

Water quality of the Grijalva river on the Chiapas - Tabasco border

Calidad de agua del río Grijalva en la frontera de Chiapas y Tabasco

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ABSTRACT. The objective was to characterize the water quality in a section of the Grijalva River and in some of its tributaries on the border between the States of Chiapas and Tabasco, in the rainy and dry seasons. Twenty-three physical, chemical and microbiological parameters as well as contaminants were determined. The values obtained were compared with the maximum permissible limits (MPLs) for water use and human consumption set out in Official Mexican standard NOM-127-SSA1-1994, and with the water quality classification scale of the Comisión Nacional del Agua (CONAGUA). The water quality in the studied section of the Grijalva River decreases as it descends to more populated areas of the State of Tabasco. Water turbidity and *E. coli* coliform levels increase, both in the river channels and in sources destined for human consumption. For the other variables evaluated, there are acceptable water quality characteristics, mainly in the dry season, except for mercury, which occurs at levels higher than those recommended. Further studies on the presence of mercury in the Grijalva River basin are recommended.

Key words: coliforms, *Escherichia*, mercury, heavy metals, turbidity.

RESUMEN. El objetivo fue caracterizar la calidad de agua en una sección del río Grijalva y en algunos de sus afluentes en la frontera entre los estados de Chiapas y Tabasco, en la época de lluvias y secas. Se determinaron 23 variables que incluyeron parámetros fisicoquímicos, microbiológicos y de contaminantes, los valores obtenidos se compararon con los límites máximos permisibles (LMP) para agua de uso y consumo humano indicados en la Norma Oficial Mexicana NOM-127-SSA1-1994, y con la escala de clasificación de calidad del agua de la Comisión Nacional del Agua (CONAGUA). La calidad del agua en la sección del río Grijalva estudiada, disminuye en su descenso a las zonas pobladas del estado de Tabasco. La turbidez y los niveles de coliformes y *E. coli* incrementan, tanto en el cauce como en fuentes destinadas al consumo humano. Para las otras variables evaluadas, se tienen características aceptables de calidad del agua, principalmente en la época seca, con excepción del mercurio, que se presenta en niveles superiores a los recomendados. Se sugiere realizar estudios sobre la presencia del mercurio en la cuenca del Grijalva.

Palabras clave: coliformes, *Escherichia*, mercurio, metales pesados, turbidez

INTRODUCTION

Water quality is directly related to the lives of rural populations, especially in places where the supply is directly from surface runoff or where communities depend on water resources for fishing

and recreational activities. The quality of water is relevant to determine its use, as well as being a management and pollution indicator (Laino-Guanes et al. 2016, Yu et al. 2016). Water quality variables allow to have a vision of a specific moment, and serve as a baseline to observe the changes or trends

in basins (Musalem *et al.* 2014). At the global level, basins are undergoing a decline in their water quality, due to their levels of sedimentation, salts and nutrients (Lintern *et al.* 2018).

About 35% of Mexico's total freshwater flows through the Grijalva and Usumacinta rivers (CONAGUA 2011). Despite this, the rural communities settled along these rivers live in conditions of extreme poverty, with severe deterioration of natural resources and limited access to good quality water (González-Espinosa *et al.* 2014, Plascencia *et al.* 2014). The combination of several biophysical, social and environmental factors generates a high degree of vulnerability to disasters caused by events such as landslides and floods, and there is great interest in the region in mining, an activity that can cause irreversible damage to the environment (Laino-Guanes *et al.* 2015).

Several studies that analyze water quality in the Grijalva basin are concentrated in the lower part of the basin, in urban areas or in major rivers, where monitoring with greater frequency is more feasible, although commonly with few parameters studied (Borbolla-Sala, *et al.* 2003). On the other hand, there are few studies in the middle and upper parts of the basin. Water quality parameters reflect water characteristics that can have different effects on human health and on aquatic ecosystems, with varying degrees of danger (Ramos-Herrera *et al.* 2012). Concentrations outside the permissible ranges cause pollution (Kulinkina *et al.* 2016). Therefore, the present study was conducted to have a water quality baseline for a section of the Grijalva River and some of its tributaries, with the objective of obtaining local data on the water quality in tributaries used by the population for consumption and economic activities.

MATERIALS AND METHODS

Study area

The study was conducted in a section of the Grijalva River, locally known as the Almandros River (Valencia-Barrera 2014). The section is located on the border between Chiapas and Tabasco

states, and is part of the Grijalva River drainage system. It has elevations ranging from 30 to 1,877 masl, with a catchment area of 56.6 km². The study area belongs to the XI Frontera Sur and 30 Grijalva-Usumacinta regions (CONAGUA 2011). It is located in the middle basin of the Grijalva River and includes territories belonging to Huitiupán municipality in the State of Chiapas and Tacotalpa municipality in the State of Tabasco. The predominant vegetation type is medium-height evergreen forest, with different degrees of disturbance, ranging from areas completely deforested for livestock farming to forest fragments with trees over 25 m in height. The most represented species are *Brosimum alicastrum*, *Cedrela odorata* and *Spondias mombin* (Ramírez-Marcial *et al.* 2014).

Six sampling points were selected in this section of the Grijalva River, two on the main river, and four in springs and tributaries (Figure 1 and Table 1). The study area is geographically isolated, not communicated and in most of the roads there is no vehicular access.

Evaluated water quality variables

Twenty-three water quality variables were analyzed, in samples taken during the rainy season (August 2011) and dry season (January 2012). For the transfer of the samples to the laboratory, they were put in refrigeration from the moment they were taken at the points until arrival at the laboratory in less than 24 h. The variables evaluated were: dissolved oxygen (DO), pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total nitrogen (N), nitrites, nitrates, total phosphorus (P), phosphates, total dissolved solids (TDS), total suspended solids (TSS), total hardness, turbidity, total coliforms and *Escherichia coli*. The content of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn was also determined.

The DO and pH were measured *in situ* at the time of taking the water sample, the DO by chemiluminescent membrane electrodes (Jiménez-Cisneros 2001) and pH by the electrochemical or specific electrodes method (APHA 1998). In the laboratory, COD was determined by the spec-

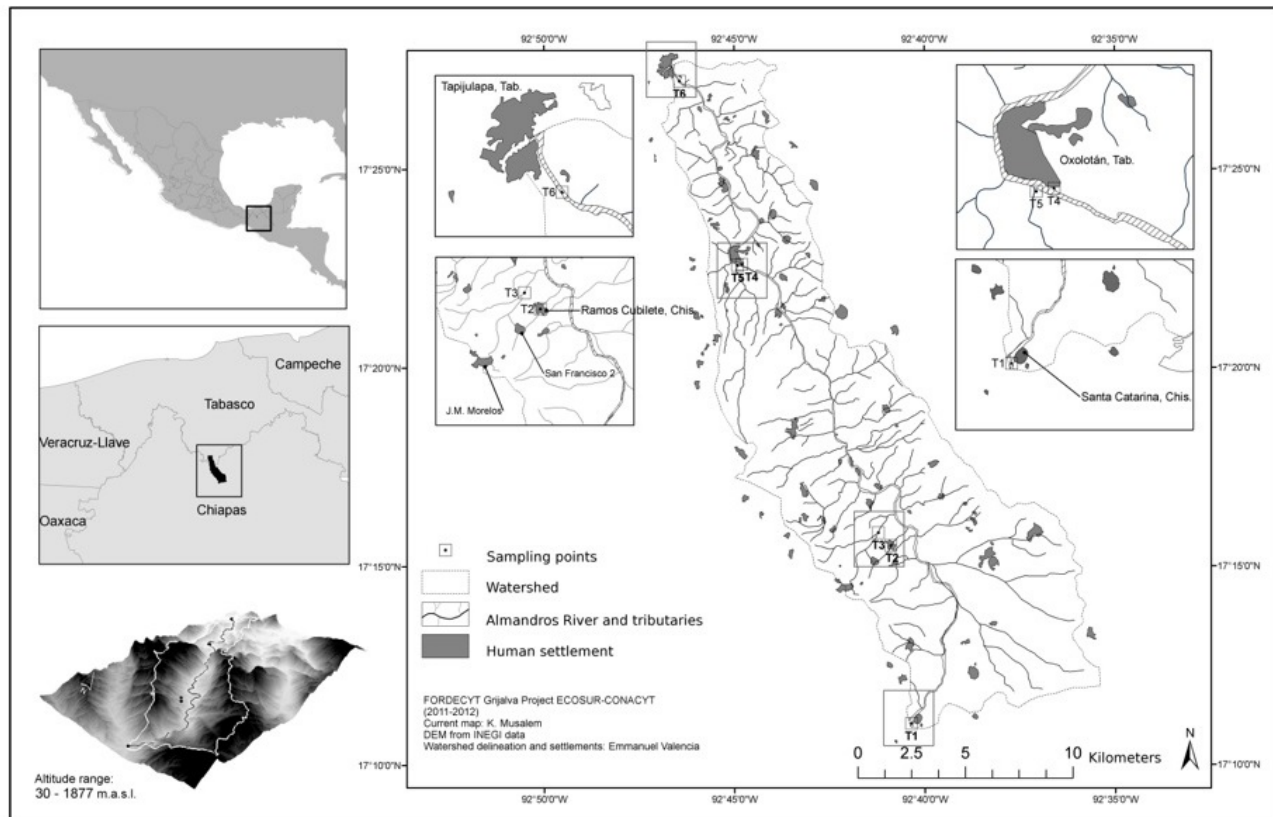


Figura 1. Location of the sampling points on the Grijalva River and its tributaries. The watershed corresponds to the delimitation of the regional module of the Grijalva Basin Project with the Pfafstetter methodology.

trophotometric method (SE 2001c), BOD by the volumetric method (SE 2001a), total nitrogen by persulfate digestion HACH 10071, nitrites by means of cadmium reduction HACH 8039 adapted from the APHA method (1998), nitrates by diazotization HACH 8507 approved by the EPA and according to the standard NMX-AA-099-SCFI-2006 (SE 2006); total phosphorus, phosphates, TDS and TSS by the molybdate HACH 10127, stannous chloride and gravimetric methods, respectively (SE 2001b), total hardness by the volumetric technique by acid-base titration, turbidity by the nephelometric method, total coliforms and *Escherichia coli* by the microbiological method of the most probable number (SCFI 1987).

Heavy metal analysis

The determination of the content of heavy metals was carried out in accordance with Official Mexican Standard NMX-AA-O51-SCFI-2001 (SE 2001e). The determination of chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) content was carried out by atomic absorption spectrophotometry, in a VARIAN SpectraAA220 model spectrometer. The limits of quantification for Cu, Cr and Ni were $200 \mu\text{g L}^{-1}$; for Pb, $190 \mu\text{g L}^{-1}$, and for Zn, $340 \mu\text{g L}^{-1}$. For quality control, WasteWaterTM Trace Metals certified reference material, triplicate sample analysis and reagent blank analysis were used.

The determination of the arsenic (As), cadmium (Cd) and mercury (Hg) content was carried out in a GBC AVANTA PM atomic absorption spec-

Tabla 1. Collection points and description of the water current studied in the Grijalva River. Source: cuencas y variables morfométricas a través del SIATL (2012).

Point	Characteristics	Basin/drainage area	Morphometric Variables*
T1	Entrance to the module or sub-basin. Main current of the Grijalva (Almandros) River at the height of the town of Santa Catarina in the Municipality of Huitiupan, Chiapas.	556 km ²	Not applicable
T2	Spring. Located in the Ramos Cubilete community in Chiapas. Spring has an approximate flow of 5 Lt/s led to a catchment tank. Commonly used for community consumption. Sample taken prior to use (corn washing, recreational use).	less than 1.66 km ²	CT: 15.66 minutes Ave. slope: 25.61% Length: 93.71 m Ave. elevation: 558 m
T3	Mountain River. Tributary of the main river with characteristics of small population and little impact by them.	less than 7.14 km ²	CT: 21.98 minutes Ave. slope: 18.87% Length: 4 721 m Ave. elevation: 636
T4	Flood zone. At the height of the community of Oxolotán, Tabasco. Water mirror formed by floods and filtrations, parallel to the main river. With permanent flow (even in dry season) to the main river.	Not applicable	Not applicable
T5	Mountain river before connecting to the main river. Tributary on the left bank of the Grijalva (Almandros) River, in the community of Oxolotán, Tabasco.	12.76 km ²	CT: 43.68 minutes Ave. slope: 16% Length: 9 373 m Ave. elevation: 792 m
T6	Module exit gauge point. Main current of the Grijalva (Almandros) River at the height of the community of Tapijulapa, Tabasco.	785.99 km ²	CT: 476.21 minutes Ave. slope: 2.31% Length: 76 836 m Ave. elevation: 908 m

*Morphometric variables calculated by the Water Flow Simulator (SIATL) of the Instituto Nacional de Estadística y Geografía (INEGI). CT = concentration time, Ave. slope = average slope, Ave. elevation = average elevation.

trophotometer, with flame and a GBC HG 3 000 model hydride generator. The samples were digested in a Lanconco semi-micro Kjeldahl digester. The limits of quantification of these analyzes for As and Hg were 0.05 $\mu\text{g L}^{-1}$, and for Cd, 0.4 $\mu\text{g L}^{-1}$. Four treatment blanks and a triplicate for quality control were analyzed for each element, in addition to triplicate analysis of certified reference material. The determination was made according to ET-QU03 procedures (EAA 2008).

Maximum permissible limits and comparative analysis of means

The water quality results were compared with the maximum permissible limits (MPLs) of Offi-

cial Mexican Standard NOM-127-SSA1-1994 (SS 1994). The COD and BOD results were analyzed with the CONAGUA water quality classification scale (SEMARNAT 2015). To find out whether there are differences between the seasons in which the water samples were taken, Tukey's range test ($p \leq 0.05$) was performed with INFostat software (Di Rienzo *et al.* 2015).

RESULTS

Dissolved oxygen (DO) and pH

In the dry season, the highest DO values were found at all sampling points, except for the spring sample (T2) that showed the highest DO in the

rainy season (Table 2). In general, the flood zone (T4) had the highest DO concentrations (12.9 mg L^{-1}), while the spring had the lowest DO contents (5.5 mg L^{-1}). By sampling season, the rainy season had the lowest pH (Table 3), but in both sampling periods the pH was within the MPLs indicated in the Official Mexican Standard.

Total dissolved solids (TDS) and total suspended solids (TSS)

The TDS values detected at the sampling points, in the two seasons of the year, do not exceed the MPLs of the Official Mexican Standard (Table 2). In the dry season, higher TDS contents were detected, except for point T4. The highest TDS content was found in the spring (T2, 680 mg L^{-1}) and the lowest in the mountain river (T5, 380 mg L^{-1}). For the TSS content, the highest values were found in the rainy season, and the highest levels were found at the entry points to the module or sub-basin (T1) and the outflow of the module or sub-basin (T6) with 186 mg L^{-1} and 304 mg L^{-1} , respectively, while the lowest concentrations were in the spring (T2) and the mountain river before its connection to the main river (T5), with 1 mg L^{-1} at both points.

Chemical oxygen demand (COD) and biochemical oxygen demand (BOD)

At all sampling points the COD and BOD values were higher in the rainy season (Table 3), with the water quality in the dry season being adequate at all sampling points for COD and BOD. In the rainy season, water quality varies from excellent to acceptable, although the outlet of the module or sub-basin (T6) has water with high COD values. For BOD, in the rainy season the water quality varies between good and acceptable.

Mineral content

The highest nitrogen concentrations were found in the rainy season, with the exception of the spring (T2), which had the highest nitrogen content during the dry season (Table 3). The concentrations of nitrates and nitrites at all sampling points, in

both seasons of the year, do not exceed the MPLs established in the Official Mexican Standard, with the highest nitrate contents occurring in the rainy season.

P and phosphate concentrations lower than 0.1 mg L^{-1} were found at all sampling points and at both times of the year.

Turbidity and hardness

Turbidity values are higher in the rainy season at all sampling points, except for the spring (T2), where turbidity values did not exceed the MPLs established by the Official Mexican Standard of 5 UTN. The highest values were found at the entrance to the module or sub-basin (T1) and at the module exit gauge point (T6) in the rainy season, with 179 UTN and 311 UTN, respectively. The hardness values found at all sampling points and in both seasons of the year did not surpass the MPLs of the Official Mexican Standard (Table 3).

Total coliforms and *Escherichia coli*

The presence of total coliforms and *E. coli* was detected at all sampling points in both sampling seasons. For total coliforms, the values found in both sampling periods exceeded the MPLs of the Official Mexican Standard, with the values found in the rainy season being higher. The highest coliform values were found at the entrance to the module or sub-basin (T1) and at the module exit gauge point (T6) with values of $15\,531 \text{ NMP } 100 \text{ m L}^{-1}$ and $24\,196 \text{ NMP } 100 \text{ m L}^{-1}$, respectively. For *E. coli*, the highest concentrations were found in the dry season at all sampling points (Table 3), with the highest bacterial concentrations found at points T1 and T6.

Heavy metal content

The presence of arsenic (As) was detected at all sampling points during the rainy season (Table 3), but does not exceed the MPLs indicated in the Official Mexican Standard, while mercury (Hg) was detected in the dry season at all sampling points, and in the rainy season it was detected only at the mouth of the mountain river (T5). Both elements had their highest values in the dry season, with sta-

Tabla 2. Concentrations of dissolved oxygen (DO), pH, total dissolved solids (TDS), total suspended solids (TSS), chemical oxygen demand (COD) and biochemical oxygen demand (BOD) at sampling points during the rainy and dry seasons.

Point	DO (mg L ⁻¹)		Ph		TDS (mg L ⁻¹)		TSS (mg L ⁻¹)		COD (mg L ⁻¹)		BOD (mg L ⁻¹)	
	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry
T1	7.6	9.2	7.9	8.5	420	590	186	4	32	3.4	9.4	NA
T2	6.2	5.5	6.8	7.2	660	680	2	1	6	2.7	NA	NA
T3	7.6	7.7	8.1	8.4	420	440	20	6	37	4.2	4.2	2.4
T4	10.7	12.9	7.7	8.2	570	460	21	6	29	2.3	6.2	1.9
T5	7.0	8.7	7.8	8.3	380	410	51	1	19	2.8	4	2
T6	7.8	8.4	8.1	8.4	450	530	304	4	43	3	18.5	2.1

NA = sample not analyzed.

Tabla 3. Concentrations of total nitrogen (N), nitrites, nitrates, total phosphorus (P), phosphates, turbidity, total hardness, total coliforms, *Escherichia coli*, As and Hg detected at the sampling points during the rainy and dry seasons.

Point	N (mg L ⁻¹)		Nitrates (mg L ⁻¹)		Nitrites (mg L ⁻¹)		P (mg L ⁻¹)		Phosphates (mg L ⁻¹)		Turbidity (UTN)	
	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry
T1	2.8	0.2	2	0.2	0.01	0	0.04	0.07	0.04	0.07	179	8
T2	2.3	2.6	1.2	1.1	0.01	0	0.05	0.05	0.05	0.05	2	3
T3	1.2	1	0.6	0.8	0.01	0.01	0.03	0.04	0.03	0.04	19	9
T4	1.1	0.3	0.2	0	0.01	0.01	0.06	0.05	0.06	0.05	24	10
T5	1.4	0.3	0.3	0.1	0.01	0.01	0.04	0.05	0.04	0.05	55	5
T6	0.5	0.3	0.4	0.1	0.01	0.01	0.04	0.08	0.04	0.08	311	8

Tabla 3. Continuation.

Point	Hardness (CaCO ₃ /100 mL)		Tot colif (NMP/100mL)		<i>E. coli</i> (NMP/100mL)		As (μg L ⁻¹)		Hg (μg L ⁻¹)	
	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry
T1	182	243	15 531	7 701	12 033	1 785	< 0.05	0.64	< 0.05	4.62
T2	295	281	3 784	839	161	86	< 0.05	0.03	< 0.05	2.33
T3	190	174	738	2 602	462	410	< 0.05	0.30	< 0.05	1.65
T4	260	183	548	1 076	122	63	< 0.05	0.13	< 0.05	4.92
T5	173	181	3 314	987	1 529	85	< 0.05	0.56	0.20	3.23
T6	189	238	24 196	1 664	> 24 196	269	< 0.05	0.47	< 0.05	3.68

tistical differences between sampling periods. The values found at all sampling points in the dry season surpassed the MPLs indicated in the Official Mexican Standard. No presence of Cd, Cr, Cu, Ni, Pb or Zn was detected.

DISCUSSION

The presence of Hg and As was detected in the dry season, with Hg presenting higher values than the MPLs indicated in Official Mexican Standard NMX-AA-O51-SCF1-2001 (SE 2001e). Laino-Guanes *et al.* (2015) have reported similar As and Hg values in the upper part of the Grijalva River basin, while Alvarado-Arcia *et al.* (2015) report the presence of Cd in soils and sediments of the Grijalva River's main channel. Hg is one of the ten most dangerous contaminants to public health, so studies on

its bioavailability and effects on humans are justified (Bjørklund *et al.* 2017). Despite the above, there is still scarce literature for this basin and Mexico in general; in this regard, Leal-Ascencio *et al.* (2009) highlight the lack of standards for metals in Mexico. The Hg data obtained in this study range from 1.65 to 4.92 ug L⁻¹ in the dry season, which is above the range reported by Guentzel *et al.* (2017) for a lagoon system in the Papaloapan River Basin, while Guentzel *et al.* (2017) found that Hg concentrations correlated with higher TSS values. The presence of Hg can originate from natural or anthropogenic sources, with the possible causes including volcanic activity, forest fires, erosion of rocks, mining, crematoria and wastewater discharges (Pirrone *et al.* 2010, Laino-Guanes *et al.* 2015).

No presence of Cd, Cr, Cu, Ni, Pb or Zn was detected. These results coincide with those of

Laino-Guanes *et al.* (2015) who found concentrations below the MPLs for these minerals in the upper basin of the Grijalva River. However, Leal-Ascencio *et al.* (2009) report for the El Limón lagoon, in the Grijalva River basin, Zn, Ni, Cr, Cd and Cu contents higher than the MPLs, a situation that could be attributed to the accumulation of metal content in the lagoons due to the sedimentation typical of lagoon systems (Bryan and Langston 1992). The BOD values of 4 to 18.5 mg L⁻¹ in the rainy season and from 1.9 to 2.4 mg L⁻¹ in the dry season, and the average COD values of 27.6 mg L⁻¹ in the dry season and of 3.06 mg L⁻¹ in the rainy season found in the present study are within the values reported by Ramos-Herrera *et al.* (2012) for the Almandros River. For the TSS content, values between 1 and 6 mg L⁻¹ were found in the dry season, while in the rainy season the values were between 2 and 304 mg L⁻¹; in this regard, Ramos-Herrera *et al.* (2012) report an average value of 102.3 mg L⁻¹ and Laino-Guanes *et al.* (2016) values between 1.8 and 4.3 mg L⁻¹ for the dry season, while in the rainy season the values ranged between 31.1 and 548.8 mg L⁻¹.

The concentrations of total coliforms and *E. coli* exceeded the permissible values at all sampling points in the two sampling periods, which coincides with the reports of microbiological contamination

in excess of the MPLs of the Official Mexican Standard at different points in the Grijalva basin, mainly in rivers associated with urban areas (Castañón and Abraján 2009, Laino-Guanes *et al.* 2016) and even in drinking water supply systems in both cities and rural communities (Sánchez-Pérez *et al.* 2000, Galdos-Balzategui, A. *et al.* 2017).

CONCLUSIONS

The presence of Mercury and Arsenic was greater in the dry season. Although some other parameters indicate better water quality in the dry season, such as the TSS and COD content, there were no differences between sampling periods. The concentrations of total coliforms and *E. coli* exceeded the permissible values at all sampling points in the two sampling seasons.

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