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Prospective study of the levels of fecal coliforms and heavy metals of surface water in the Corona River, Tamaulipas, Mexico

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Abstract
The Corona River in Tamaulipas, Mexico, originating from the San Pedro Hill in the Sierra Madre Oriental, serves as a crucial water source for the region and flows into the Vicente Guerrero Dam. Given its significance, assessing the river's water quality is imperative. Rivers are often vulnerable to contamination from organic and inorganic discharges, which can degrade water quality. This study conducted a comprehensive assessment across eleven sampling stations along the Corona River, analyzing fecal coliforms (43-2400 Most Probable Number or MPN) and heavy metals [cadmium (0.004-0.037), copper (0.0085-0.0595), and lead (0.142-0.227 mg L^{-1})]. Elevated levels of fecal coliforms and heavy metals were detected at various stations, with contamination progressively increasing towards the river's confluence with the Vicente Guerrero Dam. These findings indicate that the water quality may deteriorate to levels unsuitable for consumption. The data presented are crucial for informing relevant authorities on the necessity of implementing effective management, prevention, control, and treatment strategies to ensure that the river water meets safety standards for various uses, including consumption, recreation, agriculture, and livestock.

Key words: analysis, cadmium, copper, lead, microorganisms, pollution, water.

Estudio prospectivo de los niveles de coliformes fecales y metales pesados de aguas superficiales en el río Corona, Tamaulipas, México.

Resumen. El río Corona en Tamaulipas, México, que se origina en el Cerro San Pedro de la Sierra Madre Oriental, es una fuente de agua crucial para la región y desemboca en la presa Vicente Guerrero. Dada su importancia, es fundamental evaluar la calidad del agua del río. Los ríos son a menudo vulnerables a la contaminación por descargas de desechos orgánicos e inorgánicos, lo que puede degradar la calidad del agua. Este estudio realizó una evaluación integral en once estaciones de muestreo a lo largo del río Corona, analizando coliformes fecales (43-2400 Numero Más Probable o NMP) y metales pesados [cadmio (0,004-0,037), cobre (0,0085-0,0595), plomo (0,142-0,227 mg L^{-1})]. Se detectaron niveles elevados de coliformes fecales y metales pesados en varias estaciones, con una contaminación que aumenta progresivamente hacia la confluencia del río con la presa Vicente Guerrero. Estos hallazgos indican que la calidad del agua puede deteriorarse a niveles no aptos para el consumo. Los datos presentados son cruciales para informar a las autoridades pertinentes sobre la necesidad de implementar estrategias efectivas de gestión, prevención, control y tratamiento, con el fin de garantizar que el agua del río cumpla con los estándares de seguridad para diversos usos, incluyendo el consumo, la recreación, la agricultura y la ganadería.

Palabras clave: Análisis, cadmio, cobre, contaminación, metales, microorganismos, plomo, río, Tamaulipas.

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INTRODUCTION

Rivers are important for the environment, generating ecosystems that favor climate regulation and soil renewal (Roldán and Ramírez 2022). The climate changes observed in recent decades show the fragility of these river systems when they are exposed to anthropogenic activities and global warming. Both factors reduce the cause of the rivers and change the permanent rivers to intermittent watercourses. This is strong evidence of the current importance of adequate water management and the study of river water quality (Heyer et al. 2008, Roldán and Ramírez 2022).

The Northern Mexican region has different river systems in arid and semi-arid areas that have been affected by global warming (Magaña et al. 2012). Permanent and intermittent rivers show special ecosystems, with intermittent rivers poorly studied because their importance for the environment is underestimated due to the temporal nature of their water flow (Heyer et al. 2008). These rivers do not have adequate water management practices and can be used occasionally as areas to discharge wastewater, with subsequent pollution problems that can be generated during the rainy season due to the transport of the contained contaminants (Cortez-Mejía et al. 2021). The dynamics in the behavior of nutrient cycles (ammonium, phosphorus, etc.), heavy metals (lead, cadmium, etc.) in intermittent rivers are different concerning permanent rivers, where the agricultural, industrial, and municipal sources of these pollutants that are released into the environment and transported to other regions during the rainy season, generating problems for ecosystems and human health (Heyer et al. 2008, Roldán and Ramírez 2022).

The Corona River is considered a permanent river in the central area of Tamaulipas, Mexico (Figure 1) and due to global warming, deforestation, and anthropogenic activities, has characteristics of an intermittent river in some areas of the river during low water levels. This river is an important source of freshwater for different social sectors in Tamaulipas [24,793 total population (12,088 female, 12,705 male)] INEGI (2020), the bacteriological quality and presence of heavy metals in the river water are little studied. Coliform bacteria constitute a heterogeneous group of wide diversity in terms of genus and species, highlighting the Enterobacteriaceae family (Delgado et al. 2008, Santiago-Rodriguez et al. 2012) and with the presence of *Escherichia coli*, *Citrobacter* sp., *Enterobacter* sp., and *Klebsiella* sp. (Marchand 2002). The presence of these bacteria is a sign of contaminated water, and fecal coliforms represent a clear indicator of risk to public health due to fecal contamination (Madigan et al. 2009). López et al. (2020) worked in the San Marcos River, Ciudad Victoria, Tamaulipas, Mexico detecting values of fecal coliforms from 2 to 1,031 colony-forming units (CFU) mL^{-1}. Galindo et al. (2005) carried out similar studies in the Cazones River, Veracruz, Mexico, and detected values of fecal coliforms from 3.6 to >1,000 most probable number (MPN) 100 mL^{-1}.

Pollution caused by fertilizers, herbicides, pesticides, organochlorine compounds, heavy metals, and oil has hurt the flora, and fauna of Tamaulipas, significantly altering the viability of aquatic life (Cedillo-Leal et al. 2016). Heavy metals (cadmium, copper, and lead, among others) are an important source of pollution for aquatic ecosystems. Heavy metals have the characteristic of being persistent in the environment, do not degrade, and are toxic to flora and fauna, in addition to the fact that different heavy metals can bioaccumulate throughout the food chain (Matos et al. 2017). Heavy metals are potentially genotoxic and carcinogenic, also change the rate of cell division and/or DNA structure, cause gene mutations and chromosomal aberrations, cell death, oxidative stress inducers, and increase the risk of various degenerative diseases (Matos et al. 2017). Due to persistence, transfer, and storage, heavy metals represent a risk to environmental health that requires special evaluation by the organizations in charge of detecting and monitoring them. Cadmium and Lead were detected in the San Marcos River, Ciudad Victoria, Tamaulipas, Mexico at levels of 0.14 and 0.4 mgL^{-1} (López et al. 2020). Wakida et al. (2008) studied the sediments of the Tecate River and Tijuana River, Baja California Norte, Mexico, detecting the presence of lead (0.9-28 mg kg^{-1}) and cadmium (1.35-5.25 mg kg^{-1}). Vázquez-Sauceda et al. (2012) detect the presence of cadmium (0.5-0.45 mg mL^{-1}, approx.) and Pd (1-4 mg mL^{-1}, approx.) in the water of the Tigre River, Tamaulipas, Mexico.

The present research evaluated the quality of surface water of the Corona River, Tamaulipas, Mexico by quantifying fecal coliforms and heavy metals (cadmium, copper, lead). These values are relevant to understanding the dynamics of contaminants in a river that is experiencing significant intermittency in the face of climate change. In addition to affecting various ecosystems and being a source of fresh water for rural communities and surrounding cities along the river.

MATERIAL AND METHODS

Eleven sampling areas were established, 5-7 km apart, along the Corona River (dry season, June 2022), which is part of the hydrological region 25 San Fernando - Río Soto La Marina, in the area central Tamaulipas, Mexico (DOF, 8 Mar 2016). The sampling points (systematic random) were selected for their accessibility, safety, no discharges, and representativeness (source of the river, intermediate, mouth at the Vicente Guerrero dam) (Figure 1). The Corona River originates in the Sierra Madre Oriental and is one of the main rivers that flow into the Vicente Guerrero Dam. This river is part of the region of Hidalgo, Güémez, and Padilla, is at 2,000 masl, is 72 km long, and covers a total of 5,605 km^2 of basin area (Figure 1). The Corona River is an important river basin in the center of Tamaulipas and a source of fresh water that supplies the Vicente Guerrero dam, which supplies fresh water to Ciudad Victoria, Tamaulipas. The river has 208.45 Mm^3 of the average annual volume of natural freshwater flow, but the current drought has put it in a difficult condition today (DOF, 8 Mar 2016).

Fifty (sterile bottle) and one hundred (amber bottle) milliliters of surface water were sampled at each of the sampling stations (Figure 1) according to the methodology of the NMX-AA-042-SCFI-2015 and NMX-AA-051-SCFI-2016. The water containers (glass jars) were submerged to a depth close to 30 cm, uncovering them in the opposite direction to the flow of the current and closing them hermetically when full. The samples were labeled, stored on ice (4 °C) for transportation, and analyzed at the Instituto de Ecología Aplicada, Universidad Autónoma de Tamaulipas.

The most probable number (MPN) of the water was evaluated by serial dilutions (10^{-1}-10^{-8}), subsequently plating 1 mL of each dilution on a plate with sterile MacConkey agar, incubating them for 24 h at 37 °C. The MPN mL^{-1} of the water was determined with the number of colonies obtained in the Petri dishes. The samples were confirmed using lactose broth, bright green broth, both with Durham bell, and peptone water and tryptophan, subsequently adding Kobacs reagent (Galindo et al. 2005, Sánchez et al. 2021).

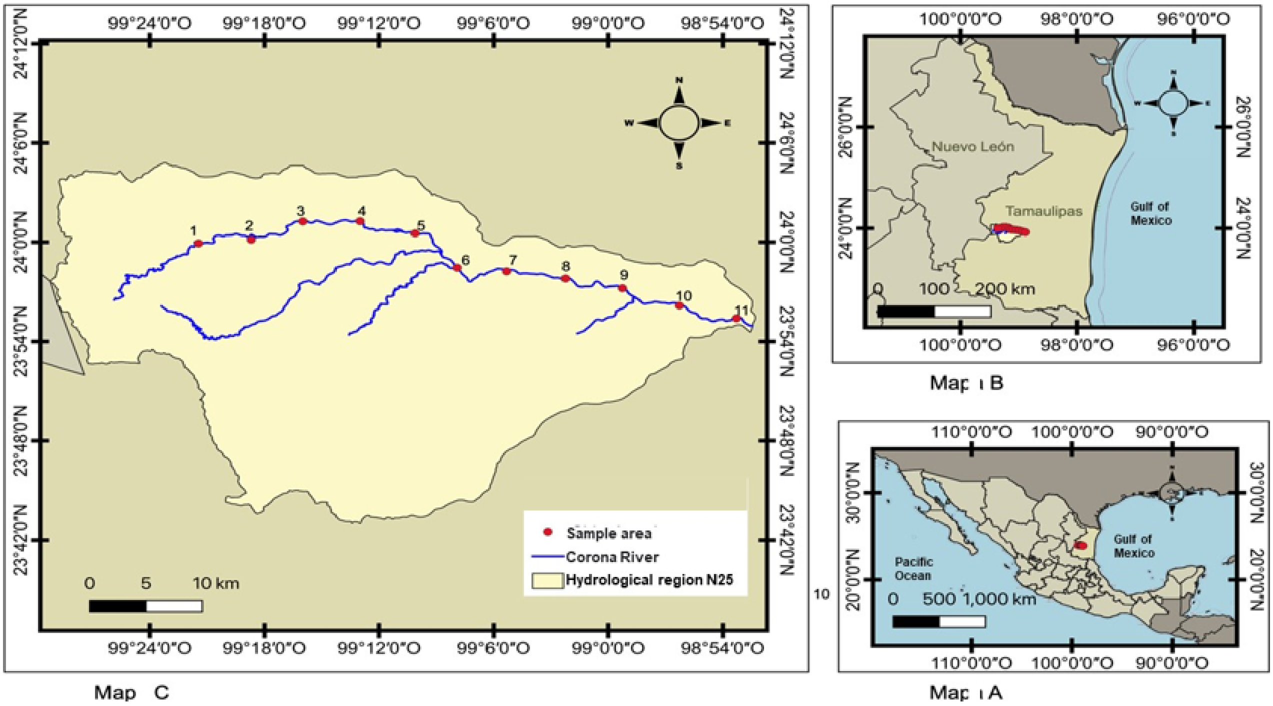

Figure 1. Study area: Corona River, Tamaulipas, Mexico.

The measurement of heavy metals began by acidifying the sample with nitric acid until obtaining a pH < 2, filtering it (0.45 µm), and storing it (4 °C) (NMX-AA-051-SCFI-2016). Cadmium, copper, and lead were evaluated according to lab instruction with a Perkin Elmer 900H atomic absorption spectrophotometer, Facultad de Ingeniería y Ciencias, Universidad Autónoma de Tamaulipas (Vázquez-Sauceda et al. 2012). The detection limits of the equipment were 0.08 mg L^{-1} for cadmium, 5 mg L^{-1} for lead, and 1 mg L^{-1} for copper. The standards were prepared from the stock standard solution for Cd (VHG Labs 5% HNO_3, 1.007 mg L^{-1} single element standard), Pb (VHG Labs 5% HNO_3, 1.003 mg L^{-1} single element standard), Cu (VHG Labs 5% HNO_3, 1.001 mg L^{-1} single element standard).The maximum permitted levels of cadmium (0.2, 0.2, and 0.4 mg L^{-1}), copper (6 mg L^{-1}), and lead (0.2, 0.2, and 1 mg L^{-1}) in river water for public use, environment, and agriculture, respectively (NOM-001-SEMARNAT-1996). The NMX-AA-115-SCFI-2015 was used to calculate the concentration of the sample using the equation of the straight line obtained from the calibration curves for each metal: $Y = mX + b$, where Y is the absorbance of the processed sample, m is the absorptivity coefficient, and b is the ordinate to the origin (Palomares 2017).

RESULTS AND DISCUSSION

Different Mexican institutions monitor water quality parameters in rivers and other tributaries (biological, chemical, microbiological, physical parameters, etc.) (Heyer et al. 2008, Sosa-Rodríguez 2012, Cortez-Mejía et al. 2021). The increase in temperature generated by climate change, a decrease in the flow of water from tributaries, and their intensive use, are generating an increase in the importance of quality studies of existing water tributaries to manage them efficiently and sustainably (Acuña 2017). The Corona River is also the main source of freshwater for the various agricultural products of the region (onion, beans, corn, melon, orange, cucumber, watermelon, sorghum, tomato, etc.), which use fertilizers and pesticides that affect the environment and can contaminate the river water when they come into contact with the river water during the rainy season and subsequently affect human health (Heyer et al. 2008).

Fecal coliforms. The World Health Organization (2017) shows that close to 50% of deaths in children under 5 years of age were due to diarrhea, caused by poor hygiene and sanitation in the intake of freshwater. Chalmers (2014) and Robertson (2014) reveal that the most common pathogens worldwide use transmission through freshwater from river sources as a diffusion route. The NMP of coliforms in the different sampling stations selected along the Corona River ranges between 43 and >2400 NMP 100 mL^{-1} (Table 1) showing that this contaminant was found in all stations with a gradual increase as it progressed. Water along the river and until its mouth at the Vicente Guerrero dam. The official Mexican standards (NOM-127-SSA1-1994 and NOM-001-SEMARNAT-1996) show that the maximum limit of fecal coliforms is 1000 and 2 MPN in 100 mL^{-1}, respectively, which indicates that almost all stations sampling monitored in the current research have a significant level of contamination for this parameter. It should be noted that the sampling was carried out during the dry season, where the last third of the Corona River presented areas with stagnant freshwater (Figure 2), and that station 11 once again presented water flow from the subsoil, which could suggest a possible natural filtration of fecal coliforms. Galindo et al. (2005) and López et al. (2020) reported lower fecal coliform levels in the San Marco River, Tamaulipas and Cazones River, Veracruz, Mexico respectively than those observed in the Corona River, possibly due to its rural nature compared to the other rivers, which cross cities with drainage services. and sewage treatment plants. However, until station 5, freshwater was at acceptable levels and of satisfactory quality to serve as a source of clean freshwater for drinking water supply and agricultural irrigation, but from season 6 onwards the water could be considered bacteriologically contaminated with fecal coliforms. Pampa, Schmidt, and Estância Velha/Portão streams show a level of fecal coliform from 141, 32000, to 305000 MPN 100 mL^{-1}, respectively in Sinos River Basin, Brazil (Benvenuti et al. 2015). Díaz-Gavidia et al. (2022) display a fecal coliform level in the Maule and Maipo Rivers, Chile ranging between 1 and 130 MPN, and 2 and 30,000 MPN 100 mL^{-1}, respectively. Both studies show that the microbial level associated with the quality of river water increases with greater urbanization. Like Ramírez et al. (2009) who emphasize that the presence of coliforms reveals the presence of contamination of anthropogenic origin in the body of water and highlights the importance of disinfecting it for consumption. On the other hand, contamination by fecal material is closely related to land use (aquaculture, agriculture, livestock, tourism, urbanization), however, sufficient plant cover helps prevent these effects (Cabello et al. 2016, Morales-Mora et al. 2022). The Corona River area has important agricultural and livestock activity and is close to rural areas where wastewater and blackwater service is incipient or non-existent, which greatly favors the presence of coliforms.

Table 1. Heavy metals levels and most probable number of fecal coliforms in the different sampling stations (dry season, June 2022) in the Corona River, Tamaulipas, Mexico (NOM-127-SSA1-1994 and NOM-001-SEMARNAT-1996).

Sampling station			**Heavy metals (mg L^{-1})**			
			Cadmium	**Lead**	**Copper**	**MPN***
1	El Olmo, Güémez	23°59’55.26”N - 99°21’27.73”O	0.004	0.142	0.0085	43
2	El Roble, Güémez	24°0’8.63”N - 99°18’40.92”O	0.013	0.175	0.0180	210
3	Benito Juárez, Hidalgo	24°1’15.14”N - 99°15’59.23”O	0.018	0.219	0.0125	240
4	Emiliano Zapata, Hidalgo	24°1’15.88”N - 99°12’59.76”O	0.021	0.307	0.0395	460
5	Las Crucitas, Güémez	24°0’32.16”N - 99°10’7.16”O	0.025	0.330	0.0345	460
6	Ceilán, Güémez	23°58’27.37”N - 99°7’54.12”O	0.024	0.274	0.0405	1100
7	El Progreso, Güémez	23°58’14.21”N - 99°5’19.43”O	0.025	0.272	0.0505	1100
8	Miraflores, Güémez	23°57’48.21”N - 99°2’14.39”O	0.024	0.232	0.0455	1100
9	Cabecera, Güémez	23°57’12.94”N - 98°59’14.68”O	0.028	0.168	0.0395	>2400
10	Cabecera, Güémez	23°56’10.08”N - 98°56’16.03”O	0.034	0.223	0.0455	>2400
11	Pastizales, Padilla	23°55’23.74”N - 98°53’17.38”O	0.037	0.227	0.0595	460

* MPN or most probable number of fecal coliforms

Heavy metals. The concentration of heavy metals in the samples from the Corona River can be seen in Table 1. Copper and cadmium are increasing along the Corona River, only copper shows an increase in stations 4-5 (Emiliano Zapata and Las Crucitas), gradually decreasing from stations 6-9 and rising at the end (stations 10 and 11). The absence and presence of heavy metals in the water of the Corona River may be related to agricultural companies or water runoff from the farm area (Rubio et al. 2005). The central region of Tamaulipas has crops such as safflower, citrus, chili, corn, melon, watermelon, and sorghum that use copper oxychloride, copper chelate, copper monohydrate, or pentahydrate as an antifungal, fertilizer, or pesticide (Heyer et al. 2008). Station 4-5 is far from citrus companies, the main crop in the region, which uses products with copper, a factor that can reduce the presence of this metal in the water. However, the decrease of this metal at station 6 reveals the importance of understanding the interaction of heavy metals with the different sedimentation processes, environment, and local flora and fauna that can alter the content of heavy metals in the water of the rivers (Galindo et al. 2005, Wakida et al. 2008, Li et al. 2015). None of the levels of copper and cadmium found are outside the maximum permissible limit (MPL) according to official Mexican standards (NOM-127-SSA1-1994; NOM-001-SEMARNAT 1996; NOM-002-SEMARNAT-1996). The sampling station with the highest concentration of lead was station 5 (0.33 mg L^{-1}) and the one with the lowest concentration was station 1 with 0.142 mg L^{-1}. NOM-001-SEMARNAT-1996 shows an MPL level of lead at 0.2 mg L^{-1}, most of the sampling stations in the Corona River are above this level, except stations 1, 2, and 9. On the other hand, NOM-002-SEMARNAT-1996 indicates an MPL of 1.0 mg L^{-1} for this metal, where no sampling station has an equal or higher value. The Mexican national standard NOM-127-SSA1-1994 indicates that the MPL for lead is 0.025 mg L^{-1}, where the present investigation reveals that all sampling stations in the Corona River have higher values of this metal (Table 1). The levels of heavy metals analyzed (cadmium, lead) in the different sampling stations of the Corona River are lower than those detected in rivers of Tamaulipas, Mexico (Río San Marcos and Río Tigre) and Baja California Norte, Mexico (Río Tecate and Tijuana River) as detected by Wakida et al. (2008), Vázquez-Sauceda et al. (2012), and López et al. (2020) suggesting that restoring the freshwater quality of the Corona River may be less difficult than in previously mentioned rivers that have greater contamination. Cedillo-Leal et al. (2016) detected the presence of heavy metals in the South of Tamaulipas, Mexico that affect the quality of freshwater, ecosystems, and regional fauna, showing that these contaminants come from anthropological, agricultural, and regional mining waste. Miller et al. (2003) show that the level of lead, cadmium, and copper in agricultural water from the Mondragón, Tasapampa, Tuero Chico and Sotomayor rivers, Pilcomayo River, Bolivia range from <0.2-81.4, <0.1-0.9, and 1.9- 17.6 μgL^{-1} respectively, where only the water from the Mondragón Riviera showed high levels of cadmium and lead, by what is indicated by their laws for the use of water for agriculture. Similar results were detected by Copaja et al. (2016) to determine the levels of cadmium (0.03 mg L^{-1}), copper (0.0006 mg L^{-1}), and lead (0.07 mg L^{-1}) in the water of the Mediterranean rivers, Chile.

This research highlights the importance of having current information about contaminants, and how this can help to adequately understand their ecological impact on the Corona River and the quality of its freshwater. It should be shown that as the flow of the Corona River decreases and meets the product of human activities, the levels of fecal coliforms and heavy metals increase (Table 1), possibly due to the lack of adequate drainage, sewage, and sewage systems. oxidation lagoon, livestock activities (animals drink directly from the river), and agricultural activities where water runoff from crops ends up in the river. This contamination can affect the quality of water and food grown in the area, directly damaging the ecological, tourist-economic, and health services in the Corona River area. The sustainable development of communities and the efficient management of water resources must be supported by collaborative work between local public administration, civil society organizations, scientists, and businessmen as the fundamental axis of said development. Likewise, thanks to this work, gives rise to future research regarding the quality of water in the central region of Tamaulipas, since this fundamental resource is currently threatened, and its analysis, management, and care require greater interest. in society, science, and technology.

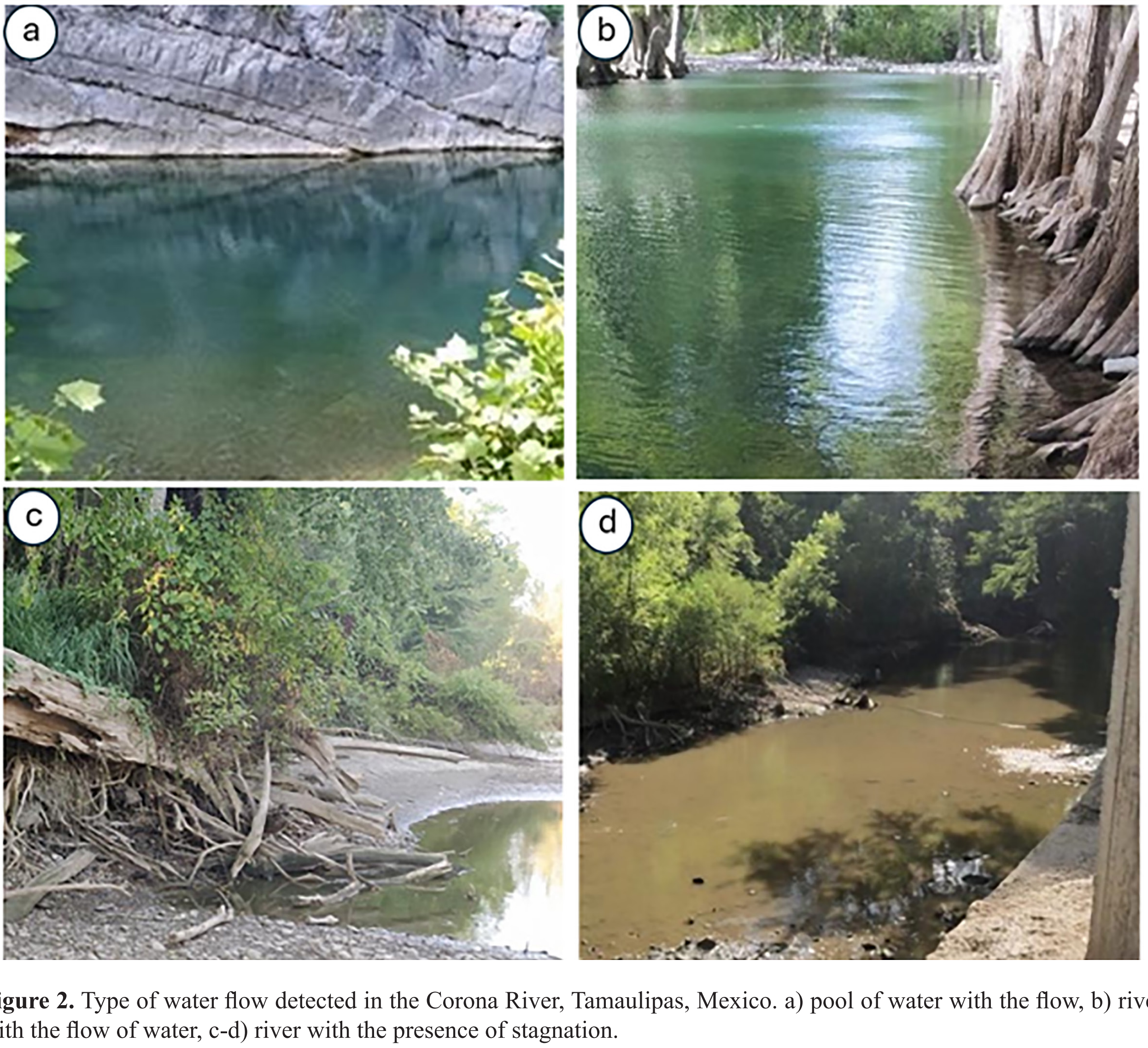

Figure 2. Type of water flow detected in the Corona River, Tamaulipas, Mexico. a) pool of water with the flow, b) river with the flow of water, c-d) river with the presence of stagnation.

Limitations of the Study. The study of water quality has limitations in the type of analysis, the length of time and period in which the study was conducted, the size and number of samples, and the specific use of water (agriculture, livestock, tourism, urban use, etc.). This generates different pollutants and changes the management actions to improve water quality. Some elements change the understanding of water quality, such as when sampling is through because this is carried out at a certain point in time (a few months, a couple of seasons, a year) and does not consider changes in water qualities, or long-term water quality. Another limitation of this type of study is that it is limited to a set of parameters, without considering other parameters that are also pollutants (pesticides, nitrogen products, other heavy metals or germs, etc.). The way of viewing pollutants is another element that impacts water quality studies, since by limiting it to human health the general perspective of the impact of toxic elements on the environment is lost.

CONCLUSION

The results observed for the different analyses determined the presence of higher levels of fecal coliforms and heavy metals than those established in the Mexican Standards in different sampling stations, generating a gradual increase in contaminants as the water of the Corona River advanced until its end in the Vicente Guerrero dam. This study shows the importance of increasing studies on these topics to make better use of freshwater in rural regions where there are permanent and/or intermittent rivers.

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