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Impact of the Citrus Industry on the Water Quality of the Filobobos River in Veracruz, Mexico

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Abstract: Veracruz, Mexico, boasts abundant water resources. However, the region is facing challenges stemming from population growth and industrial expansion, leading to a notable increase in wastewater discharge into surface water bodies. This discharge has resulted in significant alterations to water quality. In this study, we analyzed the water quality in the Bobos River, Veracruz, with a focus on sustainability. A total of 12 samples were collected from various points along the reservoir. Parameters including temperature, pH, dissolved oxygen (DO), conductivity, total nitrogen (TN), nitrate, chemical oxygen demand (COD), total phosphorus (TP), phosphate, dissolved solids (DSs), and fecal coliforms (FCs) were measured and analyzed. The pH levels ranged from slightly acidic (6.40 ± 0.71) to slightly alkaline (8.65 ± 0.07), with the lowest dissolved oxygen concentration recorded at 0.15 ± 0.07 mg L^{-1}. Conductivity varied between 0.26 and 3.81 mS. Total nitrogen concentrations ranged from 0.21 ± 3.8 to 0.491 ± 1.3 mg L^{-1}. Dissolved solid concentrations were measured at 0.39 ± 0.05 mg L^{-1}, while the final sampling point exhibited elevated values for temperature, nitrate, chemical oxygen demand, total phosphorus, and coliforms (30.35 ± 0.21 °C, 0.35, 389.00 ± 11.31, 13.20 ± 0.85 mg L^{-1}, and 3.2 × 105 ± 3.707107 × 10^4, respectively). To address these concerning trends and safeguard public health and environmental integrity, the implementation of continuous monitoring and stringent control measures is imperative.

Keywords: water pollution; Bobos River; physicochemical parameters; urban development; industrial development

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1. Introduction

Urbanization, population growth, and industrial and agricultural development can significantly impact river quality [1]. Research indicates a strong correlation between urbanization [2] and water quality deterioration. As cities expand, water pollutants, including chemicals, heavy metals, and nutrients [3], increase. In many developing countries, insufficient public policies fail to adequately protect natural resources like water [4,5]. This is particularly evident in rivers receiving untreated wastewater, which diminishes their dilution and self-purification capacities. The economic repercussions of river pollution affect vulnerable sectors, including fishing [6], livestock [7], and agriculture [8], and pose extinction risks to ecosystem organisms [9].

In Mexico, major population centers are often located along riverbanks, leading to over 70% of water bodies exhibiting some contamination and severe issues regarding availability and access to this resource [10]. Approximately 40% of generated wastewater, both industrial and domestic, is discharged into surface water bodies without prior treatment [11]. Veracruz State, Mexico, boasts significant water resources, with 17 hydrographic basins and 24 rivers. However, these rivers are impacted by wastewater from population centers and industries, making it unclear if they have any treatment processes. Mexican standards NOM-001-SEMARNAT-1996, NOM-002-SEMARNAT-1996, and NOM-003-SEMARNAT-1997 set limits for wastewater discharges.

All water, for public or industrial use, must undergo treatment before reintroduction into the cycle. Unfortunately, Veracruz has only a few registered treatment plants, with 74 urban wastewater treatment plants identified in 2002, treating only 30% of wastewater. The number of treatment plants in the 212 municipalities of Veracruz is insufficient, leading to inadequate treatment of urban wastewater that only focuses on certain parameters such as solids, carbon, and coliforms and can be considered as non-functional.

Access to clean drinking water is indispensable for fostering human health and promoting sustainable development. Regrettably, human activities pose a threat to water quality across diverse regions globally, and the Bobos River basin in southeastern Mexico stands as no exception to this concerning trend. Specifically, the discharge of waste originating from the citrus industry significantly compromises the river's water quality. Hence, this study undertakes a comprehensive physicochemical and microbiological assessment of water quality within the Bobos River, with a primary focus on analyzing the detrimental impact caused by the citrus industry in the area. Furthermore, it endeavors to address environmental sustainability concerns surrounding industrial operations by advocating for the implementation of sustainable measures aimed at mitigating adverse effects and fostering the preservation and conservation of the Bobos River and other water bodies alike.

2. Materials and Methods

2.1. Description of the Bobos River Basin

The study area encompasses the Nautla River basin, traversing the municipalities of Plan de Arroyos, Tlapacoyan, Martínez de la Torre, San Rafael, and Nautla, located in Veracruz, Mexico, until its convergence with the Gulf of Mexico. The basin exhibits a maximum elevation of 3299 m and a minimum of 6 m, spanning approximately 121 km in its main channel. Its average slope measures 3.25%, with a retention time of 520 min. The region sustains a population of 366,500 inhabitants, residing in approximately 97,500 occupied dwellings.

It is noteworthy that roughly 92,500 homes are equipped with piped water infrastructure, while 3400 lack such access. Additionally, 90,500 households benefit from sewerage systems, while 6500 do not. Notably, there are settlements close to the Bobos River (Figure 1).

2.2. Sampling

2.2.1. Area of Study

The study area encompasses the Nautla River basin, situated in the states of Puebla and Veracruz, Mexico, spanning a total area of 3544 km^2. This basin extends across several municipalities, including Puebla, Teziutlán, Martínez de la Torre, Misantla, and Nautla. The Nautla River, with a length of 121 km, eventually merges into the Gulf of Mexico. The relief of the basin is predominantly mountainous, featuring altitudes ranging from 50 to 3299 m above sea level. The region exhibits a warm and humid climate, characterized by annual precipitation levels varying from 1000 to 3500 mm [12].

On the other hand, the Bobos River basin, situated in Veracruz, Mexico, encompasses an area of 1417 km^2 and extends over a length of 77 km. The Bobos River itself measures 58 km in length, with an average slope of 1.5%. The region experiences an average annual precipitation of 2229 mm, with 75% of rainfall concentrated during the June to October season. However, intensified agricultural and livestock activities, coupled with deforestation and urbanization, have heightened the basin's susceptibility to soil erosion and sedimentation [13].

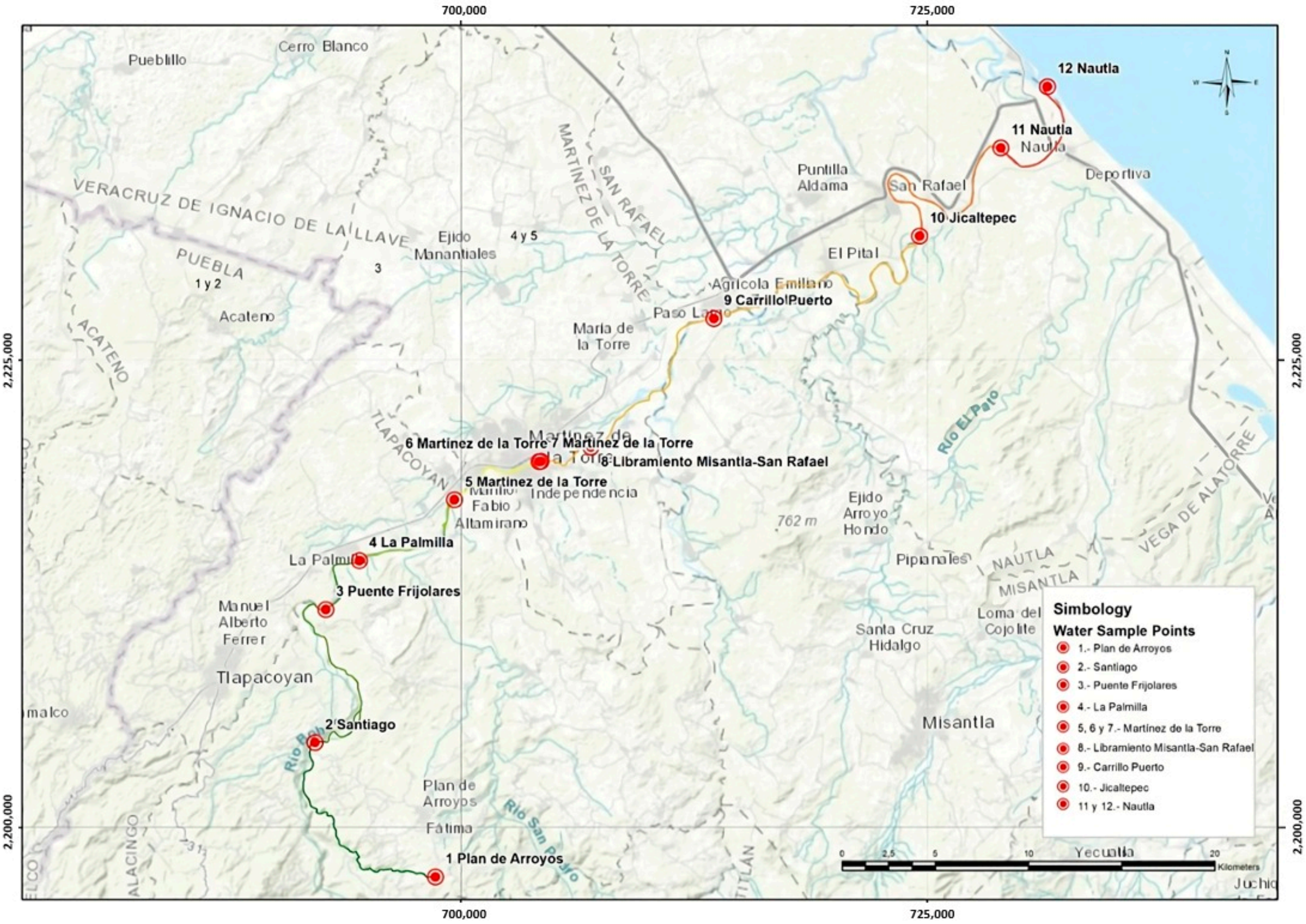

Figure 1. Location of the study area and sampling site in the Bobos River basin.

2.2.2. Water Samples

Six water samples were systematically collected at twelve distinct points along the Bobos River (Figure 1) in the summer season (June) of 2022. The sampling points were sequentially numbered in ascending order as the river flowed downstream, ranging from SW1 to SW12. High-density polyethylene containers, each with a capacity of 2 L, were employed to gather the water samples. Concentrated nitric acid was added to the containers to attain a pH level below 2, ensuring preservation during transportation and subsequent analysis.

Following collection, each container was meticulously labeled with the corresponding date, name, and location of the sampling site. Subsequently, the samples were securely stored in coolers, adhering to established transportation protocols and guidelines [14,15]. Sampling was conducted between 6:30 am and 9:00 am.

pH was measured at each site immediately after sampling using a portable pH meter (HANNA Instruments, Smithfield, RI, USA, HI98130).

Electrical conductivity was measured at each site immediately after sampling using a portable meter (HANNA Instruments, Smithfield, RI, USA, HI98130).

Temperature was measured at each site immediately after sampling using a portable meter (HANNA Instruments, Smithfield, RI, USA, HI98130).

Dissolved oxygen was measured at each site immediately after sampling using a portable meter (Milwaukee, Mulund West, Bombay, Maharashtra, India, model 600).

Parameters such as chemical oxygen demand (COD) [16], total nitrogen, NO_3, total phosphorus (TP), PO_4, and fecal coliforms were determined at the Wetlands and Environmental Sustainability Laboratory located at the Instituto Tecnológico Nacional de México Campus Misantla, Veracruz. Samples were preserved at 4 °C until processing; the techniques used were taken from the Mexican Standards which are based on the standard methods for water and wastewater analysis [15].

The research point was determined using a "sample survey method", which is a sampling method carried out by dividing the research area into points that are expected to represent the study population.

The determination of sampling points was based on consideration of ease of access, costs, and time so that the points were considered to represent the water of the Bobos River.

The initial step in determining the location of river water sampling is to know the geography of the river and the activities around the watershed [17–19].

2.2.3. Quantification of NaOH (Sodium Hydroxide) (%)

The quantification of NaOH percentage was performed using the titration method, where drops of phenolphthalein were added, and titration was carried out with sulfuric acid (0.1 N). The NaOH percentage was determined using the following formula:

$$\%\text{NaOH} = \text{Volume of acid used} \times \text{Acid normality} \times \text{meq of NaOH } (0.04) \times 100/\text{Weight of the analyzed sodium sample}.$$

2.3. Statistical Analysis

To investigate the relationship between water quality factors, correlation analysis and principal component analysis (PCA) were performed using Statistical Package for the Social Sciences software (SPSS, ver. 25.0; SPSS Inc., Chicago, IL, USA).

3. Results and Discussion

3.1. Temperature and Dissolved Oxygen

Temperature and dissolved oxygen (DO) stand as pivotal parameters in the assessment of water quality within aquatic systems. In this study, we observed significant variability in water temperature across the Bobos River basin, influenced by both geographic location and human activity (Table 1 and Figure 2).

Dissolved oxygen (DO) emerges as a critical parameter defining water quality and the vitality of aquatic ecosystems [20]. Aquatic flora and fauna, including fish, rely on oxygen for survival. For instance, fish cannot endure prolonged periods in water with dissolved oxygen levels below 5 mg L^{-1} [21]. Reduced levels of dissolved oxygen in water signal contamination and serve as crucial determinants in water quality assessment, pollution management, and treatment procedures [22].

The increment in water temperature along the river can be attributed to the convergence of tributaries with elevated temperatures and the reduction in water velocity as the river broadens. In certain instances, notable increases in water temperature stem from the discharge of industrial wastewater [22]. Regular monitoring of temperature levels and other water quality variables is imperative to ensure the sustainability of the river ecosystem in the Bobos River basin, even though water temperature values fall within normal ranges.

Our study unveiled that the highest dissolved oxygen (DO) value in the river was documented at SW4, accompanied by an average temperature of 28.68 ± 0.32 °C. Notably, there exists a temperature differential of 10 °C between the lowest and highest points. Rajesh et al. [23] note that for every 1 °C elevation in river water temperature, there is an approximate 2.3% decline in DO saturation level concentrations. However, our study did not discern this relationship, potentially influenced by climate-change-induced warming of river water [24] and supplementary anthropogenic heat emissions [25]. In a study conducted by Sousissi et al. [26], analyzing 25 water bodies, the average annual temperature was determined to be 28 °C.

Table 1. Temperature and DO concentration.

Parameter	Temperature (°C)	DO (mg L^{-1})
SW1	20.21 ± 0.28	0.15 ± 0.7
SW2	26.7 ± 0.14	0.25 ± 0.07
SW3	27.35 ± 0.07	3.80 ± 0.42
SW4	29.60.71 ± 0.12	6.45 ± 1.06
SW5	30.25 ± 0.64	0.30 ± 0.14
SW6	29.80 ± 0.4	2.64 ± 0.05
SE7	29.55 ± 0.07	0.70 ± 0.14
SW8	29.40 ± 0.42	0.25 ± 0.021
SW9	30.50 ± 0.57	0.15 ± 0.07
SW10	30.20 ± 0.14	0.25 ± 0.07
SW11	30.30 ± 0.14	0.35 ± 0.21
SW12	30.35 ± 0.21	0.60 ± 0.14

DO: dissolved oxygen; SW: water sample point; ±: standard deviation.

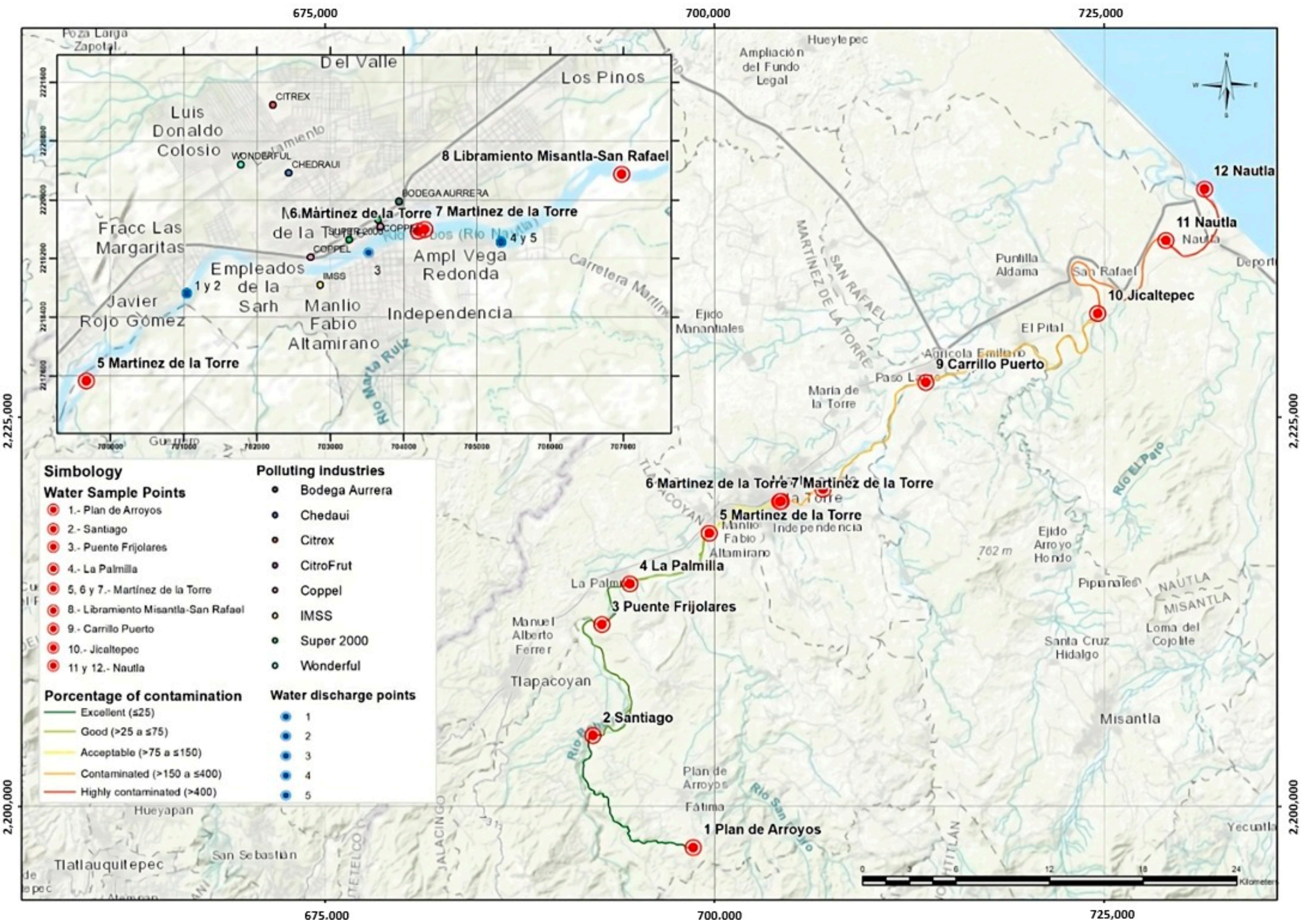

Figure 2. Localization of the study area and industries.

The optimal DO concentration in a healthy water body ranges from 8 to 12 mg L^{-1}, with concentrations below 8 mg L^{-1} posing adverse effects on the survival of aquatic species [27]. As depicted in Table 1, values observed at the assessed points are <6 mg L^{-1} (excluding SW4), limiting the presence of aquatic life in general. Another factor influencing DO levels is the turbulence of the current due to air, which aids in its dissolution in water. A water body registering a dissolved oxygen level $\leq$ 2 mg L^{-1} or $\leq$30% saturation is categorized as hypoxic [28]. Oxygen depletion or low oxygen content typically arises from a combination of heightened biological productivity and diminished water exchange [29].

The influence of water temperature on dissolved oxygen (DO) levels, particularly in polluted conditions, has been extensively documented [30]. Elevated temperatures can exacerbate low DO levels by accelerating the decomposition of organic matter, thereby inducing alterations in ecological and environmental conditions, such as heightened eutrophication through increased nutrient discharge into sediments [31]. Furthermore, when dissolved oxygen levels plummet, fish and other aquatic organisms struggle to survive. Cold water has a higher capacity to retain oxygen, whereas warm water tends to dissolve less oxygen. In this study, no significant correlation was observed between these variables. Samples SW1 and SW7 exhibited identical DO values despite temperature variations.

It has been established that water temperature can significantly influence the amount of dissolved oxygen in water, particularly under polluted conditions. Elevated temperatures can exacerbate low dissolved oxygen (DO) levels by intensifying the decomposition of organic matter, thereby inducing changes in ecological and environmental conditions, such as an increase in eutrophication through enhanced nutrient release into sediments. Additionally, when dissolved oxygen levels plummet, fish and other aquatic organisms face survival challenges. Colder water possesses a higher capacity to retain oxygen, whereas warmer water tends to dissolve less oxygen. However, in this study, no correlation was identified between these parameters.

The samples SW1 and SW7 exhibited identical dissolved oxygen (DO) values despite temperature variations. The results obtained in this study ranged between 0.15 ± 0.07 and 6.45 ± 1.06. In a comparison between these findings and those from a study on the Bagmati River, where the dissolved oxygen fluctuated between 2.1 mg L^{-1} and 8.4 mg L^{-1}, such a wide variation can be attributed to a higher organic load originating from urban areas. There exists an approximate difference of 6 units between the data obtained in this study and the findings of Giri et al. [32], where the main source of contamination is industrial.

3.2. pH and Conductivity

pH stands as a critical determinant influencing water quality and the viability of aquatic life. When pH levels deviate from the optimal range, adverse impacts on aquatic flora and fauna can occur [33], potentially indicating the presence of contaminants. The pH of most natural waters typically falls within the range of 6.5 to 8.0 [29], primarily regulated by the carbonate system. However, the ideal pH for river water should hover around 7.4 [34].

In this study, pH levels generally remained within the anticipated range for freshwater bodies, albeit exhibiting slight alkalinity or acidity at certain points (Table 2). Notably, Point SW4, situated near population (Figure 2), registered the highest pH levels, hinting at potential human-induced alterations in water quality at this locale, with variations observed from slightly acidic to slightly alkaline. It is noteworthy that certain aquatic organisms struggle to thrive in acidic environments. Except for SW6, pH values trended slightly above optimal levels, tending towards alkalinity; this point is in close relation to the companies located in the area. The presence of human settlements around SW3 may contribute to this pH elevation owing to wastewater discharge with higher pH levels than natural waters.

Table 2. pH and conductivity at the sampled points.

Sites	pH	Conductivity (mS cm^{-1})
SW1	7.85 ± 0.02	0.30 ± 0.14
SW2	8.60 ± 0.14	0.27 ± 0.01
SW3	8.55 ± 0.07	0.28 ± 0.01
SW4	8.65 ± 0.07	0.27 ± 0.01
SW5	7.50 ± 0.14	0.26 ± 0.03
SW6	6.40 ± 0.71	0.72 ± 0.03
SW7	7.75 ± 0.08	0.70 ± 0.01
SW8	8.25 ± 0.21	0.34 ± 0.04
SW9	7.75 ± 0.04	0.75 ± 0.02
SW10	7.77 ± 0.05	0.54 ± 0.04
SW11	7.78 ± 0.05	0.37 ± 0.02
SW12	7.87 ± 0.09	3.81 ± 0.04

SW: water sample point; ±: standard deviation.

Therefore, sustained monitoring of pH levels within the watershed remains imperative to avert adverse impacts on aquatic life and the broader aquatic ecosystems (Figure 2). Extreme pH conditions can render a water body inhospitable to life, with low pH proving particularly detrimental to fish and immature insects. Additionally, acidic water accelerates the leaching of heavy metals, posing toxicity risks to fish.

Pure water exhibits low electrical conductivity due to the absence of ions in the solution. Conversely, river water harbors dissolved ions, rendering its conductivity proportional to the concentration of dissolved mineral salts and temperature [35]. Table 2 delineates the conductivity values documented in this study, revealing notable variations among the different sampling points. Notably, SW12 exhibited the highest and significantly disparate conductivity value compared to other points ($p < 0.05$). Elevated electrical conductivity in natural water bodies is primarily attributed to household and commercial waste, salts dissolved via natural runoff, regional geology, and human activities. A substantial alteration in conductivity signals potential discharge or pollution sources in a water body [36,37].

River conductivity typically fluctuates between 50,000 and 1,500,000 mS cm^{-1} [38]. Conversely, Rios-Villamizar [39] assessed the water quality of various Amazonian rivers (Tapajós, Incoloros streams, Cuparí, Jutaí, Tefé, and Juruá), noting diverse electrical conductivity levels, with values of 0.014331, 0.01512, 0.0599, 0.00871, 0.007367, and 0.19114 (mS), respectively. Compared to the findings of this study, these values appear diminutive.

Low conductivity (ranging from 0 to 0.2 mS cm^{-1}) serves as an indicator of pristine or baseline conditions. Mid-range conductivity (ranging from 0.2 to 1 mS cm^{-1}) represents the typical background for most rivers and lakes, as evidenced by the observations at SW1 to SW9. Conductivity levels beyond this spectrum could suggest unsuitability for certain animal species. Elevated conductivity (ranging from 1 to 10 mS cm^{-1}) signifies saline conditions [40], as observed at SW12.

3.3. Total Nitrogen, NO_3^-, and Total Phosphorus, PO_4^-

Nitrate, a chemical compound resulting from the combination of nitrogen and oxygen, occurs naturally in trace amounts in drinking water. However, elevated nitrate levels detected in surface waters may signify contamination stemming from the presence of industrial and municipal fertilizers [41].

In this study, total nitrogen concentrations exhibited an ascending trend from SW1 to SW12, with a notable disparity ($p < 0.05$) among sampling points. Furthermore, it was noted that both total nitrogen and nitrate ($N\text{-}NO_3^-$) concentrations, along with the $NT/N\text{-}NO_3^-$ ratio, were notably higher at points SW6 to SW12. This suggests either unfavorable conditions for the oxidation of nitrogen to nitrate in the riverbed or the presence of an additional nitrogen source, such as nearby human settlements or industrial discharges proximate to the sampling sites.

Elevated nitrogen concentrations in surface waters can adversely impact the aquatic ecosystem, leading to diminished dissolved oxygen levels and toxicity to aquatic species. Moreover, intensified agricultural, livestock, and industrial activities, coupled with population growth and industrial centers within a watershed, can substantially alter nitrogen and phosphorus concentrations in water [42] (Figure 2). It is worth noting that nitrate also poses a health risk, with the permissible limit in water intended for human consumption set at 10 mg L^{-1} [43]; this limit was not exceeded in our study.

Phosphorus originates from various sources, both natural and anthropogenic, including soil, rocks, wastewater treatment plants, runoff from fertilized areas, and industrial activities [44]. Surface water sources of phosphorus encompass agricultural and urban runoff, soil erosion, wastewater treatment plant discharges, atmospheric deposition, and industrial operations, according to a 2021 report by the Minnesota Natural Resources Council. The report highlights that phosphorus can also leach from sediments accumulated at the water body's bottom, subsequently fueling algal blooms and compromising water quality [45].

Orthophosphate, the oxidized mineral form of phosphorus, mirrors total nitrogen's pattern, indicating suboptimal conditions for the oxidation of phosphorus to orthophosphate from SW1 to SW5 and from SW6 to P12 (Figure 3b).

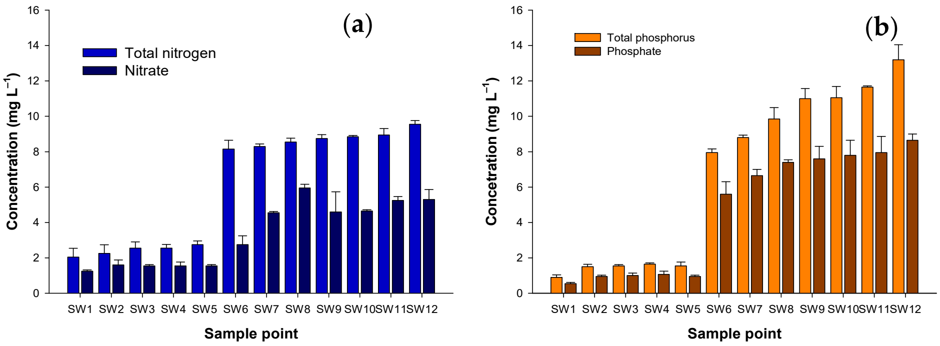

Figure 3. (**a**) Total nitrogen and nitrate concentrations; (**b**) total phosphorous in the river channel evaluated.

The concentration of phosphorus in domestic wastewater typically ranges from approximately 4 to 50 mg L^{-1} [46]. Within this study, values falling within this range were observed, specifically at points SW6 to SW12. These findings suggest potential wastewater discharges into the river, likely attributed to the proximity of human settlements along the water body's banks, as depicted in Figure 3b. The highest phosphate concentration was detected at SW12, surpassing values reported in a study by Fadiran et al. [47], ranging between 0.01 and 0.09 mg L^{-1}. Upon comparison with studies conducted in rivers within the Manzini and Lubombo regions of Swaziland, it becomes apparent that the average phosphate levels exceed the recommended threshold of 2.0 mg L^{-1} set by the SWSC (Swaziland Water Service Corporation). Specifically, the values obtained in this study are up to 23 times higher than those reported by Fadiran et al. [47]. This discrepancy may arise from material originating from higher elevations reaching the site and being retained due to flatter relief.

Furthermore, total nitrogen levels in water tend to increase downstream, attributed to the cumulative total nitrogen transported by water from its source to its terminus. The EPA (Environmental Protection Agency) has established recommended limits of 0.05 mg L^{-1} of total phosphate in lake inlets and 0.1 mg L^{-1} of total phosphorus in runoff. It is essential to acknowledge that these limits are established to uphold water quality standards and safeguard the environment.

3.4. Total Nitrogen/Total Phosphorus Ratio

The nitrogen/phosphorus (N/P) ratio in river water serves as a pivotal indicator of aquatic ecosystem health and profoundly influences the growth of aquatic organisms such as algae, plants, and phytoplankton. In this study, the dynamics of these two parameters exhibit similar trends (Figure 4a). An imbalanced N/P ratio can precipitate excessive growth of algae and aquatic plants, culminating in eutrophication and adverse impacts on water quality and dependent organisms. Typically, an N/P ratio of 16:1 is deemed optimal for the growth of aquatic organisms in freshwater. However, N/P ratios may vary contingent on geographical location and specific environmental conditions [48], as evidenced in Figure 4b of this study.

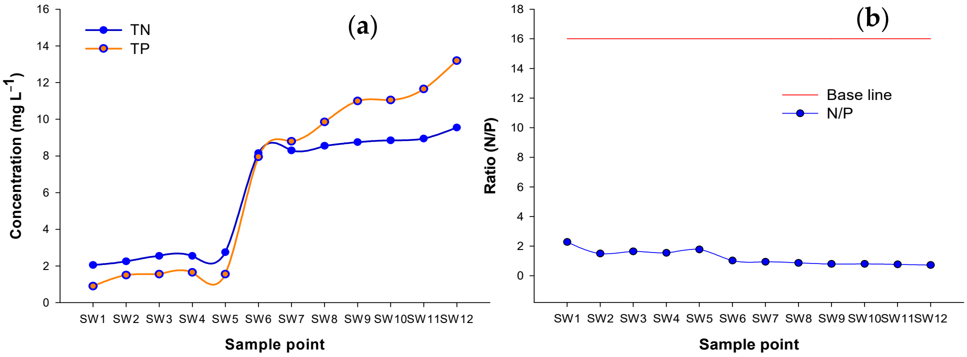

Figure 4. (**a**) Ratio between NT and PT; (**b**) N/P ratio. TN: total nitrogen; TP: total phosphorous.

The influx of phosphorus (P) and nitrogen (N) into freshwater systems can trigger the overgrowth of aquatic plants, oxygen depletion, and deleterious alterations in aquatic fauna diversity [49]. Total nitrogen (TN) and total phosphorus (TP) stand as primary nutrients instigating water body eutrophication [50]. Phosphate and nitrate emerge as critical limiting nutrients, fostering eutrophication in freshwater systems [50].

3.5. Chemical Oxygen Demand (COD) and Total Dissolved Solids (TDSs)

Sources of COD include leaves and woody debris, dead plants and animals, animal manure, effluent from pulp and paper mills, wastewater treatment plants, feedlots, feed processing plants, failing septic systems, and urban stormwater runoff. Discharges of wastes with high COD levels can cause water quality problems such as severe dissolved oxygen depletion and fish kills in receiving waters [51].

High COD levels not only pose water quality concerns but also raise public health apprehensions. The decomposition of organic matter in water can engender the formation of toxic organic compounds, such as trihalomethanes, which have been associated with an escalated risk of cancer and other health maladies. Thus, COD emerges as a pivotal parameter for gauging the presence of organic compounds in contaminated wastewater [52].

A study by Lee et al. [53] assessed COD levels in four rivers in South Korea, revealing values ranging from 0.8 mg L^{-1} to 11.6 mg L^{-1}. In contrast, in the present study, values ranged from 0 mg L^{-1} to 381 mg L^{-1} (Figure 5a), denoting higher contamination levels in the examined samples. Another study by Perez-Castresana et al. [54] scrutinized the contamination of the Atoyac River in the metropolitan area of Puebla, Mexico, unveiling average COD values of 130.91 $\pm$ 39.52 mg L^{-1} in the wet season and 260.60 $\pm$ 75.32 mg L^{-1} in the dry season. Conversely, the average value obtained in this study was 185.06 $\pm$ 169.23 mg L^{-1} (Figure 5a), indicating substantial variability among sampling points and an intermediate concentration compared to the Atoyac River study. The COD concentration significantly escalated downstream (SW7-SW12). In another study that evaluated only six points, COD concentrations were documented at 118.8 mg L^{-1} at the first point and 138.6 mg L^{-1}, implying mild contamination [17]. In this research, values ranged from 0 to 389 $\pm$ 11.31 mg L^{-1}, considered severe.

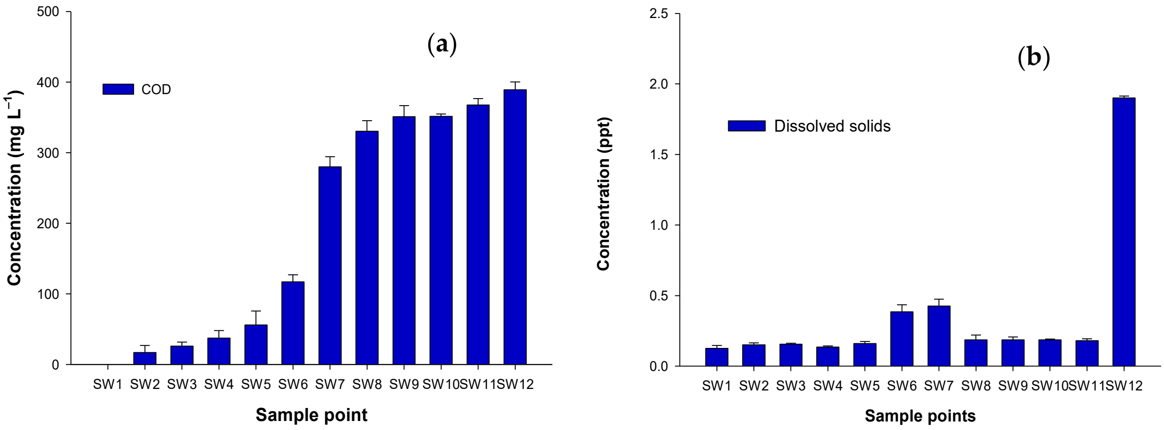

Figure 5. (**a**) Concentration of COD and (**b**) concentration of dissolved solids.

The variation in dissolved solids was noteworthy ($p < 0.05$) for SW6, 7, 12 (Figure 5b). Dissolved solids' composition may encompass salts, metals, metalloids, and dissolved organic matter [55]. Processes contributing to organic dissolved solids in streams involve the release of organic molecules during biological growth (e.g., by plant roots and microbes) and the decomposition of organic matter within the stream or on its banks. As per the NOM-001-SEMARNAT-1996 standard, the TSS content should be less than 150 mg L^{-1} for agricultural use, less than 75 mg L^{-1} for urban public use, and less than 40 mg L^{-1} to preserve aquatic life [56].

The most substantial concentration with a significant difference ($p < 0.05$) was noted at SW12 (refer to Figure 5b). Dissolved solids in water are a focal point in environmental research due to their potential impact on water quality and human health.

According to a study by Akpan et al. [57], average values of 156.1 mg L^{-1} were reported, approximately half of the average obtained in this study (350 ± 20 mg L^{-1}). Dissolved solids may encompass salts, metals, and dissolved organic matter, stemming from biological processes such as organic matter decomposition and plant and microbe growth. In another study in the Usumacinta River, an average of 265.7 mg L^{-1} was documented, a value close to that found in this study.

Elevated concentrations of total dissolved solids can diminish water clarity, contributing to reduced photosynthesis and elevated water temperature. Excessively high or low dissolved solid concentrations may impede growth and lead to the demise of numerous aquatic organisms. Dissolved solids induce toxicity through salinity increments, alterations in water ionic composition, and toxicity of individual ions. Salinity rises have been shown to prompt shifts in biotic communities, curtail biodiversity, exclude less-tolerant species, and induce acute or chronic effects at specific life stages [58].

3.6. Fecal Coliforms (FCs)

According to the World Health Organization (WHO), coliform bacteria represent a group of microorganisms found abundantly in human and animal feces. Their presence in water may signify fecal contamination and, consequently, the potential existence of other associated pathogens [59]. Coliform bacteria, originating from untreated sewage, and septic tanks, among other sources, can lead to severe illnesses such as gastroenteritis or diarrhea [60]. Fecal bacteria groups such as Escherichia coli (the most commonly isolated organism in clinical laboratories [61], *Klebsiella*, and *Enterobacter*, typically found in the gastrointestinal tract of warm-blooded animals [62], serve as indicators of water quality. Their presence correlates with some of the most challenging-to-detect pathogens, including *Salmonella*, *Shigella*, and *Vibrio*, which can cause gastroenteritis, dysentery, typhoid, and cholera.

Table 3 delineates the distribution of fecal coliforms at the twelve study sites along the Bobos River. A discernible increase in the concentration of these microorganisms from SW1 to SW12 is observed. As depicted in Figure 2, this escalation in coliform density primarily stems from the type of discharge present at each sampling point. The study identifies a significant variation ($p < 0.05$) in CFU values across different sampling points (refer to Table 3). Vigilance over fecal contamination in water utilized for industrial and recreational purposes remains imperative owing to the economic and public health implications. Total and fecal coliform concentrations exhibit low levels at upstream stations and gradually escalate toward downstream stations, a trend akin to findings in [60].

Table 3. Fecal coliform concentration.

Water Sample Point	FCs (UFC 100 mL^{-1})
SW1	$0 \times 10^0 \pm 0 \times 10^0$
SW2	$7.255 \times 10^2 \pm 1.0677 \times 10^2$
SW3	$1.005 \times 10^3 \pm 5.657 \times 10^1$
SW4	$1.215 \times 10^3 \pm 1.3435 \times 10^2$
SW5	$8.16625 \times 10^4 \pm 7.425 \times 10^1$
SW6	$8 \times 10^4 \pm 8.48528 \times 10^3$
SW7	$1.175 \times 10^5 \pm 3.53553 \times 10^3$
SW8	$1.91 \times 10^5 \pm 5.65685 \times 10^3$
SW9	$2.2 \times 10^5 \pm 2.12132 \times 10^4$
SW10	$2.322 \times 10^5 \pm 4525.48 \times 10^3$
SW11	$2.385 \times 10^5 \pm 3.53553 \times 10^3$
SW12	$3.2 \times 10^5 \pm 3.707107 \times 10^4$

FCs: fecal coliforms.

These investigations underscore the significance of monitoring fecal contamination in surface waters and advocate for the implementation of control measures to curtail disease dissemination, thus safeguarding public health and the environment. Ongoing monitoring endeavors are requisite to evaluate water quality across diverse regions and institute suitable measures aimed at minimizing fecal contamination in water sources.

3.7. Quantification of NaOH (%)

Sodium hydroxide (NaOH) is a caustic substance commonly present in wastewater from drain and oven cleaners, paint and varnish removers, degreasers, dishwasher detergents, and alkaline batteries. It is utilized in the manufacturing processes of aluminum, rayon, and biodiesel and various organic synthesis procedures. Additionally, it is a frequent byproduct in chlorine production [63] and is found in pharmaceuticals such as Clintest® [64]. NaOH can significantly alter water pH [65], and its detection in drinking water may signify contamination or system malfunctions. In wastewater, NaOH detections may indicate industrial discharges or the use of cleaning products.

Proper identification and control of NaOH are paramount for preserving water quality and mitigating any adverse environmental and public health effects. However, NaOH was detected at points SW5, SW6, and SW7 in this study, with concentrations of 6.8%, 5.6%, and 3.9%, respectively. These findings could be attributed to discharges originating from settlements and industries in the study area. While the Mexican Official Standard NOM-001-SEMARNAT-2021 outlines acceptable levels of wastewater contaminants for release into national water bodies, it does not specifically address NaOH.

Concerns regarding the presence of contaminants are particularly pertinent to the local population, which utilizes these bodies of water for recreational and aquacultural purposes. Given the high level of contamination in the water, immersion in it may lead to health issues. Reports from residents suggest that contact with this tributary's water can result in skin rashes, itching, diarrhea, and respiratory illnesses. To date, there is a lack of research evaluating these conditions, underscoring the urgency of addressing this matter to safeguard the well-being of the community.

3.8. Statistical Analysis

3.8.1. Pearson Correlation

Correlation analysis determines whether a relationship exists between two variables and the degree of association between them. A positive correlation (direct relationship) is indicated when r > 0, with values closer to 1 signifying a stronger correlation. In this study, all correlated variables exhibit positive correlations, with some displaying coefficients greater than 0.90, indicating a robust connection among them. The correlations identified include SS/temp, TN, NO_3, TP, PO_4, COD, and FCs, as shown in Table 4.

Table 4. Correlation matrix of physicochemical and bacteriologic parameters in Bobos River.

Parameter	SW	Temp	pH	DO	Cond	DSs	TN	NO_3	TP	PO_4	COD	FCs
SW	1											
Temp	0.713 **	1										
pH	−0.280	−0.206	1									
DO	−0.334	0.086	0.253	1								
Cond	0.558	0.250	−0.135	−0.151	1							
DSs	0.515	0.237	−0.133	−0.120	0.991 **	1						
TN	0.909 **	0.604 *	−0.451	−0.383	0.460	0.424	1					
NO_3	0.896 **	0.546	−0.158	−0.452	0.415	0.384	0.931 **	1				
TP	0.949 **	0.591 *	−0.354	−0.408	0.531	0.486	0.985 **	0.947 **	1			
PO_4	0.933 **	0.589 *	−0.353	−0.412	0.481	0.439	0.992 **	0.960 **	0.996 **	1		
COD	0.952 **	0.588 *	−0.189	−0.458	0.470	0.420	0.936 **	0.974 **	0.970 **	0.970 **	1	
FCs	0.956 **	0.866 **	−0.203	−0.441	0.617 *	0.561	0.911 **	0.927 **	0.967 **	0.950 **	0.968 **	1

** The correlation is significant at the 0.01 level (two-sided). * The correlation is significant at the 0.05 level (bilateral). Cond: conductivity; sampling site: SW; temperature: Temp.

The examination of possible correlations between independent variables confirms a statistically significant correlation between the sampling point and the parameters listed in Table 4. The Pearson correlation coefficient reveals that as the distance from the discharges to the sampling point increases downstream, there is a corresponding rise in parameter concentrations. This suggests that pollutants evaluated are transported by the current and not naturally purified. The correlation between SS and PO_4 may be attributed to agricultural areas along the river, where diffuse pollutants, such as fertilizers and livestock feces, introduced by rainfall, contribute to coliform bacteria appearing and increasing in conducive aquatic environments [60].

A correlation between temperature and TN, TP, PO_4, COD, and FCs was observed, consistent with the findings of Tee et al. [66], who noted a linear increase in chemical oxygen demand (COD) with rising temperatures. Sources of nitrate and phosphorus include wastewater treatment plants, runoff from fertilized lawns and agricultural lands, faulty septic systems, runoff from animal manure, and industrial waste discharges [67]. Additionally, according to [68], nitrate concentration (NO_3-N) increases with stream temperature.

Conductivity (EC) and total dissolved solids (TDSs) are parameters used to characterize water salinity levels. These two parameters are correlated and are typically expressed by the equation TDSs = k EC (at 25 °C). The relationship is influenced not only by salinity content but also by material content [69,70]. Furthermore, a positive correlation was identified between TN/NO_3, TP, PO, COD, and FCs in this study, similar to the findings reported by Seo et al. [60].

3.8.2. Principal Component Analysis (PCA)

Principal component analysis (PCA) involves creating linear combinations of variables. In terms of factor loadings, a high loading is determined to be greater than 0.75, while a moderate loading falls within the range of 0.40 to 0.75. Loadings below 0.40 are regarded as insignificant according to the referenced study [71]. These techniques aim to condense the number of variables into a limited set of indices, such as principal components or factors, while endeavoring to maintain the relationships inherent in the original dataset [72,73].

The results of applying PCA for pollutant concentrations in Bobos River are reported in Table 5. According to the results of the initial eigenvalues, the three principal components were considered, which account for over 94% of the total variance. Principal component analysis for different pollutants (Table 5) is presented.

Table 5. Principal component analysis of evaluated variables.

Parameter	Component		
	PC1	**PC2**	**PC3**
TN	**0.931**	0.250	−0.108
NO_3	**0.919**	0.185	−0.232
TP	**0.921**	0.326	−0.146
PO_4	**0.936**	0.272	−0.152
COD	**0.922**	0.257	−0.203
SW	**0.909**	0.371	−0.005
FCs	**0.945**	0.135	0.216
DO	−0.211	−0.024	**0.897**
Cond	0.281	**0.957**	−0.024
SD	0.245	**0.966**	0.001
Temp	**0.740**	0.043	0.552
% of Variance	61.230	21.350	11.890
Cumulative Variance (%)	61.230	82.580	94.470

Cond: conductivity; sampling site: SW; temperature: Temp.

The first component (PC1), with 61.23% of the total variance, shows strong and positive loadings related to TN, NO_3, TP, COD, SW, and FCs, and Pearson analysis results indicated a strong correlation between metals (TN, NO_3, TP, and COD). Industry is also a significant source of anthropogenic contamination. Anthropogenic sources of COD are significant, arising mainly from industrial activities such as agri-food [74].

In PC1, a close correlation among parameters, including SW (sampling point), suggests that the sampling point exerts influence over the measured parameters. While temperature and DO may not emerge as predominant variables, ref. [75] underscores their significance, as they impact myriad life processes of organisms, along with various abiotic factors within the ecosystem.

The second component (PC2), with 21% of the total variance, is a positive weighting factor of Cond and SD. This correlation was also shown in the Pearson's correlation.

The third component (PC3) solely comprised DO, with 11% of the total variance. The DO did not correlate with any other parameter, but the presence of oxygen plays a critical role in the transformation of nitrogen and phosphorus compounds in river water [76], underscoring the importance of monitoring oxygen concentration variability in water as a tool for recommending the sustainable use of aquatic environments [52]. While it was anticipated that a correlation or clustering would be discovered between temperature and the presence of FCs in certain components, such a relationship was not observed in this analysis. This implies that FC growth may be associated with nutrients and water pH.

The primary contaminants influencing rivers worldwide include untreated sewage, the proliferation of harmful algal blooms, biodiversity degradation, and oxygen depletion due to high concentrations of chemicals. Industrial wastewater, sewage from metropolitan areas and scientific laboratories, and surface runoff from urban areas constitute the principal sources of urban wastewater [77].

3.9. The Environmental Impact of Martinez de la Torre, Veracruz, on the Bobos River

Demographic growth, urban development, and human activities in surrounding areas have significantly impacted the environment, especially in the upper parts of watersheds, where industry, population, and rainfall directly affect urban areas. The world is urbanizing at a rapid pace, and it is essential to observe the interaction between urban centers, watersheds, rivers, and slope areas to prevent risks and ensure the water supply is suitable for human consumption, which is crucial for achieving sustainable development. An example of the effects of demographic and urban growth can be observed in Martínez de la Torre, Veracruz, where as early as 1970, there was a growing and cumulative housing problem due to population growth [78].

In warm climates such as Veracruz, a population of more than 150,000 inhabitants consumes approximately 350 L of water per day and produces 262.50 L of wastewater per day. The main sources of pollution are the population living along the river (municipal wastewater) and the citrus industry in the municipality, whose wastewater is discharged into the studied water body. In 2020, the population of Martínez de la Torre will reach 108,842 inhabitants, while Tlapacoyan will have 61,337 inhabitants, San Rafael 30,351 inhabitants, and Nautla 10,130 inhabitants, totaling 210,660 inhabitants that will affect the study area [79]. These inhabitants generate wastewater and, in turn, use water from the basin and the studied water body, which can have a significant impact on water quality. Given a daily water consumption of 350 L per person in a population of this size, it is estimated that approximately 38,069,700 L of water is consumed per day, generating approximately 262.50 L of wastewater per person per day in this region. Therefore, it is calculated that the population of Martínez de la Torre generates about 28,542,750 L of wastewater per day.

After China, Mexico is the second country in the world that uses the most wastewater in agricultural activities and is the Latin American country that irrigates the most hectares with untreated wastewater [80]. An example of this is Mexico City, where wastewater is discharged into the Tula River basin, providing water to an area that is scarce due to climatic conditions [81,82]. Although this provides economic benefits to farmers in the region, the same cannot be said for the study area, as wastewater discharged into the Bobos River basin flows into the open sea, and its effects have not yet been evaluated.

The results obtained show that there is an accumulative effect in this area since nature is not able to clean the existing pollutants in time and space. This phenomenon is visible in the points SW6-SW12, where the highest concentration of pollutants is recorded downstream. According to the Water Quality Index (WQI) developed by [83], the presence of COD > 200 mg L^{-1} in surface waters indicates that they have been heavily affected by both urban and non-urban wastewater discharges. In this study, values up to 389 mg L^{-1} were detected, indicating a situation of high pollution.

The alteration of river flows and the transport of sediment downstream are responsible for the most significant environmental impacts, endangering aquatic life and riparian ecosystems. This problem poses a threat to the survival of an entire watershed, as evidenced by various studies. Considering that the world's population is expected to reach 9 billion by 2050, the demand for water, food, and energy is expected to increase significantly, with estimated increases of 55%, 60%, and 80%, respectively. This situation puts tremendous pressure on natural water systems, making it imperative to reduce the use of water resources. One possible solution would be to limit water consumption to 150 L per person per day, which would allow the generation of only 100 L of wastewater per person per day. This approach would help prevent the depletion of water resources and reduce the continuous discharge of large volumes of wastewater into surface water bodies.

Martínez de la Torre is a city in Veracruz, Mexico, known for its citrus production, particularly lemons and oranges [84]. Despite being known for its citrus industry, it has negatively impacted the local environment, particularly water quality and public health. In addition to contamination during the citrus production chain, the industry has been responsible for contamination with organic waste from juice exporting companies such as Citrusper, Citrex, Citrofrut, and Sicar Farms. These companies have been discharging contaminated water into the Bobos River for many years [85] (Figure 6a). However, it was not until 2014 and 2015 that PROFEPA initiated administrative proceedings against Citrofrut, S.A. de C.V., and Cítricos Ex, S.A. de C.V., primarily for irregularities in wastewater discharges and the characterization of the sludge generated in the treatment plant.

(**a**) (**b**)

Figure 6. (**a**) Discharges of wastewater from two major citrus companies (1 and 2); (**b**) environmental conditions of a transect of the Bobos River (SW5-7).

So far, there is no additional information on the characterization of the Bobos River. However, it is known that the inhabitants of this community are economically dependent on aquaculture activities. They deplore this serious pollution, which is gradually reducing the fish population. The local population points out that the citrus companies located in this region are the main culprits for the death of crustaceans and fish because they dispose of polluting liquids in the tributary of the river [86]. The production of these companies generates wastes that harm the environment, especially the water body of the Bobos River (Figure 6b), streams, and aquifers near the areas where they are disposed of. In addition, these wastes have a significant negative impact on the local flora and fauna, affecting fishermen and residents of the area. The pollution also has a significant impact on the air and soil quality in this industrial area and is not limited to the city's waters.

To address these problems, more sustainable policies and practices are needed in citrus production. Some solutions include the implementation of cleaner agricultural practices and the promotion of composting methods for the disposal of organic waste generated by the citrus industry.

3.10. Preventive Measures to Avoid Contamination of the Bobos River and to Maintain Sustainable Development in the Region

The Bobos River in Veracruz is a crucial water source for the region, making it imperative to take preventive measures to avoid its contamination. Some measures that can be implemented include promoting sustainable agricultural practices, as a significant portion of pollution in the Bobos River stems from agriculture. Hence, initiatives should be undertaken to endorse sustainable practices aimed at reducing the use of chemicals and pesticides in crops. Crop rotation is also an option worth considering, as it helps diminish the accumulation of pests and diseases in the soil, even in perennial crop areas.

Large citrus orchards can introduce cover crops during fallow periods to shield the soil from erosion and enhance its health. These crops can serve as natural nutrient reservoirs, thereby reducing the need for chemical fertilizers. Moreover, integrated pest management practices can be adopted, encompassing mechanical, biological, and cultural techniques to control pests, rather than relying solely on pesticides. Organic agriculture, rooted in natural and sustainable practices, can substantially curtail the use of chemicals in farming and the pollution of the Bobos River.

Educating employees on sustainable and responsible production and waste management practices and fostering awareness regarding environmental protection and the significance of the Bobos River are commendable industry practices. Rigorous monitoring and control are indispensable to ensure compliance with environmental standards and forestall river contamination. Environmental monitoring systems and periodic audits can help identify areas for improvement.

Competent authorities must establish regulations and restrictions for industries utilizing the Bobos River for their operations. Quantitative limits should be imposed on the discharge of chemicals into the river, with penalties enforced against violators. Communities neighboring the Bobos River should have sewage treatment systems to prevent contaminated water from entering the river. Encouraging citizen participation through local communities can aid in preventing Bobos River pollution by actively engaging in river protection and care. Public involvement in cleaning and monitoring activities should be encouraged.

Pollution of the Bobos River poses a threat not only to the health of people in the region but also to the sustainability of the local ecosystem. Hence, the community must take preventive measures to avert river pollution and promote sustainable development. Some actions the community can take are as follows:

Refrain from littering the Bobos River and establish appropriate waste disposal sites.

Control the use of pesticides and fertilizers in homes and farmlands, opting for more natural methods. Promote reforestation by planting trees along the riverbanks and nearby areas to maintain water quality and protect the Bobos River ecosystem.

Reforestation is an important measure to maintain water quality and protect the Bobos River ecosystem. The community can promote reforestation by planting trees along the riverbanks and in nearby areas. Trees will help maintain water quality by absorbing nutrients and pollutants and providing habitat for aquatic organisms. Environmental education is another way to raise awareness about the importance of caring for the Bobos River and the environment in general. Environmental education programs should be established in schools and the community to raise awareness about the importance of protecting the river and the local ecosystem. In addition, river cleaning activities should be promoted to encourage community participation in the conservation of the Bobos River.

Establish environmental education programs in schools and the community to raise awareness about the importance of protecting the river and the local ecosystem. Promote river cleaning activities to encourage community participation in Bobos River conservation efforts. Implement wastewater treatment systems to reduce pollutants discharged into the river. Encourage industries to adopt cleaner and more efficient technologies to reduce emissions and pollution. These measures can help preserve the Bobos River and ensure its sustainability for future generations.

4. Conclusions

The water quality of the Bobos River in the state of Veracruz is compromised due to severe contamination, as evidenced by the obtained results and existing regulations. To safeguard the river and mitigate further negative impacts, it is imperative to regulate wastewater discharges effectively. Furthermore, additional studies are warranted to devise appropriate measures, given the limited information available on the water quality of the Bobos River. Ensuring a sustainable supply and equitable distribution of water resources while upholding sustainability mandates stringent regulatory oversight and ongoing environmental monitoring of existing policies and regulations.

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