made								

4. DISCUSSION

4.1. Physical-chemical parameters

The Hydrogen potential (pH) of the waters collected at the upstream site presented almost neutral values of 7,112 to 7,450. In the rainy season, it presented a pH of 6,250; however, pH rarely represents a problem for the soil and crops, since most of the nutrients are available at pH 5.5 — 6.5 (Ayers and Westcot, 1985). The pH value at the downstream site was between 7,120 to 8,679 with a slight alkaline tendency in the dry season, which could decrease the capacity of water buffering (CCREM, 1987). The highest conductivity values were found in the dry season (743 to 1283 $\mu S.cm^{-1}$) at the site called downstream because in the dry period the concentrations of the salts tend to increase because there is no dilution by the water of rain which indicated significant to excessive mineralization. According to the FAO (Motsara & Roy, 2008), waters with an EC less than 225 $\mu S.cm^{-1}$ are considered adequate for irrigation. The TSS was found at the upstream site between 92.0 and 176.4 $mg.L^{-1}$ and the downstream site, above the maximum value (180.7 and 186.6 $mg.L^{-1}$) at the time dry exceeding the Mexican guideline NOM-001-SEMARNAT-1996, protection of aquatic life. The National Water Commission of Mexico (CONAGUA, 2016), classifies river water as surface water with indications of contamination to contaminated and of poor quality at both sampling sites, which is attributed to discharges of raw wastewater, waters with a high content of suspended material and with restricted use for irrigation. Settling solids did not exceed the value set by the guidelines to be compared. Alkalinity results vary in the range of 89.0 to 222.0 mg.L^{-1} at the upstream site and from 103.8 to 228.5 mg.L^{-1} at the downstream site, thus exceeding the value of the USEPA guideline, protection of aquatic life, chronic, in the four sampling campaigns. The average alkalinity is high range (> 150 mg.L^{-1}) and in both sites, it is exceeded by 11 times in the dry season, which implies the capacity of the waters to buffer acid spills and indicate a high fertility potential since the waters extract the CO_2 from the dissolved carbonic acid (Espinosa & Rodríguez, 2016).

4.2. Dissolved organic matter

The BOD_5 results were found from 95.0 to 172.1 mg.L^{-1} upstream and from 49.0 to 122.9 mg.L^{-1} downstream, exceeding the value of the guideline NOM-001-SEMARNAT -1996, protection of aquatic life, in the four sampling campaigns for the upstream site and three of the four campaigns for the downstream site. CONAGUA classifies it as polluted to heavily polluted surface water, with a strong impact of raw, municipal and non-municipal wastewater discharges at both sites. The COD results obtained were from 174.7 to 296.5 mg.L^{-1} for upstream and from 137.5 to 221.3 mg.L^{-1} for downstream, thus exceeding that established by CONAGUA, for contaminated water a heavily contaminated (COD> 200) at both sites. The high demand is caused by the contribution of organic matter received by the river. According to Custodio y Llamas (Custodio & Llamas, 2001), it indicates that there is contamination when the BOD_5 concentration exceeds 1 mg.L^{-1} and when the COD concentration exceeds 10 mg.L^{-1}. Turbidity peaked in the dry season for both sites, mainly due to suspended biotic and abiotic causes such as material carryover, industrial and domestic discharges, and solid waste such as dead animals and soil erosion (CCREM, 2002).

4.3. Anions and cations

Upstream chlorides (Cl^-) were found between 27.64 to 33.51 mg.L^{-1} and for the downstream site between 70.42 to 192.29 mg.L^{-1}. In the dry season, at the downstream site, the concentration exceeded the value established by the CCME guidelines for protection for agricultural use, INEN for agricultural use and FAO for agricultural use by 2 times, indicating residual domestic and industrial contamination since chlorides are typical indicators of this type of anthropogenic contamination (Marín, 1996). Sulfates (SO_4^{2-}) at the upstream site ranged from 41,723 to 85,193 mg.L^{-1} and at the downstream site from 53,263 to 188,387 mg.L^{-1}. The high concentrations of sulfates are contributed by industrial and domestic activity, among which is the use of chemical products such as dyes, fertilizers, and the contribution of the semi-industrial tannery due to its disposal in the leather coloring stage. The calcium (Ca) corresponding to the upstream site was between 16.66 to 75.45 mg.L^{-1}, where the highest concentration occurred in the dry season. Concentrations of 24.65 to 41.94 mg.L^{-1} were found at the downstream site, with high concentrations in the dry season. The concentrations of magnesium (Mg) found at the upstream site were between 7.51 to 10.17 mg.L^{-1} and for downstream between 9.55 to 11.75 mg.L^{-1}, presenting the highest concentrations in the dry season. The carbonate and bicarbonate ions combine with calcium and magnesium to form a precipitate in the form of $CaCO_3$, leading to moderate alkalization (pH_{max} 7.45) and downstream (maximum 8,679) and high concentrations in alkalinity. The concentrations found for potassium (K) were between 14.17 to 15.85 mg.L^{-1} for the upstream site and 13.94 to 17.03 mg.L^{-1} for downstream, concentrations that were maintained with little variation, the anthropogenic origin of which may be related to the use of fertilizers such as NPK. According to Rodier, J., in natural waters, if it does not exceed 10 mg.L^{-1}, it does not offer any health problems for the population (Rodier, 1981). The concentrations of sodium (Na) found at the upstream site were between 39.64 to 107.38 mg.L^{-1} and downstream they ranged from 56.55 to 134.19 mg.L^{-1} values that exceed the maximum admissible according to the FAO and INEN guidelines for irrigation for 2 times.

4.4. Nutrients

High concentrations of ammonia were found at the upstream site of 16.6 to 22.0 mg.L^{-1}, and 18.24 to 23.05 mg.L^{-1} downstream. Upstream, in the four samplings, the values regulated by the USEPA protection of aquatic life, acute and chronic by 9 times, the CCME (protection of aquatic life) by 13 times, and the INEN protection of aquatic and wildlife in more than 1000 times. Downstream it exceeds USEPA, protection of aquatic life, acute by more than 3 times and chronic by more than 18 times, CCME (protection of aquatic life) by 75 times and INEN, protection of aquatic and wildlife, in more than 1000 times. These results indicated recent contamination since the presence of this ion favors the microbial multiplication. The ammonium ion concentration rises when the medium is strongly reducing ($P.R_{prom}$ = 224 mV upstream and $P.R_{prom}$ = 285 mV downstream) (Fernández & Vásquez, 2006). The concentrations of iron found upstream ranged from 0.652 to 2,600 mg.L^{-1} where the highest was recorded in the dry season, these exceed the values set for the guidelines CCME protection of aquatic life and INEN, protection of aquatic life and wild in the four sampling campaigns 9 times. The 2.6 mg.L^{-1} value exceeds the U.S. EPA Aquatic Life, Chronic and NTON Category 2-A and 2-B by 3 times. While concentrations at the downstream site varied from 0.644 to 1.389 mg.L^{-1} where the highest concentrations were recorded in the dry season. The normed values for use in irrigation are not exceeded.

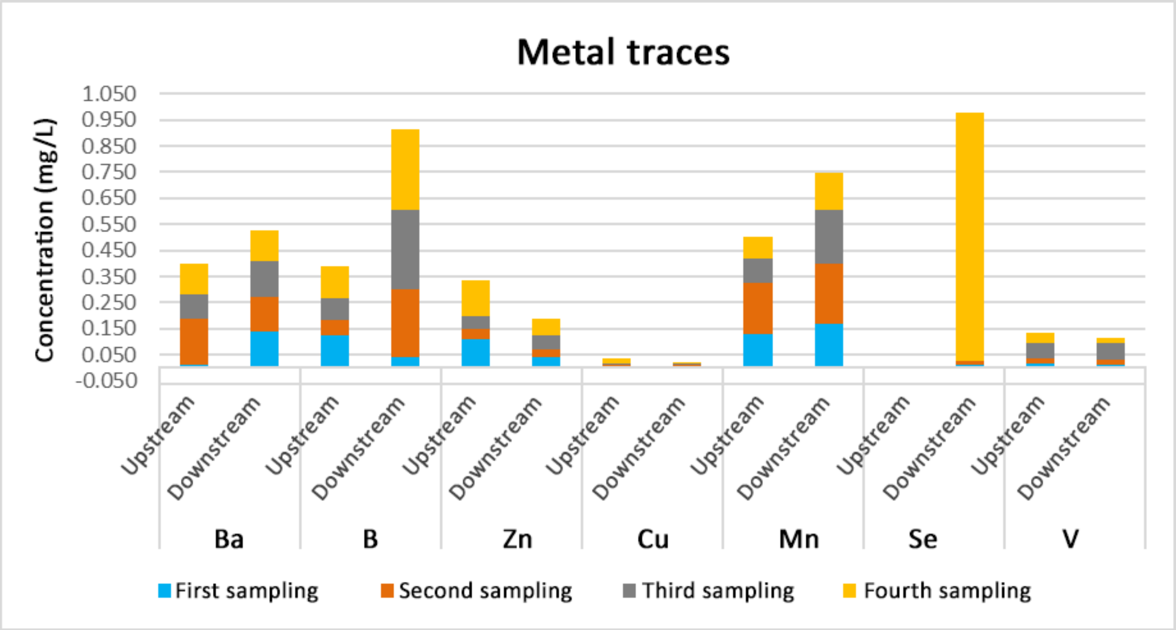
4.5. Other elements/compounds

The concentrations found for total sulfide are from 0.259 to 7.90 mg.L^{-1} for the upstream site and 0.338 to 1.057 mg.L^{-1} for the downstream site. Sulfur is an essential component of living matter. A large amount of organic matter present in both sites was evidenced by the high concentration in oils and fats, turbidity, BOD_5, and COD, this decomposes due to the presence of heterotrophic and anaerobic bacteria, thus reducing sulfate to sulfur, primarily as H_2S (CCREM, 1987). Hexavalent chromium was found to be 22 μg.L^{-1} in the first sampling campaign at the upstream site exceeds USEPA guidelines for acute and chronic aquatic life, CCME protection of aquatic life and use of irrigation water, 2 times for USEPA and 22 times for the CCME aquatic life, which makes the water in this area more toxic, relating it to the presence of scattered artisan tanneries located in neighborhoods east of the city such as the El Coyolar neighborhood.

4.6. Metals, metalloids, and non-metals

4.6.1. Trace elements

Barium (Ba) presented concentrations upstream in the range of 0.096 to 0.176 mg.L^{-1} and downstream in the range of 0.116 to 0.137 mg.L^{-1}. Boron (B) presented concentrations at the upstream site in the range of 0.063 to 0.122 mg.L^{-1} and downstream from 0.039 to 0.311 mg.L^{-1}, presenting the highest concentrations in the dry season. The results obtained using the ICP-OES spectrometric technique, with previous acid digestion (HNO_3) did not exceed the values established by the guidelines to be compared in the study. The found concentrations of boron can be attributed to the fact that spring waters generally contain appreciable amounts of boron, especially in geothermal areas. It may also be due to the domestic use of borates/perborates in detergents and softeners, and household bleaches such as borax and boric acid (CCREM, 1987). Upstream zinc (Zn) concentrations were found in the range of 0.038 to 0.135 mg.L^{-1}, where the highest concentrations occurred in the first and last sampling; while downstream it presented concentrations in the range of 0.031 to 0.065 mg.L^{-1}, and the highest concentrations in the dry season. The copper (Cu) concentrations found upstream are less than the detection limit, but in January a concentration of 22 μg.L^{-1} was found, which exceeds the standard values of the following guidelines: USEPA protection of life aquatic, acute 2 times, USEPA protection of aquatic life, chronic 2.5 times, CCME, protection of aquatic life 8 times, and INEN protection of aquatic and wildlife. High copper concentrations are usually related to anthropogenic activities and the bacterial decomposition of organic matter since copper has a high affinity for it. The results for manganese (Mn) at the upstream site exceeded the standard value for the INEN guideline, protection of aquatic and wildlife by 2 times in the rainy season. At the upstream site, concentrations varied in the range of 0.084 to 0.192 mg.L^{-1} and the lowest concentration was recorded in the dry season with a low redox potential (177.4 mV). The redox potential between the months of September to November was the highest recorded (277 mV_{prom}) and the pH changes were variable, registering a value of 6.25 in the month of May and 7,367 in the month of September. The concentrations of manganese found downstream varied from 0.141 to 0.231 mg.L^{-1}, with the lowest concentration being recorded in the dry season. The results exceeded the regulated values of the CCME, INEN and FAO guidelines for irrigation water, the INEN protection of aquatic and wildlife by 2.3 times with an average redox potential in those two months of 278 mV$_{prom}$. The Redox potential measured in the field in January is the highest recorded (301 mV). Downstream manganese exceeded the CCME, INEN and FAO guidelines for irrigation water in the months of September to November, which could be related to very little growth in plants (ATSDR, 2012). Selenium (Se) at the upstream site was not detected by the ICP-OES spectrometric technique. At the downstream site, in the dry season, the last sampling was 0.949 mg.L^{-1}, thus exceeding the standard value of all the guidelines to be compared. U.S. EPA, acute and chronic 47 times and 190 times respectively; CCME aquatic life for 950 times, CCME irrigation for 47 times; INEN, aquatic life 95 times and INEN irrigation 47 times; NTON for vegetable irrigation 95 times; FAO irrigation for 47 times. The concentrations of vanadium (V) found at the upstream site ranged from 0.015 mg.L^{-1} to 0.061 mg.L^{-1}, whereas downstream they ranged from 0.014 mg.L^{-1} to 0.065 mg.L^{-1}. In all cases, the results did not exceed the values established by the evaluated guidelines.



Graph 1. Graph of concentrations of trace elements in the four sampling campaigns, in the two selected sites. Source: self-made

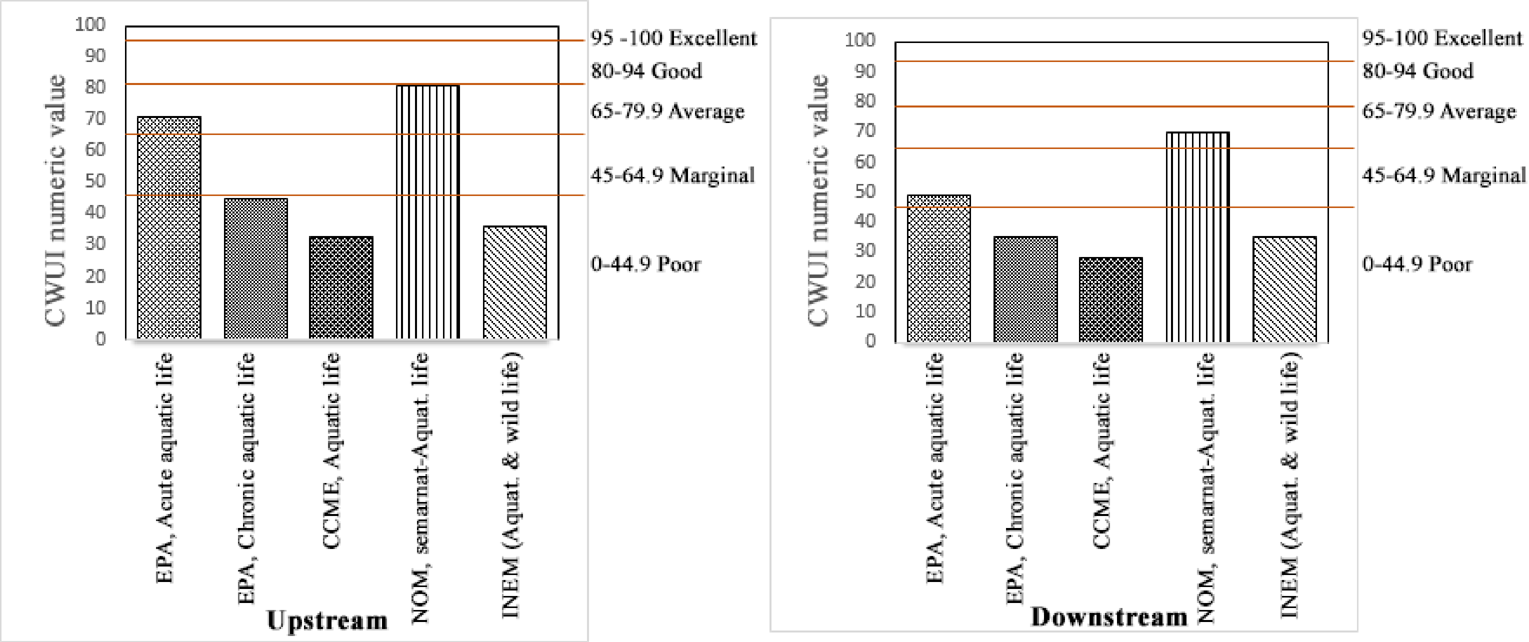
The found concentration of aluminum (Al) upstream was 0.435 to 3.002 mg.L^{-1} and at the downstream site it varied from 0.340 to 1.334 mg.L^{-1}. The highest concentrations occurred in the dry season at both sites, up to 2.25 times higher upstream. Downstream they turned out to be 15 times greater than that established by the chronic U.S. EPA and 13 times greater than the CCME and INEN.

The $Chromo^{3+}$ concentrations found at the upstream site were found to be less than the detection limit (0.002 $mg.L^{-1}$). At the downstream site, Cr concentrations were found between 0.626 $mg.L^{-1}$ to 39.719 $mg.L^{-1}$ in January. The concentrations found exceeded the value established by the U.S. EPA guidelines for the protection of aquatic life, acute and chronic, CCME protection of aquatic life, and the INEN protection of aquatic and wildlife. In the rainy season, the result for the month of September exceeded the values established by the U.S. EPA by 2 times and 14 times, the value of the CCME by more than 115 times and the value of the INEN by 21 times. In this same month, the values of the CCME for irrigation use were exceeded by more than 210 times, NTON Category 2A-2B by 21 times, and FAO used irrigation by more than 10 times. The value of 39,719 $mg.L^{-1}$ exceeds all the values established by the different guidelines by a wide margin: U.S. EPA acute and chronic aquatic life by 70 times and more than 530 times, respectively. CCME aquatic life, irrigation by 4 400 times, more than 8 thousand times and 790 times, respectively. NOM-001-SEMARNAT-1996 protection of aquatic life and use irrigation 40 times and 26 times, respectively. The INEN protection of aquatic and wildlife and the NTON Category 2A and 2B for 790 times. FAO used irrigation 400 times. These very high margins are due to the direct influence of the majority of artisanal and semi-industrial tanneries located along 3.5 km of the selected transect, whose agglomeration of 30 tanneries begins in the Laborío neighborhood until the Sutiaba neighborhood, which discharges directly to the river without prior treatment, the wastewater coming mainly from the leather tanning process and the use of chromium salts ($Cr_2(SO_4)_3$), and it is common for each artisan tannery to use its formulations based on its empiricism and experience with obsolete equipment (Palacios & Zapata, 2011) (MIFIC, 2008).

4.7. Water Quality Index

4.7.1. Water quality index for the protection of aquatic and wildlife

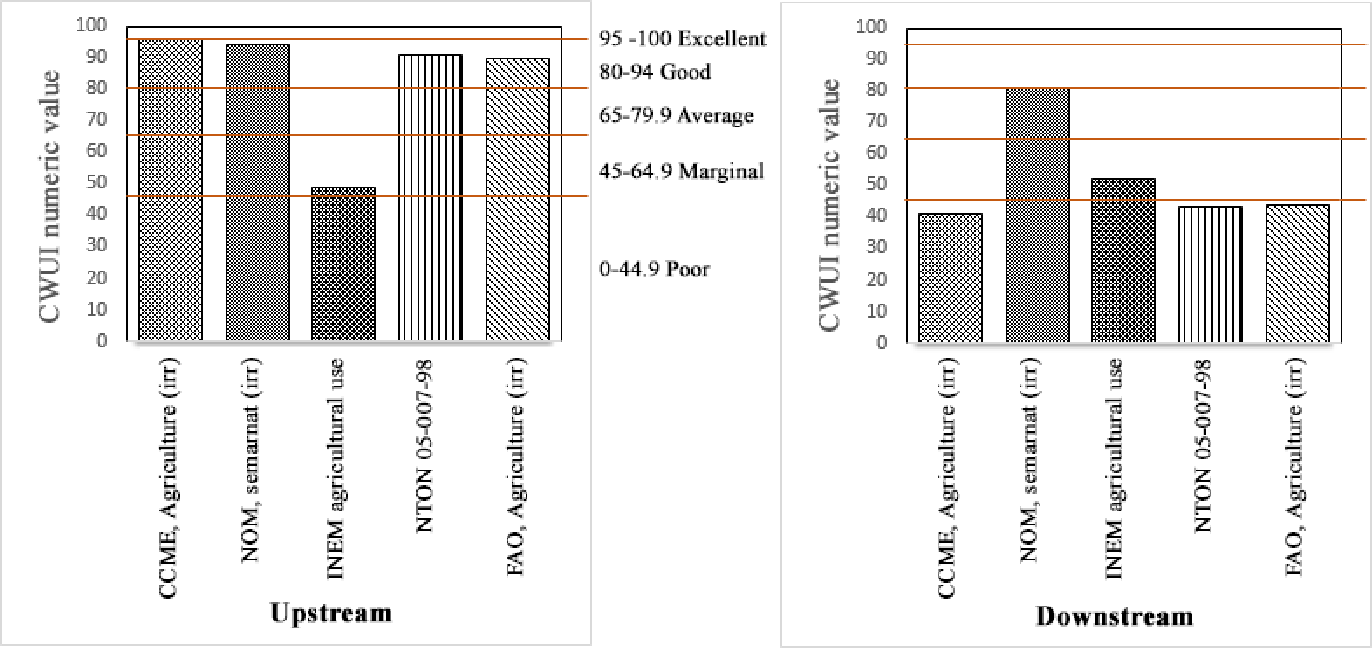
At the upstream site the quality index ranged from 33 to 81 (poor to good category). The parameters included in the calculation range from 11 to 18. The CCME and INEN guidelines categorized the water as poor, the USEPA categorized it as fair (CWQI = 71) and NOM-001-semarnat-1996, as good (CWQI = 81). Implying that quality is almost always threatened or impaired and usually deviates from natural levels by a considerable margin. The parameters that decreased water quality at this site were Al, Cr^{6+}, Cu, Fe, Mn, Zn, oils and fats, BOD_5, total suspended solids, and ammonia. At the downstream site, the quality index ranged from 28 to 70 (poor to fair category) from almost always deteriorated quality to usually protected. The parameters that decreased the water quality at this site were Al, Cr^{3+}, Cu, Fe, Se, oils and fats, total suspended solids, and ammonia. The attribute that most influenced both sites was the amplitude (F3) that represents the quantity by which the values of the parameters or failed tests did not meet their quality objectives.



Graph 2. The behavior of the water quality (CWQI) of the Río Chiquito for the use of aquatic life protection. Source: self-made

4.7.2. CWQI for agricultural use (irrigation)

At the upstream site, use in irrigation, the quality index ranged from 49 to 96 (marginal to excellent category). The parameters included in the calculation vary from 15 to 21. The INEN guideline categorized water as marginal and FAO, NTON and NOM-001-semarnat-1996 categorized it as good (CWQI between 90 and 94). The parameters that decreased the quality of the irrigation water at this site were pH, Al, Cr^{6+}, Fe, oils and fats, and alkalinity. The attribute that most influenced the quality indices was the frequency (F1) that represents the percentage of "failed" variables that do not meet their objectives at least once during the investigation period. Downstream, the quality indices ranged from 41 to 52 (poor to marginal category) with the exception of NOM-001-semarnat-1996, which gave an index of 81 (regular). The parameters that decreased the quality of the irrigation water at this site were Al, Cr^{3+}, Cu, Fe, Se, oils and fats, total suspended solids, and ammonia. The attribute that most influenced the quality indices was the amplitude (F3).



Graph 3. The behavior of the water quality (CWQI) of the Río Chiquito for agricultural use (irrigation)

5. CONCLUSIONS

- The water quality of the downstream and upstream sampling sites was found to be deteriorated, classifying it according to parameters BOD_5, COD, and TSS, as contaminated to heavily contaminated. Most of the physical-chemical parameters (alkalinity, oils, and fats, sulfates, ammonium, sulfide, chromium^{6+}) and metals evaluated (Fe, Mn, Cr^{3+}, Cu, Se, Zn) in the study exceed by more than 50% the different guidelines used for different uses.

- The calculation of the water quality index of the selected sites for water uses for protection of aquatic life and irrigation use, using the CWQI, categorized the water quality of the river for protection of aquatic life as marginal for upstream and poor for downstream and, for agricultural use (irrigation) as regular for the upstream site and marginal for downstream. The use of the CWQI in this investigation simplified the interpretation and the tendency of the deterioration for the right decision making for the hydric body, the reason why it is recommended in specific studies like this one.

- High concentrations of chromium at the downstream site exceeded the value established by the different guidelines by a wide margin (U.S. EPA, CCME, NOM-001-Semarnat, INEN, NTON, and FAO). So the water quality at this site is highly polluted.

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