Lat. Am. J. Aquat. Res., 45(2): 403-409, 2017
DOI: 10.3856/vol45-issue2-fulltext-15

Research Article

Nitrogen and phosphorus in the subtropical Presidio River, northwestern Mexico

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ABSTRACT. The aim of this study was to assess its nitrogen and phosphorus concentrations in the Presidio River, because it receives large volumes of wastewater with high loads of detergents and fertilizers. The mean concentrations of total nitrogen and phosphorus determined between February 2008 and January 2009 were 640 and 167 µg L^{-1}, respectively. The permissible phosphorous concentration established by the Official Mexican Standard NOM-001-SEMARNAT-1996 for pollutants discharge into rivers is 5000 µg L^{-1}. However, according to international standards on phosphorous concentrations in continental water bodies, the Presidio River may be considered hypereutrophic.

Keywords: nitrogen, phosphorus, utrophication, Presidio River, Mazatlan.

INTRODUCTION

In recent decades, human activities, in particular agriculture, caused increased nutrient concentrations in continental and coastal water bodies (Mbonimpa *et al.*, 2014). These lead to high chlorophyll levels (Hu *et al.*, 2014), excessive growth of seaweeds, seagrasses and nuisance algae, onset of toxic algal blooms (Schmidt *et al.*, 2012; Steffen *et al.*, 2014) and occurrences of anoxia and hypoxia (Carvalho-Aguiar *et al.*, 2011), showing that eutrophication is a significant problem worldwide (Rulkey & Rusch, 2004; Lenhart *et al.*, 2010; Nyenje *et al.*, 2010).

The main activity of the Mexican State of Sinaloa is agriculture, with 618.8×10^3 and 716.8×10^3 ha dedicated to irrigated and dryland (rain-dependent) agriculture, respectively (INEGI, 2007). Irrigation is mainly through the 11 rivers flowing through the state, but information on its effect on the state of eutrophication of Sinaloa rivers and other public water bodies is scant, hindering the establishment of effective policies regulating the activities related to water use, such as agriculture, food and drinks manufacture and processing, recreation, or the state's industries involved in water treatment (Llanes-Ocaña, 2004; Arias-Patrón, 2005).

The Presidio River is not exempt from for these problems, since it is the main water source for the 8,435 ha of the 111th Irrigation District (CONAGUA, 2012), in which the main activities are agriculture and animal husbandry. These generate large volumes of wastewater, containing mainly fertilizers, organic matter and household detergents. However, the degree of its eutrophication has not been the object of previous studies. This was the aim of this work, in which we report total phosphorus, total nitrogen and dissolved oxygen concentrations, as well as temperature and pH levels registered at ten sampling sites between February 2008 and January 2009.

MATERIALS AND METHODS

Geographic location and sampling site

From its source**,** the Presidio River (located in México) flows for 48 km in the State of Durango and for 167 additional km in a southeasterly direction across the State of Sinaloa, until it reaches the Pacific Ocean. Its catchment area is 5614 km^2 and its ecoregion (ATP-55 = Área Terrestre Prioritaria 55), which covers 3472 km^2, lies between coordinates 23°05’57”, 23°59’47”N and 105°33’11”, 106°17’17”W (Arriaga *et al.*, 2000).

Corresponding editor: Ricardo Prego

The climate of the ecoregion is warm and humid with average annual temperatures above 22°C and over 18°C during the coldest month. Annual mean rainfall ranges from 500 to 2500 mm while the driest month between 0 and 60 mm. Soil is classified as eutric regosol (RGe, 7%) and litic leptosol (LPq, 27%). Inland, the main economic activity is agriculture, while fishery and tourism are important in coastal areas (Arriaga *et al*., 2000).

The sampling sites were selected considering the presence of human settlements, with urban or agricultural wastewater discharges and classified as Humayes (site I), Copales (site II), Iguanas (site III), Cortina (site IV), Recodo (site V), Siqueros dam (site VI), Walamo (site VII), Ostial (site VIII), Tapo Botadero (site IX) and Garzas (site X), for geographic locations see figure 1. The first two were located five km above the Picachos Reservoir, at the time still under construction, the third was between the inlet and the dam, the fourth at the site of the dam and the remaining continued downriver to the Pacific Ocean. Under the hypothesis that in spite of the river's self purification (Ifabiyi, 2008) total nitrogen and phosphorus would be continuously increasing, the sampling sites were located downstream of the wastewater discharges of local communities, and the last (Garzas) was on the coast, where the river flows into the Pacific Ocean (Fig. 1). For the first five months sampling was on eight sites (Humayes, Copales, Iguanas, Cortina, Recodo, Siqueros, Tapo Botadero and Garzas). One additional sampling point (Walamo) was added in July and a second one (Ostial) in August. The data of these two sites were not used for statistical comparisons between sites.

Sample collection and analytical methods

Starting in February 2008 and until January 2009, surface water temperature, dissolved oxygen (DO) and pH values were measured monthly *in situ* with a multiparameter water quality meter (Hanna Instruments HI 9828), and surface water (20 cm) samples were collected at each site, using hydrochloric acid-cleaned, distilled water-rinsed 2-L polypropylene sampling bottles. Samples were collected on base-flow.

One mL of sulfuric acid was added to each water sample for preservation, samples were stored at 4ºC in an ice box and carried to the laboratory for analysis. Total nitrogen (TN) is reported as sum of all nitrogen species determined with APHA (1999) standard methods 4500-NH_3 C, 4500-N_{org} B, 4500-NO_2^- B (ammonia, organic N and nitrites, respectively) and nitrates by using method 352.1 (US-EPA, 1971). For Total phosphorous (TP), all samples were filtered through 0.45-µm membrane filter and was determined as PO_4^{-3} after sulfuric acid-nitric acid digestion and determined using colorimetric method (4500-P B4 and 4500-P C). Sample values were determined from standard curves with a variability less than 5%. All samples were analyzed in duplicate and Hach standard solutions were used for the respective calibration curves.

Data processing

The data of temperature and pH were normal and homoscedastic (Kolmogorov-Smirnov and Bartlett's tests). The mean values of each month, calculated with the data of all sites, were compared with one way ANOVA tests for repeated observations and multiple comparisons Holm-Sidak tests. The remaining data were not normal or not homoscedastic, or both, and their mean values were compared using the equivalent non parametric test for repeated observations (Friedman's) and Dunn's tests. The same tests were used to compare the annual mean values of all variables calculated for each site. In all cases, the significance was $\alpha = 0.05$.

RESULTS

Temporal variations of temperature, pH, dissolved O_2, Total nitrogen (TN) and Total phosphorous (TP)

The monthly mean water temperature, calculated considering all sites, increased continuously from the initial 25.03°C (February, 2008) to the maximum yearly value of 33.35°C determined in June, after which it decreased, fluctuating between 30.93 and 23.95°C from July to December, and increasing slightly in the following month (January 2009). Statistical comparisons indicated that the significantly lowest value was in December. This was different from the mean temperatures determined in September and October (but not in August), as well as from all values obtained between March and July (Table 1).

There were no clear trends in the case of pH and O_2 concentrations. The lowest pH value was in August. With the exception of July and September, the remaining months had significantly higher values, and the highest was in June. In the case of O_2, the highest and lowest concentrations were in November 2008 and January, 2009, respectively. The remaining months showed high variations, with intermediate mean values (Table 1).

With the notable exception of January, 2009, and to a lower extent of July, August and December 2008, the monthly mean O_2 concentrations were close or above the saturation values calculated as in USGS (2014), using O_2 solubility in freshwater at normal atmospheric pressure.

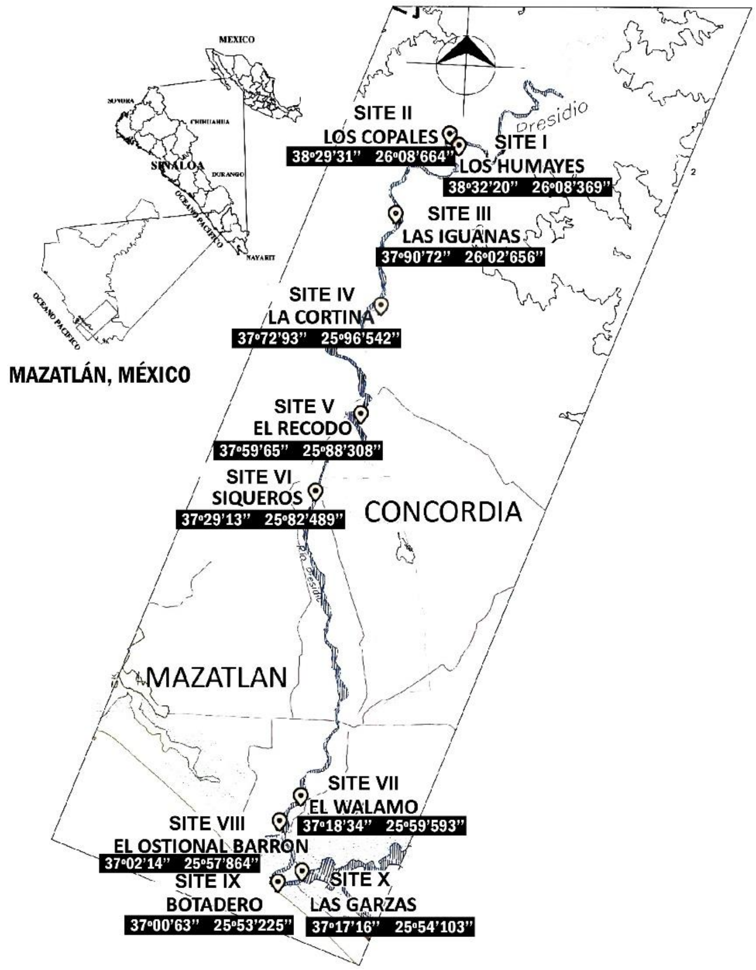

Figure 1. Localization of the Presidio River and the study sites.

In the other hand, TN concentrations increased significantly from the lowest mean concentration determined in February 2008 and reaching maximum values between June and July. In the following three to four months it remained approximately stable, and finally decreased to less than 30% of its highest annual value during the remaining two months of this study (Table 1).

TP varied irregularly within low values (<0.1 mg L^{-1}) between February and June. It showed a sudden strong increase in July and remained approximately stable between approximately 0.35-0.40 mg L^{-1} in the following three months, with no significant difference between mean monthly values. Concentrations decreased significantly in October, reaching values of <0.1 mg L^{-1} by the end of this study (Table 1).

Spatial variations of temperature, pH, O_2, TN and TP

Annual temperatures ranged between 26.1 and 28.9°C (sites I and IX, respectively). The data tended to be higher downstream, but there was no significant difference between sites, whereas pH values tended to be higher upstream, up to site V. This, as well as sites II and III, immediately before and within the Picachos reservoir, had mean pH values significantly higher than sites IX and X, close to the river mouth and the sea (7.6 and 7.4, respectively).

With the exception of site IV, located immediately below the dam, the mean annual O_2 concentrations ranged from 8.6 to almost 9.0 mg^{-1} between sites I and V, remained close to 8.1 mg L^{-1} in sites VI to VIII and decreased further in the last two sites, where values were significantly lower than at sites II and III (Table 2).

The concentrations of TN and TP showed limited geographic variability. The first varied from approximately 0.60 mg to 0.82 mg L^{-1} (sites III and V, site IX, respectively) without any significant difference between sites ($P > 0.05$). In the case of total P, the highest mean values were those of sites VII and VIII, where sampling started during summer, when nutrients had their higher mean monthly values (Table 1).

Table 1. Monthly mean values (standard deviation in parenthesis) of water temperature, pH, dissolved O_2 and TN and TP concentrations of sites I to X of Presidio River. % Sat: average O_2 saturation. Different letters indicate significant difference: a≤ab≤b≤bc≤c≤cd≤d. One-way block ANOVA, α = 0.05, *non parametric (Friedman's) test.

Month	Temp (°C)	pH	O_2* (mg L^{-1})	O_2 (% Sat.)	TN* (mg L^{-1})	TP* (mg L^{-1})
Feb 2008	25.03ab	8.17b	7.77bc	94	0.068a	0.014a
	(2.37)	(0.54)	(2.32)		(0.161)	(0.009)
Mar 2008	28.15c	8.44b	8.67 bc	111	0.417ab	0.055ab
	(2.99)	(0.61)	(2.64)		(0.149)	(0.020)
Apr 2008	28.43cd	8.51b	7.74abc	100	0.372ab	0.046ab
	(1.71)	(0.62)	(2.46)		(0.173)	(0.012)
May 2008	30.73cd	8.46b	7.40abc	99	1.004bc	0.032a
	(2.72)	(0.62)	(2.03)		(0.503)	(0.013)
Jun 2008	33.35d	8.87b	8.71bc	122	1.231c	0.079ab
	(1.14)	(0.52)	(1.42)		(0.396)	(0.034)
Jul 2008	30.93cd	7.70ab	5.36ab	72	1.235c	0.407c
	(1.13)	(0.23)	(1.39)		(0.300)	(0.220)
Aug 2008	25.59ab	7.13a	6.04ab	74	0.666bc	0.361c
	(1.19)	(0.56)	(1.24)		(0.150)	(0.180)
Sep 2008	26.98b	7.66ab	10.73bc	135	0.769b	0.344c
	(2.08)	(0.17	(4.32)		(0.318)	(0.185)
Oct 2008	28.40c	7.46a	10.26bc	132	0.842bc	0.201b
	(1.04)	(0.19)	(2.42)		(0.301)	(0.095)
Nov 2008	25.50ab	8.40b	14.14c	173	0.566bc	0.109ab
	(2.06)	(0.28)	(2.54)		(0.153)	(0.019)
Dec 2008	23.95a	8.38b	4.61ab	55	0.336b	0.087ab
	(1.49)	(0.19)	(0.59)		(0.121)	(0.021)
Jan 2009	25.40ab	8.52b	1.63a	20	0.343b	0.091ab
	(1.67)	(0.34)	(0.83)		(0.114)	(0.030)

In the remaining sites values ranged between 0.094 and 0.185 mg L^{-1} (sites III and VI, respectively), and the mean value of site III was significantly lower than those of sites VI and VIII (Table 2).

DISCUSSION

Temperature, pH, dissolved oxygen

The temperature cycle of Rio Presidio is similar to that observed between 2008 and 2009 in a reservoir located in the neighboring state of Nayarit by Rangel-Peraza *et al.* (2009), and reflects the regional climate, which is characterized by a cold and a warm dry season from November to February and from March to June, respectively, and by a warm, rainy season from July to October. In the case of geographic distribution, although the differences are not significant, the tendency to higher temperatures downriver than upriver is the most probable effect of the progressively longer time of exposure to the high temperatures typical of the Mexican Pacific coastal plain.

Depending on the nature of the soil types in the respective catchment areas, most river waters have pH values between 6.5 and 8.5 (Tepe *et al.*, 2005; LCRA, 2014), although this range may be modified by the type and intensity of biological processes such as photosynthesis and respiration. All values determined in this work fell within this range and, while the February through June progressive increase was most probably due to the photosynthetic activities of phytoplankton and phytobenthos, which caused at the same time the high dissolved O_2 concentrations observed during the same months.

The remarkable pH decrease in the following two months could have been due to acid rain from the close to 115 ton of sulfur dioxide released yearly into the atmosphere by the thermoelectric plant serving the city of Mazatlán, although the accompanying lower O_2 values would seem to indicate that these changes were probably caused by surface runoff during the rainy season, causing high turbidities, phytoplankton and phytobenthos shading and a consequent increase in oxygen demand accompanied by decreased oxygenic photosynthetic activity.

Barring sites VII and VIII because of incomplete sampling, mean pH values were within the range 8.2-

Table 2. Mean values (standard deviation in parenthesis) of water temperature, pH, dissolved O_2 and TN and TP concentrations of sites I to X of Presidio River determined from February, 2008 to January, 2009. % Sat: Average O_2 saturation. Equal or common letters indicate lack of significant difference: a≤ab≤b and a<b. One-way ANOVA for repeated observations, $\alpha = 0.05$, *Non parametric (Friedman's) test. **Sites VII and VIII not used for statistical comparisons.

Site	Temp (°C)	pH	O_2* (mg L^{-1})	O_2 (% Sat.)	TN* (mg L^{-1})	TP* (mg L^{-1})
I	26.09a	8.21ab	8.64ab	107	0.673a	0.102ab
	(3.50)	(0.69)	(4.41)		(0.559)	(0.088)
II	26.91a	8.34b	8.94b	112	0.652a	0.108ab
	(3.24)	(0.70)	(4.18)		(0.455)	(0.091)
III	27.17a	8.32b	8.90b	11	0.595a	0.096a
	(3.44)	(0.66)	(3.90)		(0.302)	(0.082)
IV	27.75a	8.04ab	7.54ab	96	0.628a	0.199ab
	(3.54)	(0.54)	(3.59)		(0.415)	(0.207)
V	28.11a	8.43b	8.97ab	115	0.604a	0.170ab
	(3.50)	(0.60)	(3.82)		(0.408)	(0.167)
VI	27.12a	8.17ab	8.10ab	102	0.637a	0.185b
	(4.43)	(0.51)	(3.64)		(0.373)	(0.186)
VII**	27.92	7.81	8.07	103	0.608	0.275
	(1.80)	(0.78)	(4.68)		(0.313)	(0.218)
VIII**	27.52	8.02	8.11	103	0.615	0.267
	(1.45)	(1.10)	(4.53)		(0.347)	(0.200)
IX	28.91a	7.62a	5.79a	75	0.822a	0.168b
	(2.39)	(0.36)	(2.58)		(0.578)	(0.207)
X	28.07a	7.41a	4.74a	61	0.617a	0.142ab
	(2.93)	(0.29)	(2.55)		(0.436)	(0.199)

8.4 down to the river mouth (sites IX and X), where values decreased to 7.4-7.6, possibly because of the high biological activity typical of the transition areas between continental and marine waters (Kjerfve, 1994; Gocke *et al*., 2003), which is consistent with the low annual mean O_2 values of these two sites.

Total nitrogen (TN) and Total phosphorous (TP)

The high seasonal variability of TN and TP concentrations are clearly related to the State's agricultural activities which usually peak between May and November, and the high concentrations coincide with the rainy season, when excess fertilizers and agrochemicals are carried to the river through ditches and surface runoff. A similar relationship on high TN and TP concentrations was attributed at river runoff in wet season for the Yangtze River (Tong *et al.,* 2017). There is no information available on the amount and type of fertilizers used in Sinaloa State, but the N and P seasonal variations suggest heavy use of nitrogenous compounds beginning in May and continuing through October-November whereas, either because of later application, of slow solubility or of low availability of P fertilizers (Syers *et al*., 2008) TP increased significantly only in July, although it decreased with a rate similar to that of TN until the lasts sampling date.

The most noteworthy feature is that there is not a clear tendency to an N concentration buildup along the course of the river, which seems to indicate that at the current rate of soil use the self-cleaning of the biological activities would be sufficient to maintain water quality within the limits indicated by Official Mexican Standard (15 mg L^{-1} for TN, NOM-001-SEMARNAT-1996) and in fact far lower than the values detected at international level in some water bodies with hypereutrophic conditions (Table 3). However, the mean annual P concentrations of all sites were higher than the threshold of 75 µg L^{-1}, which marks the boundary between mesotrophic and eutrophic conditions (USEPA, 2012), as well as the lower limit (≥77.7 µg P L^{-1}) for hypereutrophic conditions indicated for tropical/subtropical reservoirs by Fernandes-Cunh*a et al*. (2013), indicating a strong possibility of P-related deterioration of the water quality of the river. Nonetheless, this deterioration of water is more evident due that TN and TP average concentrations reported by Maybeck (1982) for in wide variety of unpolluted rivers (375 for TN and 25 for TP, µg mL^{-1}), are very less than for Presidio River.

Table 3. Average concentrations of TP and TN of some hypereutrophic water bodies.

	TN (µg L^{-1})	TP (µg L^{-1})	Reference
Meuse, Belgium	6160	487	Maybeck (1982)
L'Albufera Lake, Spain	3900	361	Martín *et al.* (2013)
Villerest Reservoir, France	2580	240	Jugnia *et al.* (2004)
Garças Reservoir, Brazil	2498	208	Escudeiro de Oliveria *et al.* (2010)
Presidio River, México	640	167	This study
Nakdong River, South Korea	4300	165	Ha *et. al.* (1998)
Mulgum River, Korea	4100	151	Kim *et. al.* (2001)
Waekwan River, Korea	4300	145	Kim *et. al.* (2001)
Nam River, Korea	3800	130	Kim *et. al.* (2001)
Sacramento, USA	417	120	Maybeck (1982)

These data were obtained when the Picachos Reservoir was not completely filled and was receiving water from the Presidio River and from the several waterways discharging into this new water body. Since the reservoir was built with the purposes of power generation and of irrigation to the fertile but water-poor agricultural soils of southern Sinaloa, further data will have to show how this change in water use might have affected the water quality downstream.

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Received: 8 September 2015; Accepted: 23 January 2017