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Articles

Evaluation of the physical and chemical quality and trace elements of water in Cupatitzio River, Michoacán

Evaluación de la calidad fisicoquímica y elementos traza en el agua del río Cupatitzio, Michoacán

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Abstract

In Mexico, around 90 % of the rivers are polluted mainly from wastewater resulting in human health issues. This work is aimed at determining the water quality of Cupatitzio River; 20 sampling sites (SS) were determined in rainy (August 2016) and dry (May 2017) seasons; 31 trace elements (TE) were obtained and 15 physicochemical parameters; three quality indices were calculated: Water Quality Index (WQI), Pollution Index (IC) and the Canadian Council of Ministers of the Environment, Water Quality Index ($CCMEWQI$). Statistical analysis was conducted to associate variables. Results show for the rainy season, the quality indices indicates that the worst quality is found in the middle watershed due to the wastewater and leachate from a landfill; in the dry season, low quality reaches the low watershed. High concentrations of Fe, Al and P trace elements are found in the middle and lower watershed. It is worth mentioning that they may be associated with the pesticides used in avocado orchards. Finally, analyses show an association between poor quality, low dissolved oxygen and the presence of reservoirs. Therefore, the river water is not fit for human use and consumption.

Keywords: Canadian Water Quality Index, Cupatitzio River, environmental metrics, physicochemical parameters, pollution index, trace elements, water pollution.

Resumen

En México, alrededor del 90 % de los ríos más importantes están altamente contaminados, principalmente de aguas residuales, lo cual resulta en problemas de salud humana. El presente trabajo tiene como objetivo determinar la calidad del agua del río Cupatitzio. Para ello se determinaron 20 sitios de muestreo en temporadas de lluvias (agosto de 2016) y secas (mayo de 2017); 31 elementos traza (ET), y 15 parámetros fisicoquímicos. Se calcularon tres índices de calidad: índice de calidad del agua (ICA), índice de contaminación (ICO) e índice canadiense (CCME WQI); se hizo un análisis estadístico para asociar variables. Los resultados se reportaron como sección de cuenta alta, media y baja. Para el tiempo de lluvias, los índices de calidad indicaron que la peor calidad se encuentra en la cuenca media debido a la presencia de aguas residuales y lixiviados de un relleno sanitario; en estiaje, la baja calidad se extiende hasta la cuenca baja. Los elementos traza Fe, Al y P se presentan en altas concentraciones en las cuencas media y baja. Cabe destacar que pueden estar asociados con plaguicidas empleados en huertas de aguacate. Por último, los análisis estadísticos presentan una asociación entre baja calidad, poco oxígeno disuelto y la presencia de embalses. Debido a lo anterior, el agua del río no es apta para el uso y consumo humano.

Palabras clave: índice de calidad del agua canadiense, río Cupatitzio, métricas ambientales, parámetros fisicoquímicos, índice de contaminación del agua, elementos taza, contaminación del agua.

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Introduction

The intensification of agricultural practices, insufficient treatment of wastewater, heavy metals, nitrates and nitrites are high impact pollutants for aquatic organisms and human health, causing water-borne diseases, mainly cancer (Arain *et al*., 2014). Another factor affecting water quality is the nonpoint source pollution derived from agricultural practices, whose activity has been increasing in the last decade due to the demand for international trade, which accounts for one fourth of the global N emissions (Liu *et al*., 2018b). Surface water quality may be evaluated with various methodologies, and through different indicators, such as: physical and chemical parameters which may in turn be evaluated by means of water quality indices, quality standards or multivariate statistics; biological indicators such as the count of benthic species; and microbiological indicators, which quantify pathogens such as fecal coliforms (Espinal, Sedeño, & López, 2013; López-Hernández, Ramos-Espinosa, & Carranza-Fraser, 2007; Storaci-Koschelow, Fernández-Silva, & Smits-Gunta, 2013). Furthermore, the impact on water quality may be indirectly estimated through simulation of hydrologic models, assessment of soil erosion or even vegetation indices (Abbaspour *et al*., 2015; Ouyang, Hao, Skidmore, & Toxopeus, 2010).

In Mexico, the outlook of water quality is critical, since of the 50 most relevant rivers in the country, 94 % are considered highly polluted as reported by the National Water Commission (Conagua, 2014). Another example is this study case; the Cupatitzio River begins from inside the Barranca del Cupatitzio National Park, in the city of Uruapan, Michoacán.

Previous studies in the Cupatitzio river have analyzed its quality through biological analyses such as the count of macroinvertebrates, count of planktonic organisms, quantification of physical and chemical parameters and the application of national standards such as the NOM-127-SSA1 (1994) (Ortega-Murillo, Díaz-Martínez, Alvarado-Villanueva, & Hernandes-Morales, 2012; Pérez-Munguia, Aguilera-Ríos, & Mora-Guerrero, 2006). However, there have not been yet applied physical and chemical indices that may express water quality numerically, which allows their comparison with other water bodies as suggested by Silva *et al*. (2013) upon applying the WQI to determine surface water quality in the Duero river in Michoacán.

Among the environmental impact activities occurred in the Cupatitzio watershed, the following must be highlighted: The change of

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land use from forestland to monoculture of avocado resulting in the loss of biodiversity; excessive use of agrochemicals polluting the body of water; overexploitation of aquifers, and untreated wastewater discharges (Bravo *et al*., 2009; Villafán-Vidales & Ayala-Ortiz, 2014). The consequence of this background is an increase in soil creep, transport of nutrients to water and, consequently, the degradation of the quality of the body of water.

The Cupatitzio river has a great relevance in the region, since it is used to supply drinking water to the city of Uruapan, it also feeds 11 agricultural irrigation dams (22 550 ha for crops) and three hydroelectric power dams that belong to the Federal Electricity Commission (Conagua, 2012). Another relevant aspect from a cultural and recreational stance is that the source of the Cupatitzio River starts inside the Barranca del Cupatitzio National Park, which is a protected natural area and it is a tourist attraction (CNANP, 2006; Ortega-Murillo *et al*., 2012).

Given the importance of the river, it is necessary to know the current status of the quality of its water and pollution sources. Therefore, the objective of this work was to determine the physical and chemical quality of the water of Cupatitzio River, main tributaries and reservoirs.

This study was carried out in October 2017 in the water laboratory of the Interdisciplinary Research Center for Regional Integral Development, Michoacán Unit, Jiquilpan, Michoacán, Mexico.

Materials and methods

Area of study

The Cupatitzio river watershed belongs to Hydrological Region No. 18 (Río Balsas), it is located to the west center of the state of Michoacán, covering the municipalities of Uruapan (80 % of the watershed), Gabriel Zamora, F. J. Múgica, Nuevo Parangaricutiro and Parácuaro. The watershed is geographically located between the extreme coordinates 102° 02´ 22" W, 19° 59′ 55′′ N and 19° 05′ 24′′ N, 102° 06′ 46′′ W; with an area of 78 260 ha and a medium height of 1 425 masl. At the upper and middle part of the watershed crosses the transverse volcanic system from east to west, finding slopes of between 15 to 60 % and ravines with 100 % slopes. At the upper part, it is adjacent to hills of up to 3 380 masl, such as the El Pilón, Capén and La Virgen hills; on the center: El Burro hill (2 700 masl), Cocucho (3 000 masl) and El Santísimo (3 280 masl); the lower middle watershed is adjacent to the hills: El Chino, La Cruz, La Charanda and El Colorado (2 100, 2 300, 2 200 and 2 120 masl respectively). The altitude of the lower part of the watershed is 320 masl and it is open to the south (Navia-Antezana, 2008). The main types of soil on the watershed are andosol on the upper watershed, luvisol and acrisol on the middle watershed and regosol and vertisol on the lower part. The climate is humid in the upper part and sub-humid in the lower part with abundant rain in summer. Among the uses of land and vegetation, there are: pine forests, oak forests, pine-oak forests, montane cloud forests, deciduous forest, traditional agriculture, bodies of water and human settlements (INEGI, 2014).

Sampling stations

On the river, there were established 20 sampling stations (Table 1, Figure 1) based on four criteria: 1) accessibility and security to the point of interest; 2) presence of reservoirs or infrastructure on the main stream; 3) main inflows or outflows, and 4) point or nonpoint sources of pollution, such as wastewater discharges or intensive agriculture near the stream being studied. The sampling was conducted in two periods: Sampling 1 (M1) during rainy season in August-15-2016, and Sampling 2 (M2) during dry season in May-14-2017. On both occasions, sampling was carried out from 9:00 am to 5:00 pm.

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Table 1. Name and coordinates of the sampling sites, upper watershed (SS 1 to 10), Middle watershed (SS 11 to 15) and lower watershed (SS 16 to 20).

SS	X	Y	Z	Name	Comment
1	807177	2150978	1700	Rodilla del Diablo	Home river
2	807263	2150720	1666	El Reveladero	Wellspring
3	807287	2150549	1679	El Puente	National park center
4	807629	2149874	1630	Parque Lineal	Output national park
5	808203	2149512	1610	Puente Manuel Ocaranza	Manuel Ocaranza Street
6	806320	2146052	1544	La Pinera	Dam
7	807868	2143245	1532	Zumpimito discharge	Dam
8	807852	2143321	1526	Zumpimito installations	Dam
9	813274	2150279	1596	Santa Bárbara	Manantial
10	813197	2150205	1599	Caltzontzin	Wellspring
11	806970	2142375	1466	Tzararacua	Waterfall
12	806441	2141333	1376	Matanguarán	Wellspring
13	806546	2141056	1376	Matanguarán canal	Hydro-electric channel
14	806861	2140531	1356	Matanguarán lixiviados	Sanitary landfill
15	806950	2134216	1057	Barranca Honda River	Over the river
16	806950	2134044	1099	Barranca Honda canal	Over the river
17	806982	2132970	897	Jicalán	Dam
18	806707	2132795	885	Jicalán-río	Jicalán river
19	809350	2128152	760	El Abrevadero	Dam
20	808659	2112158	902	Puente el Marqués	Over the river

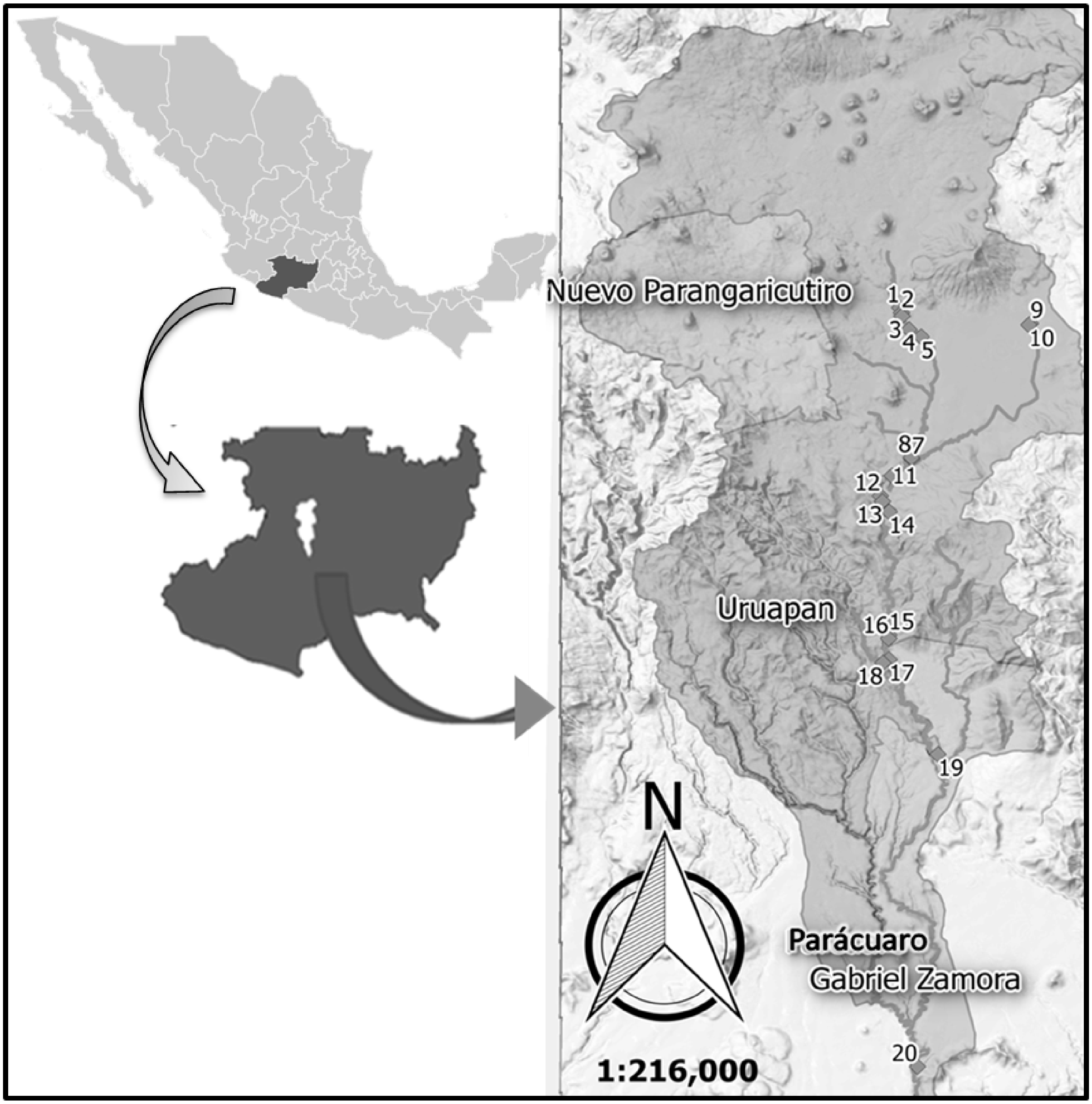

Figure 1. Map of the study area and sampling stations.

Description of sampling sites

Sites 1 to 4 are located within the protected natural area Barranca del Cupatitzio, it has a rocky landscape with shallow clear waters (1m deep and 2.5m wide). Before leaving the protected area, there are water pumps, these pumping the water of the river to supply the city of Uruapan. Site 5 is located on a linear park where the river is deeper. Site fifth is located in the streets of the city of Uruapan. Site 6 is located in the La Pinera dam, it is a tourist place and its landscape is wooded.

Sites 7 and 8 are located in the Zumpimito dam, it is a hydroelectric that retains part of the Cupatitzio River, as well as wastewater discharges from the city of Uruapan. Sites 9 and 10 are tourist places, the Santa Barbara River is born and its waters form a wetland with a wooded landscape. Site 11 is located in the Tzararacua waterfall, the water is somewhat cloudy with a brown hue and a slight unpleasant odor, at this point the river is between 9 and 12 m wide and 1.5 deep.

Site 12 is located in the Matanguarán dam, part of its waters pass into a channel (sites 13 and 16) to later be used in another hydroelectric. Site 14 is a runoff of water that comes from the top of a hill where the sanitary landfill of the city of Uruapan is located.

Site 15 (Barranca Honda) is an area with a steep slope (> 40 %), despite the agricultural practices of avocado production, this facilitates the dragging of nutrients into the river. Sites 17 and 18 belong to the Jicalán River, this is a tributary of the Cupatitzio River, its waters come together right at the dam of the same name. Site 19 is a small dam that channels water from the river into an irrigation canal. Site 20 is the end of the Cupatitzio River to give rise to the El Marquez River, the speed of the river is strong and with an average depth of 2.5 m and a width of 5 m, the water is clearer than in the middle basin but not more than in the upper basin.

Physical and chemical parameters and trace elements

Eight physico-chemical parameters (PFQ) were determined in the field for each site, a Hidrolab model DS5 multisensor was used, this equipment is robust and has eight sensors which are calibrated individually: temperature (T), hydrogen potential (pH), electric conductivity (CE), total dissolved solids (SDT), chlorides (Cl-), ammonium (NH4+), nitrates (NO3-) and dissolved oxygen (OD). Subsequently, a two-liter sample was taken to analyze in the laboratory based on the indications of each corresponding standard: alkalinity (Alc) (NMX-AA-036-SCFI-2001, 2001); total hardness (Dur) (NMX-AA-072-SCFI-2001, 2001); total phosphorus (P) (NMX-AA-029-SCFI-2001, 2001); total suspended solids (SST) (NMX-AA-034-SCFI-2015, 2015); chemical oxygen demand (COD) (NMX-AA-030-2-SCFI-2011, 2011), and biological oxygen demand for five days (BOD5) (NMX-AA-028-SCFI-2001, 2001). In addition, 31 trace elements (TE) were determined through inductively coupled plasma mass spectrometry (ICP-Masas) (the equipment used belongs to the Applied Geology Laboratory of the Faculty of Engineering at the Autonomous University of San Luis Potosí). these were: Li, B, Al, P, Sc, Ti, V, Cr, Mn,

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Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Pd, Ag, Cd, Sn, Sb, I, Ba, Hg, Tl, Pb and U. It is worth mentioning that for the second sampling session (dry season), the trace element analysis was not performed; furthermore, it was not possible to evaluate SSs 7 and 8 (Zumpimito dam) and 14 (Matanguarán leachates), due to the lack of runoff water.

Evaluation of pollutants found in the water and quality indices

The permissible limits of water pollutants (PLWP) for human use and consumption were evaluated based on two Mexican standards CE-CCA-001 (1989) and NOM-127-SSA1 (1994).

From the PFQ (physic-chemical parameters), three indices were calculated: water quality index (WQI), Conesa and Fernández (1993) (Equation (1)); pollution index (COI), by Backman, Bodiš, Lahermo, Rapant and Tarvainen (1998) (Equation (2)); and the Canadian Council of Ministers of the Environment, Water Quality Index ($CCMEWQI$) (Davies, 2006) (Equation (3)):

$$ICA = \sum_1^n (w * i) / \sum_1^n W \quad (1)$$

Where n is the nth parameter of each sampling station; w is the weight assigned to each parameter; *i* are the Values assigned to each observation pursuant to the intervals according to w. The measurement ranges of this index can take values between 0 and 100, with zero being indicative of the lowest quality and one hundred being excellent quality.

$$ICON = \sum_{1}^{n} \left(\frac{ob}{lim}\right) - 1 \qquad (2)$$

Where n is the nth observation of the sampling station, ob is the numerical value of each observation, lim is the limit prescribed by the quality standard for each parameter (PLWP) given in mg/l. This index may take values greater or less than zero, being the negative values an indicator of the best quality or less pollution.

$$CCMEWQI = 100 - \left(\frac{\sqrt{F1^2+F2^2+F3^2}}{1.732}\right) \qquad (3)$$

Where:

$F1 = \left(\frac{npf}{np}\right) * 100$:it is the number of parameter beyond the permissible limit (npf) according to the pertinent standard, over the number of parameters evaluated (np), multiplied by 100.

$F2 = \left(\frac{nof}{not}\right) * 100$: iotal number of observations beyond the permissible limit (nof) according to the pertinent standards, over the total number of observations (not) multiplied by 100.

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$F3 = (\frac{\sum_1^{not}(\frac{of}{lim})-1}{not})$: addition of the ratio divided by the observation that fails to comply with the permissible lmit (of) over the permissible limit (lim) minus 1. This quantity over the total number of observations (not). This index may take values among 0 and 100, zero as an indicator of the lowest quality and one hundred indicating excellent quality.

Statistical analysis

The results were processed and analyzed with R-software (Chambers & Colleagues, 2023), calculating: Correlation matrix, principal component analysis and agglomerative hierarchical clustering.

Digital cartography and spatial analysis

Using the free QGIS software (QGIS Development Team, 2014), maps of the use of land and vegetation (USV) were created. This process was carried out through Congedo's semi-automatic classification plugin (Congedo, 2016), for which data from the remote sensors of 7 and 8 Landsat, from the 1997, 2009 and 2016 periods, was used, with 30 m accuracy (USGS, 2016), addition to the digital elevation model to enhance map accuracy (Cruz-Cárdenas *et al*., 2010). A total of 863 459 points were grouped in the following classes: Pine-oak forest (BPE), secondary vegetation (VS), agriculture (CU), populated area (ZP). The Mahalanobis distance algorithm was used due to its great accuracy of up to 94.27 %

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(Singh, Singh, & Vásquez, 1997). Subsequently, the three indices were mapped in order to analyze the spatial distribution of water quality.

Results

The results for the PFQ and ET for M1 and M2 are completely shown on Table 2.1, Table 2.2 and Table 2.3. Then, Table 3 shows the series of parameters found beyond the PLWP prescribed by the aforementioned domestic standards. Said table presents the average value of each parameter, minimum, maximum, PLWP value, and the stations found beyond these limits.

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Table 2.1. Physical and chemical parameters for sample 1 rain season (August 2016).

Sampling 1 (rainy season, August 2016)														
SS	**T**	**EC**	**pH**	**TDS**	**Cl**	**NH4**	**NO3**	**OD**	**Alk**	**Hard**	**P**	**COD**	**BOD**	**TSS**
1	16.13	140	7.02	70.7	24.37	0.585	2.22	10	70	38.45	0.74	2	1.885	18.56
2	16.02	131.6	7.28	66.46	33.93	0.57	2.48	10.4	62	42.29	0.68	46	4.265	40
3	16.25	147.7	7.68	74.59	27.3	0.525	3.29	11	64	42.29	0.73	46	4.68	33.34
4	16.39	161.6	7.81	81.61	42.24	0.58	3.32	11	62	38.45	0.81	46	2.815	31.67
5	16.56	164	7.83	82.82	34.39	0.6	3.16	11.2	64	49.98	0.77	49	1.52	27.69
6	17.34	185.6	7.8	93.73	49.01	0.96	5.8	10.1	74	49.98	0.76	44	4.5	43.33
7	21.37	362.7	7.55	183.1	84.35	8.775	15.53	9.2	162	61.52	1.36	105	5.45	50
8	17.57	108.3	7.73	54.69	50.01	1.09	20.5	10.4	86	53.83	2.57	78	4.715	35.71
9	16.09	131.7	6.44	66.51	18.9	0.435	4.22	5.9	148	49.98	0.69	38	3.38	35
10	21.26	160.5	8.48	81.06	29.02	0.62	5.63	9.4	62	46.14	1.18	78	4.045	45
11	19.08	217	7.91	109.5	18.95	1.71	2.38	5.7	75.9	61.52	0.88	43	5	25.77
12	19.57	215.8	7.38	108.9	51.31	1.2	7.34	7.3	78	49.98	0.75	27	4.13	7.18
13	19.11	219.4	7.53	110.8	50.09	1.82	8.29	10.4	78	49.98	0.92	25	4.47	35.71
14	20.88	1.7	8.43	0.85	532.2	100.16	14.95	2.5	NA	NA	2.83	590	1.32	200
15	25.12	208.3	8.07	105.2	14.13	0.93	1.82	10.2	72	49.98	0.86	69	2.9	584
16	20.93	209.6	8.21	105.8	14.72	0.965	2.36	8.8	12	61.52	0.96	75	2.78	202
17	23.45	199.4	7.62	100.7	8.09	0.75	1.41	9.5	72	57.67	0.86	62	2.695	142
18	22.92	188.3	8.09	95.1	4.96	0.69	0.8	10.5	80	57.675	0.73	97	4.555	102
19	21.11	207.6	8.13	104.8	13.25	0.86	2.25	10.1	83.9	42.29	0.88	22	4.215	118
20	27.5	209.6	8.28	105.8	10.1	0.99	1.41	11	98	57.67	0.72	22	3.91	110

Table 2.2. Trace elements for M1.

SS	Li	B	Al	P	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As
1	5.48	12.9	25.21	155.9	6.04	4.59	21.53	1	1.46	38.37	0.01	0.01	4.21	14.58	0.04
2	4.31	8.62	0.01	130.3	6.11	3.98	20.92	1	0.01	0.01	0.01	0.01	0.01	0.01	0.01
3	4.83	15.57	75.9	189.65	7.53	7.53	23.34	0.37	7.54	73.52	0.01	0.01	22.87	94.32	0.19
4	4.51	13.79	95.03	212.7	7.05	8.68	23.18	0.66	13.18	263.45	0.01	0.01	5.93	64.87	0.4
5	4.61	17.35	82.06	354.55	6.25	6.63	21.56	0.01	8.33	72.46	0.01	0.01	5.3	54.74	0.01
6	4.32	16.53	136.55	449.85	7.46	9.9	22.11	0.28	16.7	124.95	0.01	0.01	3.88	69.36	0.33
7	1.36	85.04	570.1	1491	3.2	17.48	6.04	0.14	216.9	1147	0.49	0.71	5.49	24.57	0.36
8	2.69	8.06	217.3	142.4	6.49	9.52	21.14	0.14	73.66	150.9	0.01	0.01	2.9	11.84	0.01
9	2.56	8.01	116.05	805.95	6.45	11.51	18.57	0.86	8.05	214.75	0.01	0.08	2.84	133.8	0.37
10	3.86	8.92	48.28	264.3	7.44	5.98	21.61	0.16	0.95	45.63	0.01	0.01	4.08	9.72	0.24
11	3.22	17.36	265.75	417	6.34	13.73	21.24	0.78	426.65	474.86	0.61	1.8	2.95	16.68	1.02
12	3.16	16.13	370.45	364.35	6.02	16.27	17.99	0.01	36.87	332.21	0.01	0.04	3.62	10.86	0.36
13	3.02	20.81	53.29	610	6.79	15.42	19.97	0.55	70.82	594.11	0.05	0.38	11.31	93.7	0.08
14	0.82	494	271.75	1592.5	5.87	70.56	27.46	47.25	607.2	3367.76	9.34	21.51	31.16	68.09	6.26
15	2.91	26.16	185.55	263.75	7.02	11.5	17.13	0.19	24.34	230.76	0.01	0.01	6.49	24.5	0.14
16	2.31	18.11	143.65	269	7.05	9.49	17.88	0.11	17.74	186.01	0.01	0.01	4.75	8.58	0.53
17	0.98	15.57	207.1	115.15	5.75	6.52	8.75	8.86	57.66	583.56	0.01	1.21	1.66	22.6	0.01
18	0.29	11.99	219.75	172.65	6.7	8.17	6.38	0.01	37.03	176.76	0.01	0.1	3.16	431.3	0.02
19	1.31	15.38	489.3	302.15	6.89	16.37	13.6	0.01	76.53	423.36	0.05	0.18	5.08	26.0	0.01
20	1.82	11.21	481	175.7	6.42	7.25	15.29	0.04	27.28	324.46	0.01	0.36	5.18	10.6	0.24

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Table 2.3. Physical and chemical parameters for sample 2 dry season (May 2017).

Sampling 2 (Dry season May 2017)														
SS	**T**	**EC**	**pH**	**TDS**	**Cl**	**NH4**	**NO3**	**OD**	**Alk**	**Har**	**P**	**COD**	**BOD**	**TSS**
1	17.1	148	7.52	74	24.09	0.16	36.83	5.6	30.15	49.99	0.51	0	1.3	0.66
2	16.3	164	7.53	82	23.7	0.08	23.87	9.15	31.5	46.14	0.41	0	1.2	0.9
3	16.3	153	7.94	76	23.62	0.06	25.84	9.42	31.5	57.68	0.43	0	1	1.3
4	16.3	164	7.79	82	36.75	2.59	36.46	8.85	31.5	46.14	0.71	0	0.97	1.5
5	26.4	166	7.8	83	24.59	0.24	29.06	9.6	32.85	49.99	0.42	35	15.89	0.8
6	16.6	199	8.13	99	24.15	0.15	35.1	9.2	36	48.06	1.69	55	12.85	30.8
7	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
9	22	155	6.81	77	24.22	0.15	67.69	7.67	28.35	42.3	0.48	33	9.17	5.14
10	21.7	349	6.39	175	26.26	0.54	28.6	13.1	32.4	38.45	0.4	30	9	5.3
11	19.3	206	7.99	102	24.05	0.11	21.27	11.5	39.15	57.68	0.59	45	14.39	3.2
12	27.4	340	6.38	170	25.73	0.43	32.8	0.74	80.1	111.51	0.62	31	9	6
13	26.3	217	6.64	108	26.69	0.61	8.64	4.83	41.4	61.52	0.58	36	10.25	31.2
14	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
15	20.57	166.6	6.69	75.58	44.15	2.73	21.62	4.52	26.44	39.79	0.55	44	9.3	5.1
16	22.6	177	7.05	84	24.27	0.13	18.65	5.67	42.3	57.68	0.51	76	10.15	3.2
17	25	243	6.57	120	28.17	0.88	21.18	3.9	40.05	61.52	0.52	39.67	14.96	2
18	28.6	235	6.51	117	24.62	0.19	8.44	5.5	54.45	65.37	0.27	32	9.75	2
19	20.4	200	6.74	100	26.35	0.52	38.63	6.8	36.9	61.52	0.53	52.5	13.35	5.6
20	29	380	7.1	254	28.86	1	21.69	5.81	86.4	80.75	0.53	21.33	14.08	9.6

Table 3. Parameters beyond the permissible limits in water for M1 and M2.

Variable	$\bar{x}$	Min	Max	permissible limit	sampling stations, outside of permissible limits
			M1		
Cl	55.6	5	532.2	250	14
NH4	6.24	0.4	100.16	0.5	All except SS 9
NO3	5.46	0.8	20.5	5	6,7,8,10,12,13 y 14
DO	9.23	2.5	11.2	>4	14
P	1.03	0.7	2.83	0.1	All
COD	78.2	2	590	40	2, 3, 4, 5, 6, 7, 8, 10, 11, 14, 15, 16, 17, 18
TSS	94.4	7.2	584	500	15
Al	0.2	0	0.57	0.02	All except SS 2
Fe	0.44	0	3.36	0.3	6, 11, 12, 13, 14, 17, 19, 20
P	0.43	0.2	1.59	0.1	All
			M2		
NH4	0.62	0.1	2.73	0.5	4, 10, 13, 15, 17, 19, 20
NO3	28	8.4	67.69	5	All
DO	7.17	0.74	13.11	>4	12
P	0.57	0.3	1.69	0.1	All
COD	31.2	0	76	40	6, 11, 15, 16 y 19

DO= dissolved oxygen; COD= chemical oxygen demand; TSS= total soluble solids

Description of parameters for the rainy season (M1)

The temperature increased upon descending the watershed. This is considered normal behavior if the influence of the regional climate is taken into account. Electrical conductivity, pH and total dissolved solids similarly increased as there was a decrease in the basin and no site exceeded the PLWP. This is due to an accumulation of salts due to the physicochemical interaction with rocks and sediments along the river (Carreño-de-León, Zarazúa-Ortega, Fall, Ávila-Pérez, & Tejeda-Vega, 2018); the average of these parameters was 178.52, 7.76 and 90.15, respectively. Similarly, the pH increased upon descending the watershed and no station exceeded the PLWP; in general, a pH close to neutral was found. SDT and CE kept around the average of 178.52 mS/cm and 90.16 mg L-1 respectively; therefore, they were observed far below the PLWP. The Cl- only surpassed the PLWP in SS 14. The ammonium ion exceeded the PLWP in all the sampling stations except for SS 9 (Santa Bárbara spring), the nitrates showed their highest concentration in the middle watershed and lower values in the upper and lower part of the watershed. The oxygen presented values over 4 mg l^{-1} except at SS 14, where it just presented 2.5 mg l^{-1}. Alkalinity, hardness and BOD5 presented significantly low values with respect to PLWP. P and COD surpassed the limits in all the SS. The total suspended solids showed an increasing behavior upon descending the watershed, surpassing the PLWP only in SS 15 (Barranca Honda).

The trace elements in general showed significantly low values except for Al, Fe and P, which exceeded the PLWP. Al showed a tendency to increase upon descending the watershed, Fe appeared in higher concentrations in the middle and lower watershed. P, as expected, surpassed the PLWP in all the SS.

Description of parameters for the dry season (M2)

The temperature in M2 showed a variable behavior due to the variation in the volume of water in each zone. The pH showed values between 7 and 8 for the upper watershed, whereas in the middle and lower watershed the values had a neutral pH. The variables of EC, SDT and Cl- presented near average values and far below the PLWP in most of the SS. The ammonium was fluctuant, surpassing the PLWP in seven of the SS. NO3- presented excessive high values in all the SS, surpassing in up to five times the mean in the rainy season. The OD presented lower values than the sampling in the rainy season; however, only in one SS was below the minimum limit (0.74 mg l^{-1}, Matanguarán dam SS). The alkalinity and hardness parameters show their highest values at the middle watershed. It is worth mentioning that the alkalinity value reached half of the values obtained during the rainy season, whereas the hardness remained very similar in both seasons. The P showed again a high concentration and surpassed the PLWP in all the SS. The COD presented lower values than M1; however, it also surpassed the PLWP for five SSs (La Pinera dam, Tzararacua waterfall, over the river in Barranca Honda, and El Abrevadero dam). The SST had very low values with respect to the permissible limits.

Water Quality Index

The WQI for M1 had a range from 64 (SS 13) to 85 (SS 1) points. The lowest values were obtained in the middle watershed section (average = 72.8), whereas, in the upper watershed and in the lower watershed, the average values were 79.3 and 79.4, respectively. The WQI for M2 ranged from 54 (SS 12) to 87 (SS 2) points, obtaining low values in the middle and lower watershed (average = 66), whereas the average was 79 points at the upper watershed. Figure 2 shows the spatial distribution of the WQI results for M1 and WQI for M2.

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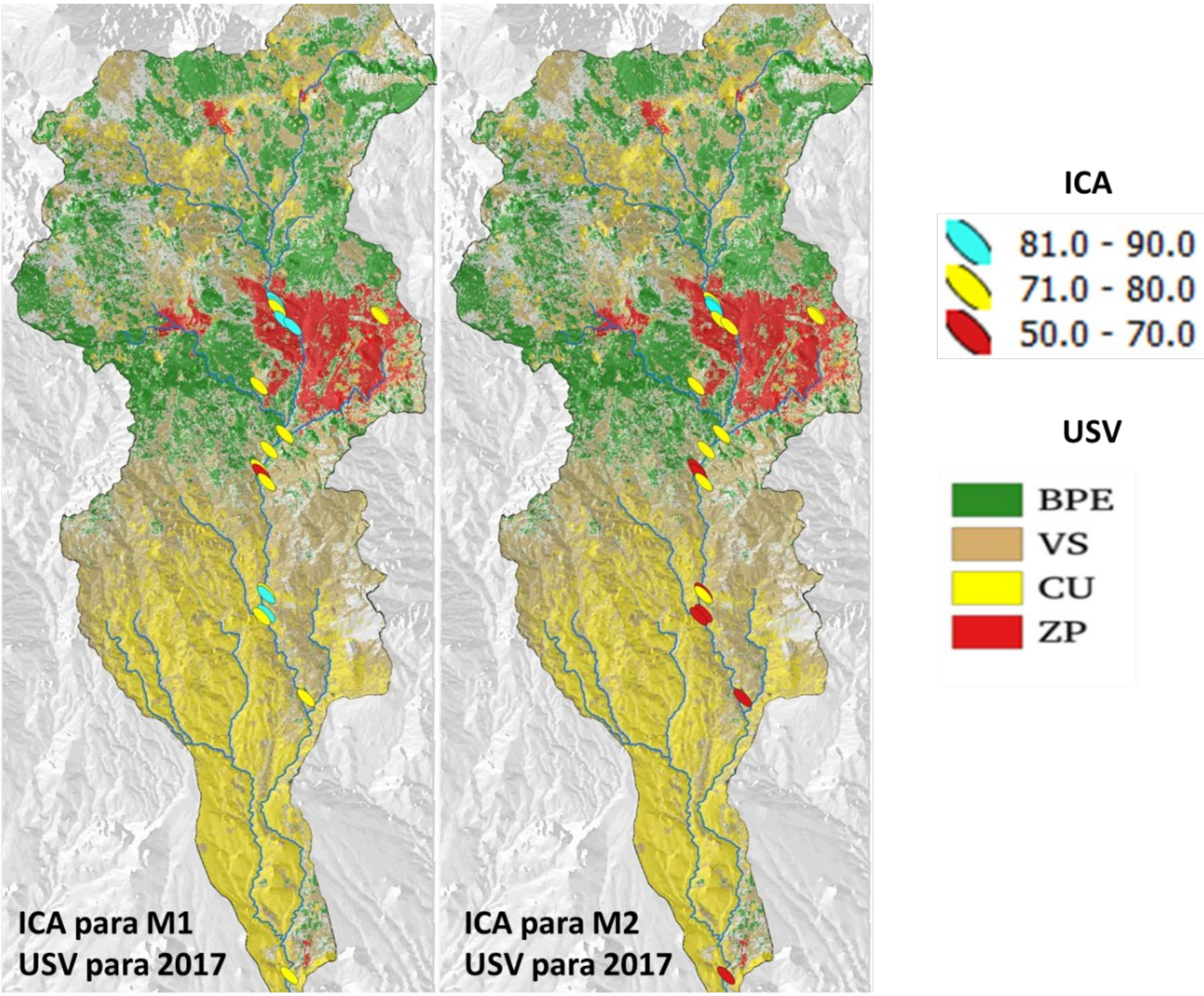

Figure 2. Water Quality Index (WQI) in color scale over the use of land and vegetation map (USV) of the Cupatitzio river watershed (M1 and M2).

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Pollution Index

The COI for M1 had a station with moderate pollution, between zero and three points (SS 13), and three stations with high pollution degree (SS 7, SS 8 and SS 14), above three points.

For the COI of M2, three SS were obtained with moderate pollution (SS 12, SS 15 and SS 19), and two seriously polluted stations (SS 4 and SS 9).

The EMs that are not mentioned in both samplings represent low pollution index zones, obtaining values below zero. Figure 3 shows the COI map for the sampling periods.

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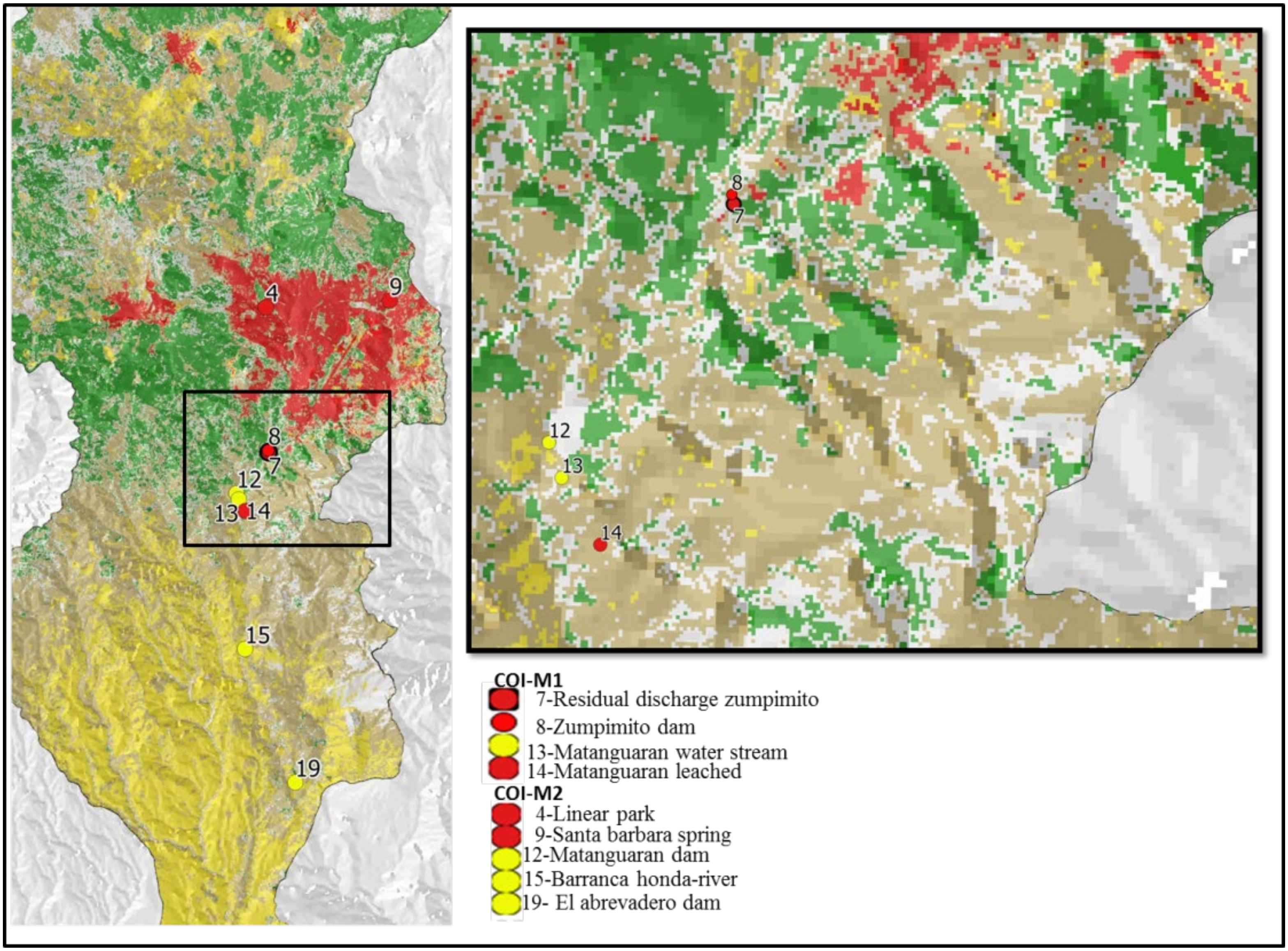

Figure 3. Map of pollution index for M1 and M2, the moderate pollution sampling stations are shown in yellow and seriously polluted stations are shown in red.

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Canadian Index CCME WQI

For M1, the quality of the whole body of water was evaluated, obtaining 55 of 100 points, which represents poor quality. The result differs from that obtained with WQI index, since if all the sites are weighted 78 points of 100 are obtained (good quality). However, it is easy to understand the result of the CCME WQI if we observe and compare among themselves the factors F1 = 36.36, F2 = 21.36 and F3 = 65. 96: where the first is the PFQ quality beyond the PLWP (7 of 14), the second is the frequency with which said limits are breached (63 of 300). Finally, F3 indicates how much the limit values are surpassed; for instance, the phosphorus limit was exceeded 10 times, 12 times for ammonium and 1.9 for COD. Evidently, F3 had the highest value, in other words, a low quality score was obtained due to the high concentrations mainly of phosphorus and ammonium.

For M2, 66 points were obtained, which is an indicator of fair quality, observing the factors F1 = 27.7, F2 = 21.92 and F3 = 47.54. It may be stated that the greatest impact on water quality is given by the amounts of the pollutants as occurred in M1. However, the Canadian index this time shows better quality than in the rainy season, mainly due to the decrease of factor F1, which corresponds to a lower PFQ number beyond the standards (4 of 14).

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Relationship of parameters of the first and second sampling

Calculating the correlation matrix for sample one (MC-1), there was obtained that the highest coefficients were (r > 0.7): Cl-, NH4+, NO3-, P and COD (Figure 4). It is worth mentioning that these parameters are the same presented beyond the PLWP, this may indicate that they have a common source.

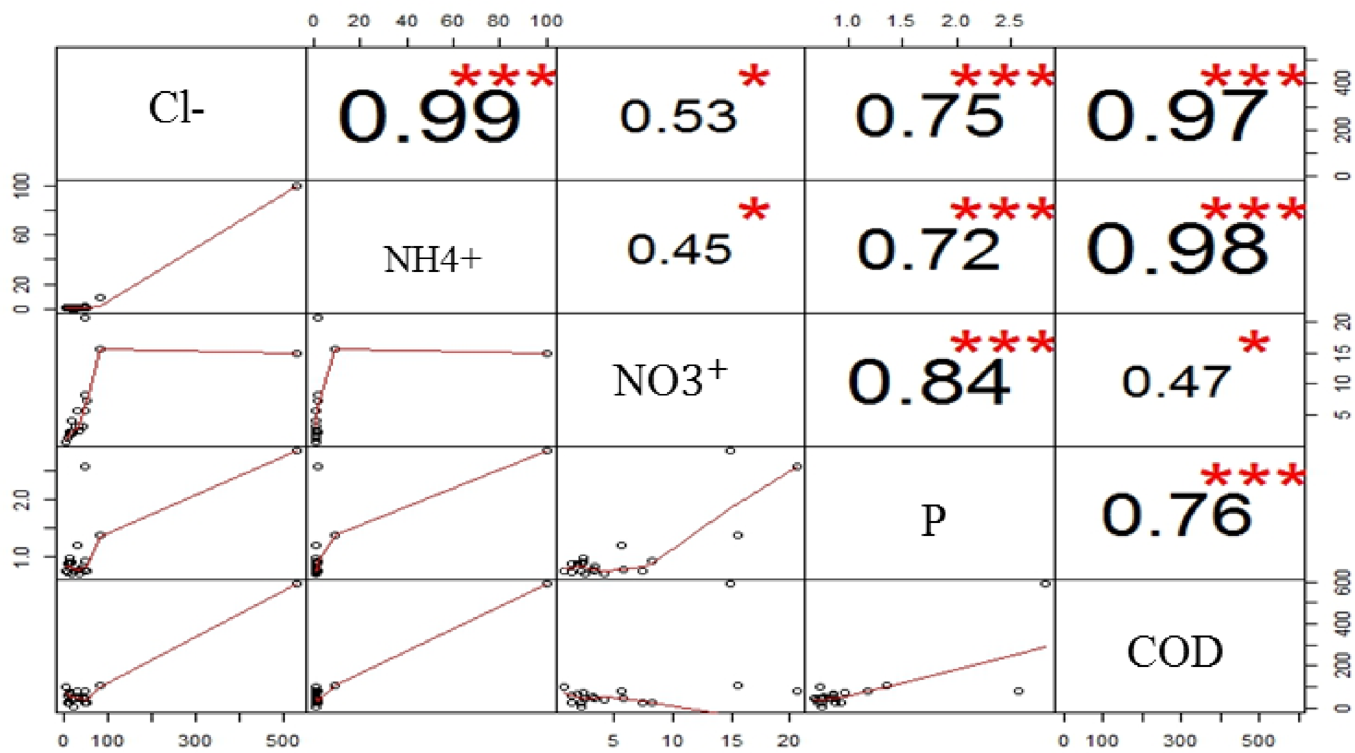

Figure 4. Correlation Matrix MC-1, The PFQ are shown with a Pearson's correlation coefficient greater than 0.7 for the first sample.

For sampling two, the correlation matrix (MC-2) showed that the PFQ correlated to *r* > 0.7 were TDS, Cl-, NH4+, Alc, Dur, COD (Figure 5). In contrast to MC-1, the dry season parameters had a lower correlation among themselves and do not coincide with the parameters beyond the PLWP.

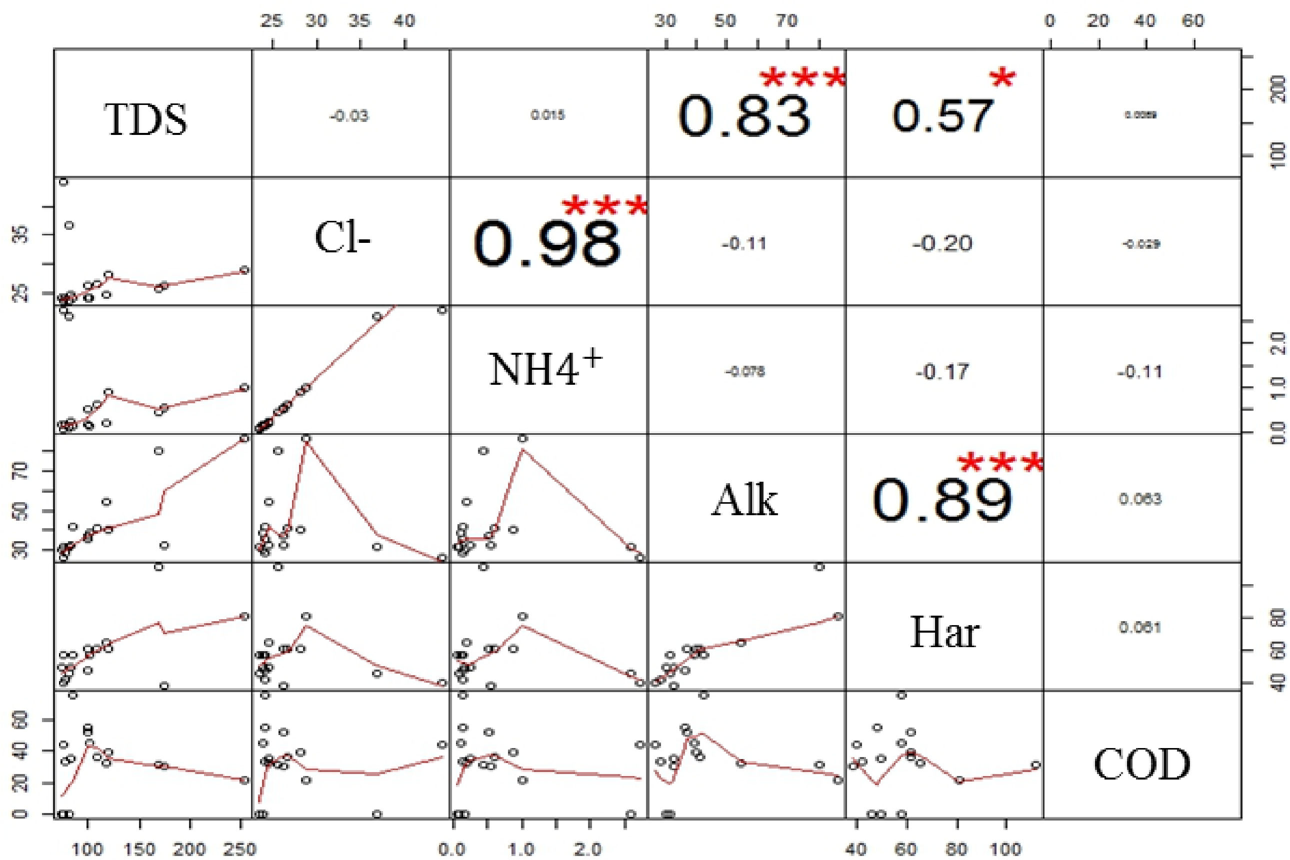

Figure 5. Correlation Matrix MC-2, the PFQ are shown with a Pearson's correlation coefficient greater than 0.7 for the second sample.

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Principal Component Analysis (PCA)

The PCA was applied to the data matrix of both samplings, obtaining 14 principal components (CP) given the 14 original variables. Of these 14 CP, the first seven were taken to perform the Cluster analysis, since they form 94 % of the variation of the original data (Table 4).

Table 4. Summary of the principal components for the physical and chemical parameter data of sampling one and two.

PC	Standard deviation	Proportion of Variance	Cumulative proportion
		Rainy season	
1	2.279	0.371	0.371
2	1.651	0.195	0.566
3	1.542	0.170	0.736
4	1.011	0.073	0.809
5	0.919	0.060	0.869
6	0.742	0.039	0.908
7	***0.693***	***0.034***	***0.943***
8	0.664	0.031	0.974
9	0.485	0.017	0.991
10	0.301	0.006	0.997
11	0.154	0.002	0.999
12	0.106	0.001	1.000
13	0.020	0.000	1.000
14	0.000	0.000	1.000
		Dry season	
1	2.203	0.347	0.347
2	1.515	0.164	0.511
3	1.418	0.144	0.654
4	1.212	0.105	0.759
5	1.067	0.081	0.841
6	0.973	0.068	0.908
7	***0.806***	***0.046***	***0.955***
8	0.577	0.024	0.978
9	0.329	0.008	0.986
10	0.310	0.007	0.993
11	0.253	0.005	0.998
12	0.129	0.001	0.999
13	0.124	0.001	1.000

Cluster analysis

The hierarchical cluster analysis technique was applied using Ward's method for both CP. The dendrograms for M1 and M2 (D1, D2) presented in Figure 6 and Figure 7 show the clustering or cluster (CL) of SSs based on the Euclidean distance between their data.

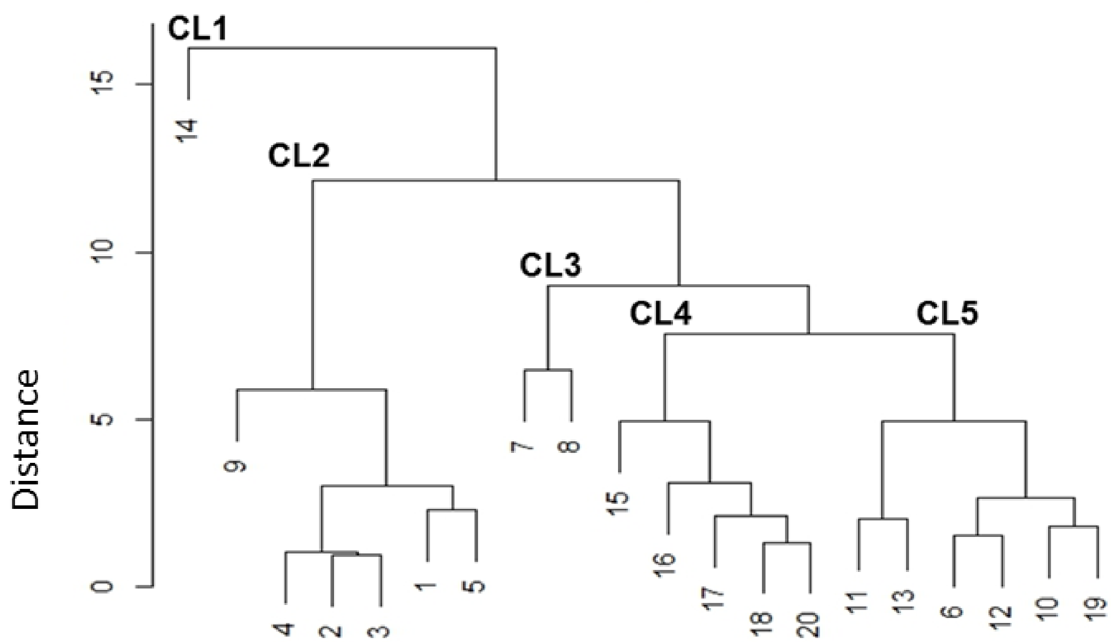


Figure 6. Dendrogram D1 for M1.

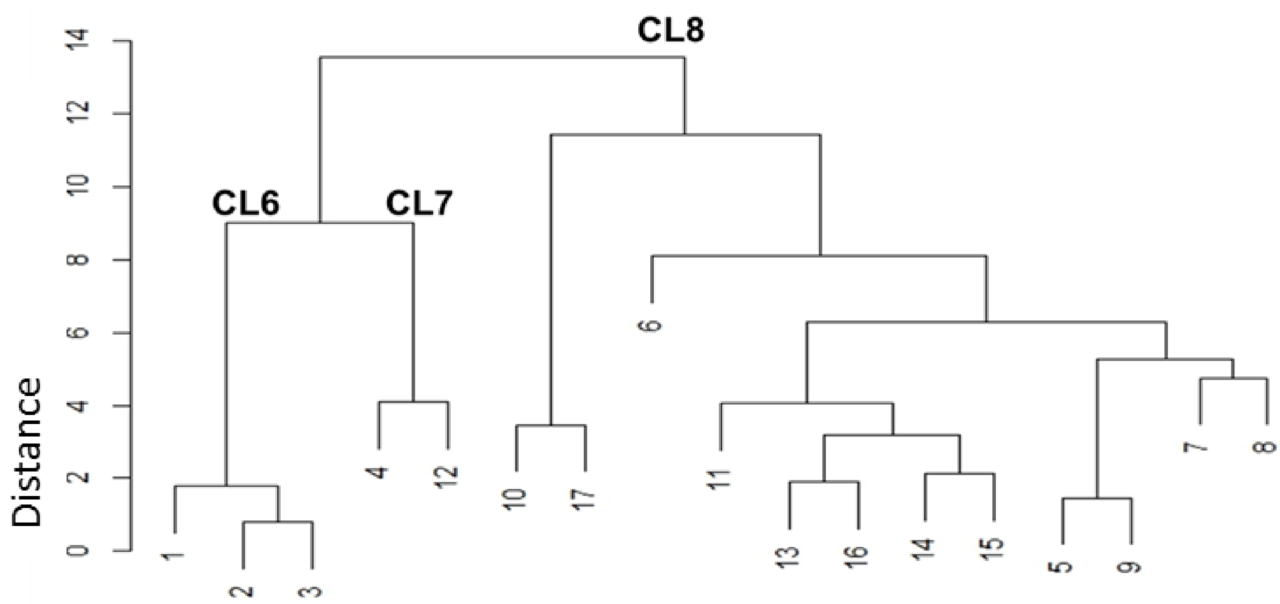


Figure 7. Dendrogram D2 for M2.

For D1, the SS 14 CL1 forms a single cluster given its unique characteristics. It is worth bearing in mind that this SS belongs to the middle watershed and has the highest COI for M1. CL3 covers the SSs located at Zumpimito dam, which represents the second highest COI. CL2 relates the SS of the upper watershed whereas CL4 groups all the SSs belonging to the lower watershed section. It must be mentioned that in these last two clusters there was found good water quality and high contents of OD. Finally, CL5 groups the SSs belonging to reservoirs and present the lowest levels of OD; therefore, there is a relation between reservoirs, poor quality, scarce OD and the middle watershed zone.

CL6 mainly shows the SSs of the upper watershed, but it has no similarity with another cluster, there is neither a comparison point between CL7 and CL8. In general, M2 does not represent patters in the distribution of its parameters as observed in M1.

Discussion

In the first sampling, there was observed that not only did the parameters beyond the permissible limits show high correlations between themselves, but also maximum values in the same sampling stations (SS 7 and SS 14). This fact suggests that said pollutants have their highest impact on water quality due to the presence of wastewater discharges and leachates from the landfill of the city of Uruapan. This would also explain the presence of trace elements such as Fe and B, which derive from industrial discharges, wastewater, paintings, textiles, varnishes and electronic pieces (Hassan, Rahman, Saha, & Kamal, 2015; Velázquez, Pimentel, & Ortega, 2011). Furthermore, the aluminum and its tendency to accumulate in the lower region of the watershed is attributed to the high use of pesticides applied in avocado orchards, as reported by Bravo *et al*. (2009), highlighting aluminum phosphide to control *Dendroctonus mexicanus*. This would explain the large amounts of Al and P found in the body of water.

Even though the greatest part of pollutants derived at least partially from wastewater, the parameters NH4+, NO3-, P and COD surpass the PLWP in sites that have not been impacted with said discharges (for example, Rodilla del Diablo spring in the upper part of the watershed). This is related to agriculture in the highest parts of the watershed and infiltration of nutrients into the aquifer, as suggested (De-Miguel-Fernandez & Vázquez-Taset, 2006).

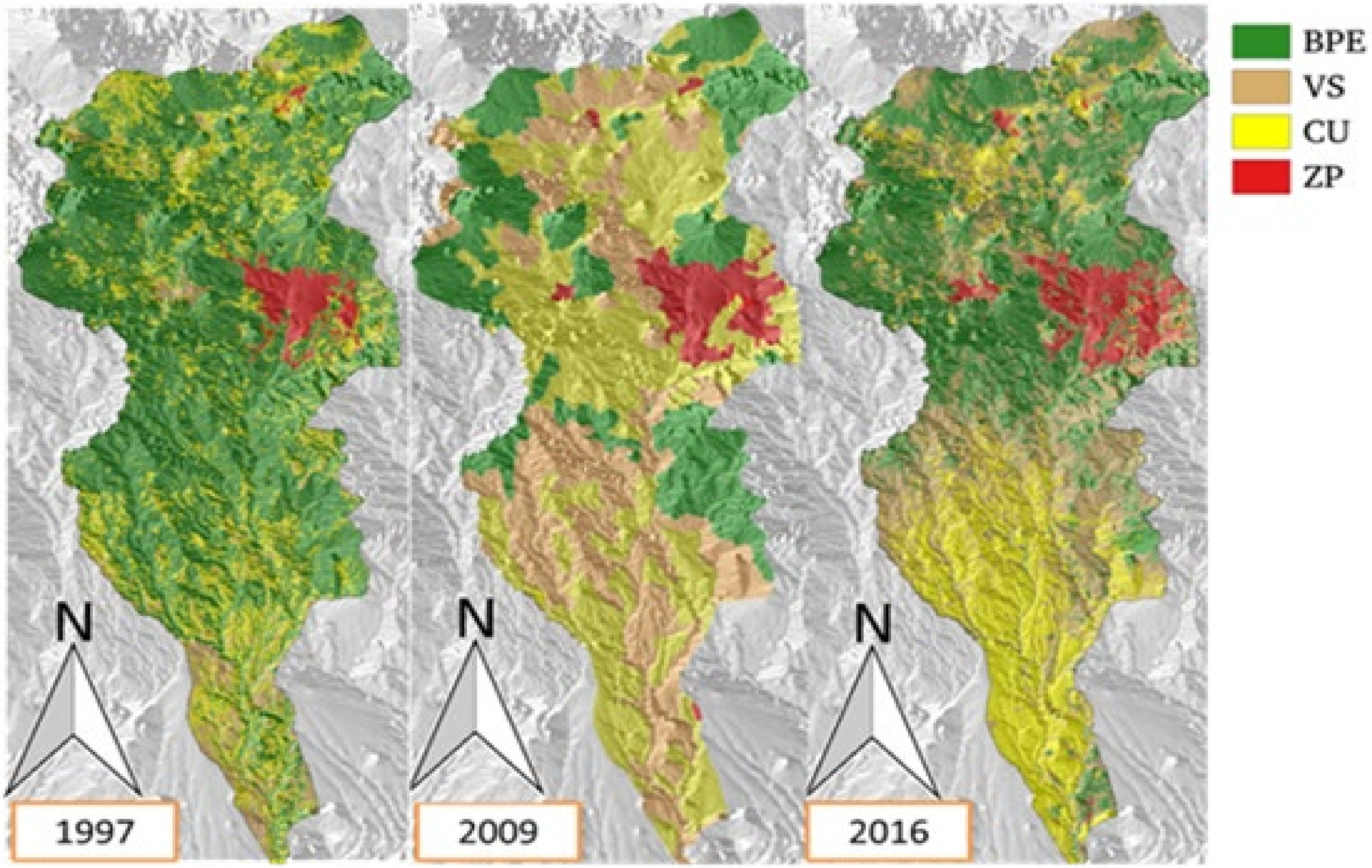
As the basin descends, the accumulation of residual waters and the increase of nitrogenous substances is noticeable mainly in the decrease of dissolved oxygen and the increase in the chemical and biological demand for oxygen. For example, SS 11 has the highest biological oxygen demand and the second lowest oxygen value. This behavior is related to the biochemical processes of nitrification and denitrification carried out by nitrosomonas bacteria and nitrobacteria, respectively (De-Miguel-Fernandez & Vázquez-Taset, 2006; Torres-Bojorges, Hernández-Razo, Fausto-Urquieta, & Zurita-Martínez, 2017).

The COD, for example, is an indicator of the presence of biodegradable or oxidizable matter (NMX-AA-030-2-SCFI-2011, 2011); therefore, the oxidation of ammonium may contribute to oxygen demand, since it is a natural process in bodies of water (Bednarek, Szklarek, & Zalewski, 2014) and this would explain the high chemical oxygen demand found in sites with no wastewater impact.

The parameter related to the best water quality was dissolved oxygen, since the SSs with the highest quality according to the WQI are those whose oxygen concentration was higher. These same SSs were grouped in the cluster analysis (Cl2 and Cl4). While the reservoirs grouped in Cl3 and Cl5 are the SSs with lower quality and with lower levels of dissolved oxygen. It should be noted that in these SSs there is the presence of water hyacinth covering most of the surface of the reservoir, this represents a physical barrier that limits the penetration of oxygen into the water (Carrión *et al*., 2012). Related to the above Sharma, Meher, Kumar, Gautam and Mishra (2014) analyzed the quality of the Ganges river, India, correlating the WQI values with the PFQs; finding a correlation of 47 % between OD and WQI, which may indicate that there is a similar behavior for this case study. This reaction shows the importance of the presence of dissolved oxygen for the oxidation of contaminants, such as $NH4^{+}$, which will be oxidized to NO_3^{-} if there is sufficient dissolved oxygen. It should be mentioned that the nitrate ion is the most stable form of nitrogen and to which it tends to all the nitrogenous substances and that the reduction of $NH4^{+}$ also has consumption of carbonates that are found in their hydrolyzed form as carbonic acid, this consumption of $HCO3^{-}$ represents a decrease in alkalinity and therefore in the pH; behavior that was observed in the middle basin in De-Miguel-Fernandez and Vázquez-Taset (2006); Pacheco-Ávila, Pat-Canul and Cabrera-Sansores (2002), and this condition was reflected in the results of SS1 (Murillo, Aguilla, Hernández, & Díaz, 2014).

For M2, the values of $NH4^{+}$ and P were reduced by approximately 30 % compared to M1, this may be related to the absence of surface runoff, that is, the dragging of nutrients and agrochemicals from agricultural soils, in addition to runoff from the landfill (SS 14).

On the contrary, NO3- increased up to eight times its concentration in comparison with M1. In general, the high concentrations of nitrates in the river may be due to three situations: the first is the change of use of land, since Espinal *et al*. (2013) relates the increase of population density and the intensification of agricultural practices to the eutrophication of the bodies of water. Figure 8 shows that this is due to the 4 % annual increase in the area of human settlements in the watershed, while forest areas are decreasing 2 % annually, thus coinciding with the reports of the National Commission of Natural Areas Protected (CNANP, 2006).



Legend	Use of soil and vegetation	1997 (ha)	2009 (ha)	2016 (ha)
BPE	Pine-oak forest	40022	31367	25559
VS	Secondary vegetation	19260	19950	27725
CU	Crops	16396	22534	18949
ZP	Human settlements	2105	4313	6028

Figure 8. Cupatitzio river watershed use of land and vegetation maps for the years 1997, 2009 and 2016.

Another reason for the increase in nitrates is nitrification, that is, oxidation of ammonium to nitrites, later to nitrates, and the increase in groundwater and surface water, due to the infiltration of nutrients from agricultural soils (Rudolph, 2015) and as would be happening in SS 1 (Rodilla del Diablo spring).

The third situation according to Bravo *et al*. (2009), the concentration of nitrates may be related to fertilization cycles and crop management in the watershed, which for the case of the avocado zone of Michoacán up to 1g L^{-1} of nitrates in leaches have been reported beyond root reach in avocado orchards; these nutrients may infiltrate the aquifer and accumulate.

Espinal *et al*. (2013), and López-Hernández, Ramos-Espinosa and Carranza-Fraser (2007) consider that the studies using more than one ecological evaluation metric or technique are more effective in analyzing data. For this reason, three indices were used with the following advantages: The WQI index, in contrast to the others, allows to timely and independently evaluate each sampling station, thereby highlighting the best quality at the sides of the watershed. The pollution index COI, even though it also presents a score per SS, was able to emphatically indicate the seriously polluted stations that the WQI could not identify, for instance: SS 14 had 75/100 points for the WQI, considered fair quality, whereas for the COI it obtained 219, which shows that this SS is seriously polluted. The Canadian index CCMEWQI, even when it granted a single quality value to the whole body (M1 = 55 and M2 = 66 points), retrieved

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unique information through its three factors (F1, F2 and F3), specifying that the high concentration of phosphorous and nitrogenous substances was the main cause of water quality degradation. Lastly, it may be stated that the statistical techniques used are environmental metrics broadly used in water quality and spatial distribution studies (Juahir *et al*., 2011) and they contributed two important points of analysis: the first was the correlation between physical and chemical parameters through a correlation matrix, subsequently said correlation was eliminated through a principal component analysis to finally analyze the relation between sampling stations with the clustering technique. Liu, Shen and Chen (2018a), and Mainali and Chang (2018) coincide with this study in the use of statistical techniques along with a use of land analysis through remote sensors to understand the distribution of water quality, as well as the origin of the pollutants.

Conclusions

The water of Cupatitzio River is unfit for human use and consumption due to its poor quality, mainly resulting from the high levels of phosphorus, ammonium, nitrates, Iron and aluminum in all the sites evaluated, during the rainy and dry seasons. These pollutants surpass the limits taking into account standard CE-CCA-001 (1989); therefore, it is unfit for human consumption.

Based on the water quality indices, it may be concluded that Cupatitzio River has fair quality water due to its high concentrations of pollutants.

The strong impact on water quality in the middle watershed is due to the discharge of wastewater and leachates from the landfill of the city of Uruapan. These sources contribute more than 70 % of the nitrogenous substances and 50 % of the total phosphorus; the rest is originated from the surface runoff.

The greatest impact on the lower watershed is due to the avocado agricultural zone, where there is observed the accumulation of Al which, according to the background, derives from aluminum phosphide pesticides largely applied in avocado orchards.

The presence of reservoirs was associated with poor water quality and low dissolved oxygen levels, which is an indicator of eutrophication of the body of water. However, this is not a permanent state, therefore, corrective and strategic actions may be taken to recover the water quality of Cupatitzio River.

Acknowledgments

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