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ANTHROPOGENIC IMPACT ON THE QUALITY OF WATER AND AGRICULTURAL SOIL IN GUADIANA VALLEY, DURANGO, MEXICO

Abstract: One of the most important effluents in Guadiana Valley, Durango is El Tunal River, mostly used for agricultural and livestock supply. This river has been polluted by agricultural activity and wastewater discharges. Thus, this study aimed to evaluate the current quality of water and agricultural soil near the river, to estimate the environmental situation of the agricultural sector and its main pollution sources. Hence, a total of 24 soil and five water samples were taken, analysing parameters of organic matter, pH, nutrients, and heavy metals(loid)s (As, Cd, Pb, Zn) in five agricultural areas. The randomised experimental design showed significant variations in soil ($p < 0.05$) of organic matter, nitrogen, As, and Pb between sampling points, confirming suitable conditions for agriculture. Although contamination by heavy metal(loid)s exists, it is below permitted levels. In contrast, the physicochemical quality of the water indicated high levels of phosphates, total dissolved solids, and total coliforms, mainly in the nearest site of a wastewater treatment plant, thus the quality of the water is not suitable for consumption and irrigation for sensitive crops. Nevertheless, rainfall contributes to improve the quality of the river by diluting pollutants. Moreover, constant use of this water might represent a risk to human health and agriculture as it could transport elements to crops or soil, becoming a severe environmental problem.

Keywords: Tunal River, agriculture, wastewater discharges, water quality index, geoaccumulation index

Introduction

Water is an essential resource for human consumption, and in recent years, its demand has substantially increased, particularly within critical economic sectors such as agriculture [1]. In Mexico, in 2017, 76.04 % of water was used in agricultural activities, corresponding to an approximate volume of 66 799 hm^3 [2]. Due to the high requirement for water, it has been settled cultivation methods such as wastewater irrigation and fertiliser application,

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which in excess, have been causing havoc in the environment [3]. This situation derives mainly from the high presence of heavy metal(loid)s, high contents of salts, and bacteriological content, creating bioaccumulation processes in soil and crops [3, 4]; indicating, a risk to human health and the environment, as stated by some studies [4, 5].

The state of Durango is located in the semiarid region of Mexico and it's highly affected by moderate drought, a situation that endangers crops and low levels of water resources [2]. Nonetheless, Durango has one of the main rates of agricultural areas, in 2018, it reached 59 892 ha with an economic value of 9.7 million Mexican pesos [6], therefore, proper water management is essential.

Likewise, one of the main water sources of Durango is the San Pedro Mezquital basin, which comprises 74.0 % of the territory of the state, and it's the main water source supply for livestock, fishing, and agriculture above all [7]; its surface water irrigates around 12 019 ha [2]. This hydrological region has several effluents, being the El Tunal River one of the most important for agriculture and livestock. The irrigation district 052 belongs to Durango where the annual volume of El Tunal River intended for public use and livestock are 0.24 and 0.06 million m^3, respectively. Also, the water of this river contributes to the volume granted for agricultural irrigation (250 million m^3) [8]. It is mainly used as a receiving mantle of municipal discharges of a wastewater treatment plant (WWTP) that operates under an activated sludge regime. It has a capacity of 600 lps to benefit more than 150 000 inhabitants [9]. Around 975 m^3 day^{-1} of domestic wastewater is discharged into the river [10], along with dead cattle near the river. Along with these activities, the quality of the river has been highly affected by wastewater and fertilisers used in agricultural areas, increasing the algae production in the river and limiting the recovery rate [8]. Likewise, Durango is known for its mining activity with extraction of gold, silver, copper, iron, lead, and zinc, in regions located near El Tunal River, contributing to heavy metal(loid)s content in the region [11]. Furthermore, the groundwater of Guadiana Valley has been used in agriculture, public use, industrial, and livestock, with a total of 147.5 million annual m^3. It is commonly found concentrations of As in a range of 0.01 mg L^{-1} - 0.20 mg L^{-1}, are attributed to natural geology, which has increased by the depth of water wells and rhyolitic rocks [8].

Therefore, the ecosystem and food security could be affected by these discharges and agricultural runoff. Thus, this study aimed to evaluate the quality of water and agricultural soil adjacent to El Tunal River to estimate the current situation that faces this effluent, and also, to identify the main sources of pollution.

Materials and methods

Study area and collection samples

The research was performed in El Tunal River in Durango, Mexico. Soil samples were taken in the spring, and water samples were taken in the spring and summer of 2021. The sample sites included a section between the following towns: El Pueblito (23.967341 N, -104.711346 W), La Ferreria (23.967341 N, -104.672034 W), Navacoyan (24.045054 N, -104.547215 W), 5 de Febrero (24.063992 N, -104.514673 W), and El Arenal (24.050381 N, -104.430614 W) with altitudes of 1887 and 1859 m between sites (Fig. 1).

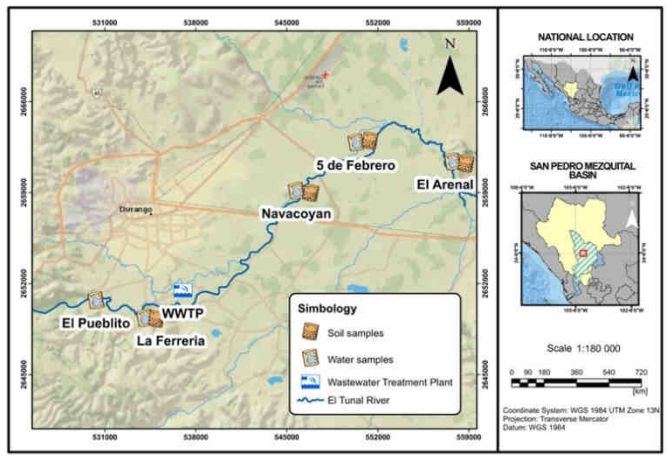


Fig. 1. Sampling sites in Guadiana Valley in Durango, Mexico

Soil samples were taken in agricultural areas: La Ferreria, Navacoyan, 5 de Febrero, and El Arenal at an approximate distance of 150 m away from the river. Therefore, a total of 24 simple samples were randomly taken (six samples per site), at a depth of 0 cm - 30 cm, according to NOM-021-RECNAT-2000 standards [12]. Likewise, water samples were taken directly from the river at each site. Procedures for the collection and preservation of water samples were followed by standard methods [13]. Also, in situ measurements of temperature (T) and total dissolved solids (TDS) were made with a HANNA® brand multi-range meter model Hi8733.

Physicochemical analysis of water and soil

Soil samples were dried, pulverised, and sieved with a 2 mm mesh. Soil texture was determined by the Bouyoucos method. Also, organic matter (OM) was determined by the Walkley & Black method and total nitrogen (N) was estimated by dividing the OM by 20, since MO contains approximately 5.0 % of N [14]. Subsequently, a saturated paste was obtained to measure pH in soil extract with a HANNA® model Hi9803. The heavy metal(loid)s: arsenic (As), cadmium (Cd), lead (Pb), and zinc (Zn) were quantified with a PerkinElmer AAnalyst 800 Atomic Absorption Spectrometer (FAAS). All physicochemical and heavy metal(loid)s analyses were realised according to the specifications of fertility, salinity, and soil classification [12].

Furthermore, water samples were processed to analyse N [15], phosphorous ($P\text{-}PO_4$) by the ascorbic acid method [16], and total coliforms (TC) [17]. The heavy metal(loid)s Cd, Pb, and Zn were estimated by FAAS (PerkinElmer AAnalyst 800), and As was determined by the hydride generator analytical technique. All metal(loid)s analyses were realised according to NMX-AA-051-SCFI-2016 [18]. The quality of surface water was evaluated by the ecological criteria for water quality [19] which establishes the water standards for agricultural irrigation. Likewise, Mexican standards were considered [20] to indicate the maximum limits of pollutants in wastewater discharges.

Geoaccumulation index, I_{geo}

Soil pollution levels by heavy metal(loid)s were estimated through I_{geo}. This index was calculated to compare the values of current loads of heavy metal(loid)s with natural concentrations, allowing to distinguish between the natural or anthropogenic origin [21]:

$$I_{geo} = \left(\frac{C_n}{1.5\, B_n}\right) \quad (1)$$

where: C_n is the metal(loid)s concentration in soil samples; B_n is the value of the element in the earth's crust and 1.5 is the correction factor to minimise variations. Results were compared with the following classes: 1) $I_{geo} < 0$ uncontaminated - moderate, 2) $1 < I_{geo} < 2$ moderately contaminated, 3) $2 < I_{geo} < 3$ moderate - heavily contaminated, 4) $3 < I_{geo} < 4$ heavily contaminated, 5) $4 < I_{geo} < 5$ strongly - extremely contaminated and 6) $5 < I_{geo}$ extremely contaminated [22].

Water quality index, *WQI*

The *WQI* was determined by combining a series of parameters that become a single value on a scale from 0 to 100 [23, 24]:

$$WQI = \sum_{i=1}^{n} q_i W_i \quad (2)$$

where: q_i - assigned value; n - total number of parameters; W_i - relative weight. Six parameters were used with the following W_i values according to a previous study [25]: TC (0.16), pH (0.11), *T* (0.10), N (0.10), P (0.10), and TDS (0.07). The q_i values were determined for each parameter by function curves [26]. This index allowed to estimate the pollution for each sampled site that allows classifying the conditions of the environment as very bad (0-25), bad (26-50), medium (51-70), good (71-90), and excellent (91-100) [27].

Statistical analysis

A completely randomised design was used, as well as an analysis of variance in soil samples to determine the significant differences in concentrations between sampling points. Also, a non-parametric test of the Kruskal-Wallis test ($\alpha < 0.05$) was used. Likewise, an analysis of Spearman's correlation was performed to establish the association between variables along with a Principal Component Analysis (PCA) to determine the contribution of each parameter. The software used for the analyses was R Studio version V4.1.2 [28].

Results and discussion

Physicochemical properties of soil

Fractions of sand ranged from 41.3 % - 86.0 %, clay from 6.0 % - 16.8 %, and silt from 9.3 % - 38.0 %. Meanwhile, the mean sand, clay, and silt fractions of the soil were 65.6 %, 11.4 %, and 23.0 %, respectively. This result indicates that the average texture of the study area is sandy loam (Table 1).

The soil was classified as moderately alkaline (pH 7.4 - 8.5) [12]. The pH showed values of 7.5 - 8.0, there were significant differences ($p < 0.05$) between La Ferreria and El Arenal (Table 2). It is important to highlight that the alkaline pH reduces the

bioavailability of heavy metal(loid)s [29] and allows them to precipitate in the soil, limiting their mobility [30].

Table 1

Comparison of means of agricultural soil texture

Sample site	Clay [%]	Sand [%]	Silt [%]	Texture
La Ferreria	15.1 ±2.3	55.3 ±7.2	29.5 ±7.8	Sandy-loam
Navacoyan	12.2 ±1.8	63.0±5.3	24.8 ±4.5	Sandy-loam
5 de Febrero	9.1 ±2.6	70.1 ±7.7	20.8 ±5.9	Sandy-loam
El Arenal	10.0 ±7.6	71.0 ±17.0	19.0 ±11.0	Loamy-sand

Table 2

Comparison of means of chemical properties of agricultural soil

Sample site	pH [-]	Organic matter [%]	Total Nitrogen [%]
La Ferreria	7.5 ±0.4 a	1.0 ±0.1 bcd	0.050 ±0.006 bcd
Navacoyan	7.8 ±0.1 ab	1.5 ±0.6 abc	0.07 ±0.03 abc
5 de Febrero	7.7 ±0.05 ab	1.9 ±0.4 ab	0.09 ±0.01 ab
El Arenal	8.0 ±0.3 b	2.1 ±0.3 a	0.1 ±0.01 a

±Standard deviation. Different letters in the same column are statistically different ($p < 0.05$)

The percentages of OM denote soils with a low number of humic substances. The OM of the sites is within the low to medium class (0.96 % - 2.15 %) [12], with significant differences between sites ($p < 0.05$). Similarly, low levels of OM (1.40 %) have been reported in this area and are related to physicochemical degradation of the soil in the state of Durango, causing low fertility with low levels of infiltration and water retention [31].

Table 3

Correlation matrix of soil physicochemical parameters

Parameter	pH	OM	As	Pb	Zn	Clay	Sand	Silt
pH	1							
OM	–0.38	1						
As	0.58	–0.47	1					
Pb	0.46	–0.62*	0.60*	1				
Zn	0.15	–0.42	0.10	0.80**	1			
Clay	0.48	–0.61*	0.71*	0.63*	0.25	1		
Sand	–0.81**	0.67*	–0.79*	–0.77*	–0.37	–0.82**	1	
Silt	0.89**	–0.46	0.77*	0.59	0.17	0.59	–0.91**	1

$^{*}p < 0.05$, $^{**}p < 0.01$

The estimated total N showed a range of percentages between 0.05 % - 0.10 %, with a mean of 0.08 %. These percentages are related to the type of soil that predominates in Durango (loam-sandy), characterised by its intermediate capacity to retain moisture and elements with high mobility such as N [31]. Similar values have been reported in previous studies in Guanajuato (0.07 % - 0.05 %) [22] and in Durango, Mexico (0.01 % - 0.98 %) [31]. These percentages assume a possible competition for N between microorganisms and crops due to the years of soil production, sowing seasons, and the use of fertilisers [22]. On this matter, it is important to analyse the correlation of physicochemical properties of soil to understand some of their associations to heavy metal(loid)s. Spearman's correlation matrix indicated relationships between the physicochemical properties of the soil (Table 3)

and is supported by PCA in a spatial distribution to determine the contribution of each parameter and its possible pollution sources for heavy metal(loid)s in the study area (Fig. 2). The element Cd was excluded in both analyses since it was a constant parameter in all of the observations and does not provide a variation in the relationships with other parameters. Also, N was excluded, since it was calculated from the percentage of the OM and the use of individual variables is essential.

The first component of PCA explained 59.20 % of the total variance and was controlled by pH, OM, As, clay, silt, and sand. The second component collected 21.70 % of the variance and was controlled by Pb and Zn. Therefore, the positively correlated variables are grouped close to each other, while the negatively correlated ones are represented in opposite quadrants. Thus, the use of chemical fertilisers affects the form of heavy metal(loid)s, as it can affect soil through ion exchange and also variate the pH value of soil and indirectly control the solubility of metal(loid)s such as As and Pb [32], decreasing its mobility and bioavailability as the pH of the soil increase [33]. Meanwhile, OM - Pb showed a high negative correlation ($r > –0.62$, $p < 0.05$), implying that Pb can bind to OM at high pH [22]. This might occur because OM can retain heavy metal(loid)s in an exchangeable form [29] since parameters such as pH, OM, soil type, moisture, and micronutrients could affect the mobility and availability of heavy metal(loid)s, by influencing the adsorption of metal(loid)s to the soil [4, 33]. Likewise, it has been reported that Pb does not leach into the soil layers, as its mobility is very slow [34]. Also, there is a strong relationship between clay content and OM content ($r > –0.61$, $p < 0.05$). Soils having granulometric composition characteristic for clay and high content of organic matter, tend to have a high sorption capacity and a strong ability to bind metallic elements. Nonetheless, this study shows a higher composition of sand and a low presence of OM. Thus, sandy soils are distinguished by a low sorption capacity [35].

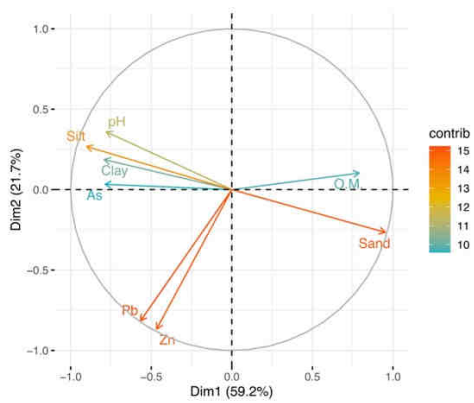


Fig. 2. PCA of physicochemical parameters of the soil

Heavy metal(loid)s and I_{geo}

The concentrations of heavy metal(loid)s showed the following pattern: Zn > As > Pb > Cd (Table 4). Statistical differences were presented in the concentrations of As, Pb, and Zn in 5 de Febrero. Hence, As was the element that showed higher values (7.3 mg kg^{-1} - 11.8 mg kg^{-1}), compared to background values [36]. Further, I_{geo} was found

between classes one and two for all the sites sampled. This shows that the soil has a low level of pollution by Zn, Pb, and Cd, but is moderated by As.

Table 4

Total concentrations of heavy metal(loid)s [mg kg^{-1}] and I_{geo} classification of soil

Sample site	As	I_{geo}	Pb	I_{geo}	Cd	I_{geo}	Zn	I_{geo}
La Ferreria	9.9 ±0.3 a	2	13.0 ±1.3 ab	1	≤ 0.2 a	1	36.1 ±2.5 a	1
Navacoyan	11.8 ±1.0 a	2	12.0 ±1.0 ab	1	≤ 0.2 a	1	33.7 ±1.3 a	1
5 de Febrero	8.5 ±0.6 b	2	7.6 ±2.5 b	1	≤ 0.2 a	1	28.0 ±1.3 b	1
El Arenal	7.3 ±0.4 b	2	11.0 ±2.0 ab	1	≤ 0.2 a	1	34.0 ±0.3 a	1
B_n	4.8		17		0.09		67	
CR[1]	22		400		37		-	
CR[2]	-		40-450		1-3		60-450	

CR[1-2]: Allowed concentration by national [37] and international standards [38]. Different letters in the same column are statistically different ($p < 0.05$)

Hence, the site of Navacoyan showed a higher concentration of As and Pb. However, none of these elements exceed the maximum limits allowed for metal(loid)s in soils [37]. On this matter, the contribution of As in PCA is lower than the rest of the metal(loid)s (Fig. 2). Nevertheless, As can be related to anthropogenic sources, contrary to Pb and Zn, which can be related to geological sources, since they are both associated in the second component and their concentrations are below background values.

There is a positive correlation between Pb - Zn - As. This correlation may occur due to a similar source such as mining, agricultural runoffs, wastewater irrigation, solid waste disposal, and vehicular use [11, 35, 39]. In the same way, it has been reported values of As (4.40 mg kg^{-1} - 221.0 mg kg^{-1}) and Pb (8.30 mg kg^{-1} - 135.0 mg kg^{-1}) within the urban area of Durango, attributed to industrial, mining activities, and the use of automobiles [11, 40]. Also, the presence of As can be attributed to the use of water from El Tunal river for irrigation due to wastewater discharges; and highly influenced by pH and OM of the soil. It is important to mention that, most of As presence is related to geogenic origin such as rock weathering, especially in arid or semi-arid areas [41, 42]. Also, the presence of As can increase during groundwater extraction, causing the oxidation and subsequent rise of sulphide minerals [43]. In the same way, it has been reported that elements of Pb and As are associated, and their pollution source emerges from fertilisers or wastewater [30]. On this matter, constant irrigation can increase the concentrations of As and could change the geochemical properties, allowing its solubilisation and absorption in crops [5].

Physicochemical properties of water

Water samples physicochemical properties are shown in Table 5. The *T* increased along the river, but it was attributed to the recollection timing. Nonetheless, in both seasons it is below the limits (35 °C). Also, the range of pH of both seasons was 6.8 - 8.3, according to the established optimal criteria of official standards to be used as irrigation water it should be in a range of 4.5 - 9 [19, 20, 44].

Meanwhile, during the dry season, the P-PO_4 surpassed the allowed permissible levels of discharges [20] it registered concentrations higher than 15 mg L^{-1} starting from Navacoyan. This concentration was reduced during the rainy season (< 10 mg L^{-1}). However, there should not be the presence of phosphate (> 1 mg L^{-1}) unless there are

phosphate fertilisers or detergents [1]. Hence, concentrations of $P\text{-}PO_4 > 5$ mg L^{-1} endanger aquatic life even when they are useful to agriculture due to their high nutrient content [45]. The results of dry and rainy seasons are above this value, representing a risk for aquatic organisms. These results might be related to low rainfall and low nutrient dilution, mainly to high concentrations of $P\text{-}PO_4$ that are generated by wastewater residues.

Table 5

Physicochemical-bacteriological parameters of the El Tunal River

Season	Sample site	*T* [ºC]	pH [-]	$P\text{-}PO_4$ [mg L^{-1}]	TDS [mg L^{-1}]	TC [NMP 100 mL^{-1}]	As [mg L^{-1}]
Dry	El Pueblito	10.5	7.1	4.2	42.9	$2.1 \cdot 10^{4*}$	0.01
	La Ferreria	14.6	6.8	3.9	47.4	$2.1 \cdot 10^{4*}$	0.02
	Navacoyan	18.3	7.0	48.4*	542.1*	$1.10 \cdot 10^{5*}$	0.02
	5 de Febrero	18.8	7.3	51.4*	587.5*	400	0.03
	El Arenal	21.6	8.0	43.5*	579.2*	700	0.03
Rainy	El Pueblito	21.2	8.1	0.2	98.0	< 3	0.01
	La Ferreria	19.3	8.0	0.2	47.7	< 3	0.01
	Navacoyan	18.0	8.0	9.4	250.2	< 3	0.01
	5 de Febrero	21.8	8.0	10.0	284.8	< 3	0.02
	El Arenal	23.1	8.3	7.5	100	< 3	0.02
MPL[1]		35	4.5-9.0	15	500	250-1000	0.1-0.2
MPL[2]		30	5.0-9.0	-	500-1000	200	-

MPL[1-2]: Maximum permissible levels according to national [19, 20] and international standards [44]

Similarly, the TDS from Navacoyan is above the maximum permissible limit during the dry season; its value increased by almost 17.50 % above ecological criteria. The sample site of 5 de Febrero showed the highest percentage. Therefore, high values of TDS suggest the existence of elements that are used by microorganisms such as Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, HCO_3^- and SO_4^{2-} [31]. The results are within the category of TDS < 500 mg L^{-1} in both sites which corresponds to the higher sites of the basin, where the risk to use water for irrigation is null (El Pueblito and La Ferreria). Oppositely, the concentration of TDS in Navacoyan, 5 de Febrero, and El Arenal (500 mg L^{-1} < TDS < 1000 mg L^{-1}), might affect sensible crops and it might have a light to moderate restriction in crop irrigation [45]. Even though the TDS were reduced with precipitations, El Pueblito increased its levels of solids, this might be attributed to a tributary that includes wastes and industrial discharges.

On the other side, the results of microbiological analysis of TC were high, as 60.00 % of the samples exceeded the standard requirement [19, 20, 44], mainly in Navacoyan. As previously stated by some authors, they suggest that those microorganisms indicate the existence of punctual and diffused pollution sources of faecal matter, attributed to lack of treatment in wastewater or cattle near the river [24]. The data above, is related to the present study, as Navacoyan is approximately 13 km from a WWTP, and livestock is developed near the river. Meanwhile, 5 de Febrero and El Arenal are below the limits, suggesting that there are only punctual pollution sources. Yet, the contamination in El Pueblito and La Ferreria also surpasses the allowed permissible levels; those are recreative areas and there is not a punctual pollution source, where it might occur some illegal discharges or irregularity by users or establishments near the river. These results represent a potential risk, as the polluted water increases the risk of acquiring diseases; coliforms might be transported during crop growth by polluted soil [46]. During the rainy season, the TC was highly reduced in all sites (< 3 NMP 100 mL^{-1}).

Although the concentrations of Cd, Pb, and Zn were not detected, the As tends to increase along the river (0.01 mg L^{-1} - 0.03 mg L^{-1}), below the allowed limits. Thus, there is no risk to be used in agriculture [19]. It is known that As has been detected in natural form in different regions of Mexico [42] and also, some authors in Durango have reported As in groundwater (0.02 mg L^{-1}- 0.09 mg L^{-1}), attributed to mineral origin and alluvial structure of aquifers [43]. It is important to mention that, the increase of As might be favoured by mineral oxidation with sulphur, such as arsenopyrite ($AsFeS_2$), which increases its concentration with underground water extraction [47].

Likewise, according to PCA (Fig. 3), parameters with high contribution during the dry season are TC, TDS, and P (Fig. 3a). The first component contributes to 64.70 % of the variability and is controlled by pH, As, T, TDS, and P, while the second component contributes 28.20 % and is controlled by TC (Table 6).

Table 6

Correlation matrix of physicochemical parameters of water (dry season)

Parameter	pH	Temperature	TDS	P-PO_4
pH	1			
T	0.70*	1		
TDS	0.60*	0.90**	1	
P-PO_4	0.50	0.60*	0.80**	1
TC	–0.71**	–0.56	–0.66*	–0.60*

* $p < 0.05$, ** $p < 0.01$

The load of TDS is attributed to the presence of primary ions as well as total alkalinity and hardness [48]. PCA showed that concentrations of TDS, P-PO_4, and TC are correlated and had highly impacted water quality during the dry season. Some authors have reported the impact of TDS on coliform bacteria, showing interaction through deposition, agitation, and suspension [48, 49]. TDS could also benefit coliform bacteria with organic and inorganic nutrients. The concentrations of TC have been associated with phosphorus concentrations [49]. A reason for the correlation between TC and P-PO_4 could be the untreated discharge from industrial complexes and WWTP.

While coliforms are bacteria that occur naturally in water and soil, TC includes *Enterobacter*, *Citrobacter*, *Klebsiella*, *Aeromonas*, *Serratia*, and *Escherichia* [48], and faecal coliforms [49]. The microbiological quality of rivers is primarily related to leaching from nearby septic tanks, to high concentrations of animal faeces, as well as other activities such as bathing, washing, dumping wastes, and the management of their waste in the watershed [48, 49].

Also, P-PO_4 and pH were negatively correlated with TC pollution as in other studies [48, 50, 51]. This implied that high values of P-PO_4 and pH in surface waters could relate to low levels of coliforms since phosphate is a major nutrient for coliform bacteria [50]. This suggests that P-PO_4 may be high because of all the phosphorus sources, thus, dissolved phosphorus is available for bacteria [51]. Also, pH affects the survival of faecal coliform bacteria in water. It has been reported that faecal coliforms die more rapidly when pH is above 8.5, even in a nutrient-rich condition [52]. This parameter affects microbial metabolisms and hence, microbial community structures by modulating the thermodynamics and kinetics of redox reactions. This implies the incidence of coliform bacteria in this study is likely to be favoured by a neutral environment [50].

Table 7

Correlation matrix of physicochemical parameters of water (rainy season)

Parameter	pH	*T*	TDS	P-PO_4
pH	1			
T	0.80*	1		
TDS	0.20	0.23	1	
P-PO_4	0.24	0.18	0.94**	1
TC	–0.26	–0.31	–0.81**	–0.62*

*$p < 0.05$. **$p < 0.01$

On the other hand, during the rainy season (Fig. 3b), the first component contributes to 42.70 % and the second component contributes to 33.60 % of the variance. The PCA (Fig. 3b) and correlation analysis (Table 7) indicated that external factors influence the surface water. Accordingly, the decrease of TDS, P-PO_4, and TC may have been caused by dilution or death of the bacteria. The concentrations of coliforms and TDS vary with seasonal changes, as well as in response to rainfall and river flow [49, 51].

Ellipses in the individual PCA indicate the dispersion and variability of parameters in both seasons (Fig. 3c). The PCA allows to distribute sample sites and seasons, and ellipses group both factors. Hence, Navacoyan, 5 de Febrero, and El Arenal are more distant among them, while El Pueblito and La Ferreria are closer, implying that they share physicochemical parameters during the rainy season.

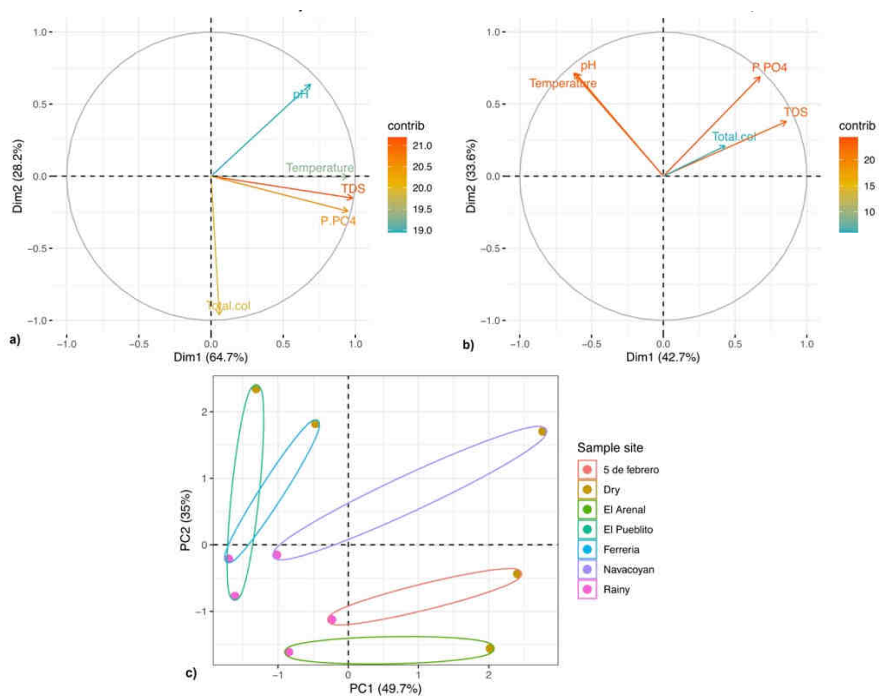


Fig. 3. PCA of physicochemical parameters of the water: a) dry season, b) rainy season, c) individual PCA in both seasons

Water quality index, *WQI*

The classification of water from the El Tunal River is shown in Figure 4, ranging from regular quality (50-69) to bad quality (26-50), according to the *WQI* values.

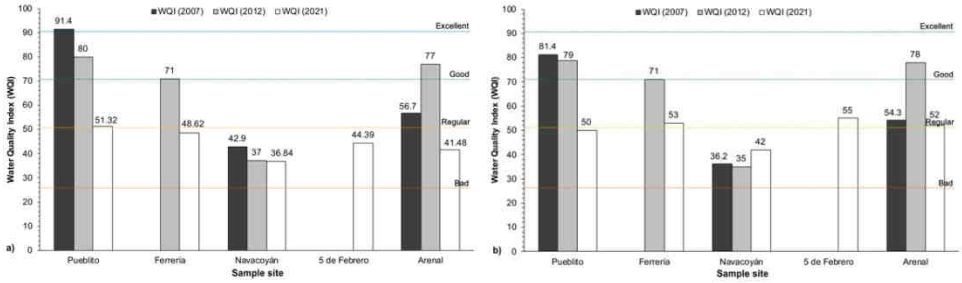


Fig. 4. Comparison of *WQI*: a) dry season, b) rainy season in the Tunal River in 2007 [10], 2012 [53], present study in 2021

The use of water in different sectors along the river is considered unacceptable and doubtful. For the recreative sector, it is recommended to avoid direct contact with water. Fishing activities and aquatic life might not be suitable for sensitive organisms or ideal only for resistant organisms. However, for agricultural activity, it is possible to use previous treatments for the majority of crops or only resistant ones [54]. These results show a contrast with the reports of 2007 and 2012. The difference in values might be attributed to natural factors that are influenced directly by the evaluated parameters such as the weather, low rainfall, and particle transport [23]. The parameter with a major contribution to WQI was TC and P, mainly in Navacoyan, where the results are similar to previous reports, as wastewater discharges of the WWTP lack an optimal capacity. The results can be compared to other studies in Mexico with a similar quality as the ones reported here [23, 55]. However, the results depend on the considered parameters and the assigned value to each one of them.

Conclusion

The pH, OM, and texture of the soil contributed to a decrease in the mobility, bioavailability, and sorption of heavy metal(loid)s. It is mostly related to anthropogenic sources such as irrigation and chemical fertilisers since the concentration is higher than background levels. The quality of the water was low due to lack of rainfall and constant discharges of wastewater, which seemed to be the main source of TC, P-PO_4, and TDS, as well as some diffuse sources such as the management of wastes near the aquatic system. Also, rainfall allowed dilution of the pollutants, increasing the quality of the river in most of the sites.

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