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Water quality and ecological risk assessment of intermittent streamflow through mining and urban areas of San Marcos River sub-basin, Mexico

Elisenda López [a], Reynaldo Patiño [b], María L. Vázquez-Sauceda [c,*], Roberto Pérez-Castañeda [c], Leonardo U. Arellano-Méndez [a], René Ventura [d], Lorenzo Heyer [d]

[a] Institute of Applied Ecology, Autonomous University of Tamaulipas, División del Golfo 356, Col. Libertad, 87019, Cd. Victoria, Tamps, Mexico
[b] U.S. Geological Survey, Texas Cooperative Fish and Wildlife Research Unit and Departments of Natural Resources Management and of Biological Sciences, Texas Tech University, Lubbock, TX 749409-2120, USA
[c] Faculty of Veterinary Medicine and Zootechnics, Autonomous University of Tamaulipas, Km. 5 Ctra. Victoria-Mante, 87000, Tamps, Mexico
[d] Faculty of Engineering and Sciences, Autonomous University of Tamaulipas, Centro Universitario, 87120, Cd. Victoria, Tamps, Mexico

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ABSTRACT

Intermittent rivers are becoming more ecologically stressed worldwide. Flow cessation occurs naturally and spatiotemporally in these systems and anthropogenic activities such as wastewater discharges can have considerable impacts. Public entities mostly monitor water quality in permanent streams, leading to insufficient monitoring of intermittent streams and consequently to their potentially inadequate management.. This study analyzed spatiotemporal patterns of water quality and associated ecological risk through the quantification of physicochemical and microbiological pollutants in the intermittent river system of El Novillo and San Marcos in Northeast Mexico. Results showed that water quality varied geographically and seasonally. Based on national and international criteria, annual averages of water quality parameters analyzed suggested that streamflow in these river systems is of poor quality and poses high ecological risk to aquatic life. In the urban area, annual mean concentrations of Cd and Pb (0.14 and 0.4 mg/L) were 77- and 10-fold higher than their respective water quality criteria (<0.0018 and 0.04 mg/L). Statistically significant ($q < 0.05$) correlations were identified in concentrations of cyanide, Cd, Cu and Pb between wastewater seeping into the river and streamflow within the urban area. These observations highlight the unique sensitivity of intermittent urban streams to anthropogenic activities and may provide useful information to enhance current water management plans for the El Novillo-San Marcos River system for the protection of ecosystem integrity and human health.

1. Introduction

In arid and semi-arid areas worldwide, many river systems are intermittent or temporary, lacking flow at some points in time and space (Arthington et al., 2014). These ecosystems are ecologically important because they support diverse plant and animal communities, particularly when viewed at timescales that encompass periods of flow, standing water, and no water (Snelder et al., 2013). Despite their importance, the hydroecology of intermittent streams is poorly understood and their ecosystem service contributions are often underestimated (Acuña et al., 2014, 2017). An example of the latter is that when they are seen and managed as permanent streams, the ecological relevance of their dry phase is often ignored and actions are taken to transform these systems into permanent streams through discharge additions from wastewater treatment plants or reservoirs (Ruhí et al., 2016).

Intermittent rivers are particularly endangered ecosystems because they often lack adequate management practices and protective policies and legislation (Datry et al., 2014). The natural variability of organic matter and nutrient transformations may be higher than in permanent streams (e.g. rapid ammonium and phosphate release from sediments), and the dynamics of these materials is more distinctly pulsed in intermittent than perennial rivers (Datry et al., 2014). In arid and semi-arid areas, effluents from agricultural, industrial and municipal sectors can

* Corresponding authors.
E-mail addresses: ealtarriba@docentes.uat.edu.mx (E. López), reynaldo.patino@ttu.edu (R. Patiño), mvazquez@docentes.uat.edu.mx (M.L. Vázquez-Sauceda), roperez@docentes.uat.edu.mx (R. Pérez-Castañeda), luarellano@uat.edu.mx (L.U. Arellano-Méndez), reneventura.houle@gmail.com (R. Ventura), lheyer@docentes.uat.edu.mx (L. Heyer).

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contribute the majority (up to 100 %) of the inflow to intermittent rivers (Larned et al., 2010; David et al., 2013; Steward et al., 2012; VanLandeghem et al., 2012), and knowledge about the ecological consequences of artificial perennial flow sustained by effluent discharge with high concentrations of contaminants is limited (Datry et al., 2014). The alterations in the quality of water of intermittent streamflow can greatly impair ecosystems and present risks to human health.

In Mexico, environmental monitoring of the main waterbodies is conducted by the federal government and is based on measurements of several parameters of water quality including physical properties, organic and inorganic constituents, and microbiological indicators (CONAGUA, 2016). Unfortunately, because of the misconception of being of lesser ecological, social and economic importance (Acuña et al., 2017), there is little information about the water quality and ecological conditions of intermittent streams exposed to anthropogenic challenges. In the central area of Tamaulipas state (northeast Mexico), a river of special concern is the San Marcos River. This intermittent river crosses the state's capital city, Ciudad Victoria and flows into the Vicente Guerrero Reservoir, the sixth largest drinking water reservoir in Mexico with a capacity of almost four million cubic meters of water (Periódico Oficial., 2015). The watershed of the San Marcos River harbors potential sources of contamination; for example, mining of serpentine (white asbestos) takes place in the upper reaches, and wastewater leakages and discharges from urban areas are observed downstream (Lera, 2016). Contaminants from these activities and sources are likely to affect river water quality and consequently its ecosystem services as well as, potentially, human health.

The main objectives of this study are to assess the environmental integrity of a small intermittent river sub-basin (San Marcos) and evaluate its probable ecological risk through water quality indices and risk quotients. The specific tasks are to determine (1) if water quality and ecological risk can be classified into different categories spatially and seasonally, (2) if the various sources of pollution within the system influence the spatial and seasonal variation in water quality, and (3) overall associations among water variables as well as correlations between metal concentrations in streamflow and wastewater. These tasks represent working hypotheses to be addressed. Measurements of physicochemical and microbiological parameters were conducted on the San Marcos River between 2015 and 2016 and analyzed using univariate and multivariate statistical approaches to explore spatial and temporal patterns. This information may serve to enhance our understanding of mining and urban impacts on the quality of intermittent streamflow and identify sources of contamination in the San Marcos River sub-basin.

2. Material and methods

2.1. Study area

The San Marcos River sub-basin drains an area of 384 km^2 (Instituto Nacional de Estadística y Geografía (INEGI)., 2010) and is located within the San Fernando-Soto la Marina Hydrological Region in the state of Tamaulipas, northeast region of Mexico (Fig. 1). The upper area of the watershed is formed by the Mata and El Novillo Rivers, born in the Sierra Madre Oriental (1500 mamsl). The middle basin is formed mainly by the San Marcos River, with an approximate length of 41.7 km (Instituto Nacional de Estadística y Geografía (INEGI)., 2010); San Marcos River crosses through Ciudad Victoria (320 mamsl) and flows into the Vicente Guerrero Reservoir (140–150 mamsl) (Gónzalez Rodríguez, 2005).

The climate types in this watershed are sub-humid semi-warm with rains in summer, semi-arid very warm as well as warm (Instituto Nacional de Estadística y Geografía (INEGI)., 2010). Near the upper reach (El Novillo station), the annual average temperature and rainfall are 22.4 °C and 86.1 mm (CONAGUA, 2013). In the urban area (Victoria station), the annual average temperature and rainfall are 24 °C and 76.5 mm (CONAGUA, 2019). According to the available climatological data, the rainy season extends from May to October (Supplemental Figure S1). The El Novillo and San Marcos rivers are intermittent, with periods with little if any water mostly within the dry season (Gónzalez Rodríguez, 2005).

The upper area of the San Marcos River sub-basin, commonly known as the El Novillo Canyon, has been set aside for environmental conservation; it is located within the Altas Cumbres Protected Natural Area (ANPAC) and provides ecosystem services to the population (Periódico Oficial., 2015). Terrestrial ecosystem services derived from ANPAC include important natural land cover and forests with aesthetic, productive and recreational benefits, biodiversity of terrestrial species (e.g. cougar, American black bear, golden eagle), and hiking (hiking and biking trails). Aquatic ecosystem services include an aquifer source (water pumping station commonly known as "La Peñita") and surface water that provides drinking water to the population, aquatic biodiversity, and swimming (pools located near to the upstream). The overall sub-basin serves as the main water source to the state's capital city, with a population of 346,029 habitants (Instituto Nacional de Estadística y Geografía (INEGI), 2015). The main water sources for domestic use are

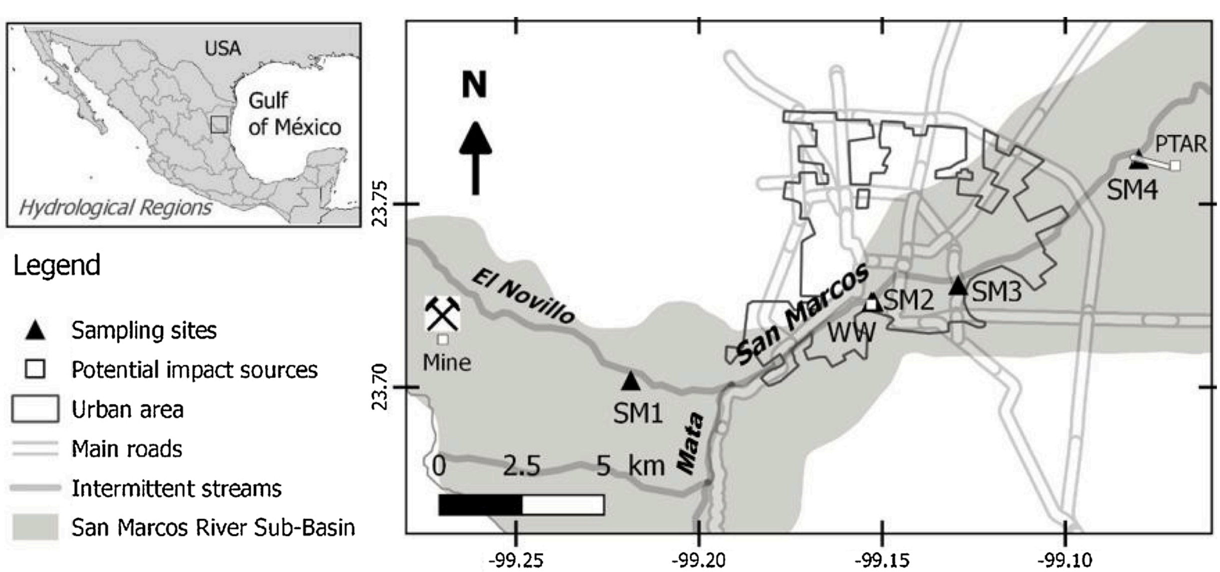


Fig. 1. Study area of water sampling sites in the San Marcos River sub-basin, Mexico. Triangles: sampling sites (SM1-SM4 and WW). PTAR: Wastewater Treatment Plant.

El Novillo Canyon in the upper basin and Vicente Guerrero Reservoir in the lower basin (Periódico Oficial., 2015). Despite its importance as a source of potable water, little information is available about the potential for anthropogenic activities over the sub-basin watershed to affect its water quality. These activities include runoff from mining of serpentine in the upper area and municipal sewage seepage, domestic waste disposal, and motor vehicle cleaning waste (Lera, 2016) in the lower urban area.

2.2. Sampling sites

The following sites were selected to evaluate water quality variability in the San Marcos River sub-basin (Fig. 1) in a downstream direction: a mining-rural area (SM1); a wastewater (raw sewage) site inside a collector (WW); two sites within the urban area (SM2 and SM3); and a post-urban area site (SM4). The first site SM1 is in a mining-rural area in El Novillo River receiving runoff from mining transportation (mineral transported in trucks falling onto watershed) as well as non-point pollutants from subsistence agriculture and scattered households without sanitation. Inside the urban area, the WW site presents wastewater seepage to the river through the subsoil from a continuous wastewater pipeline on the riverbank. The SM2 and SM3 sites are also inside the city limits 100 and 2600 m respectively downstream of the WW site, and SM3 also receives non-point runoff from motor vehicle cleaning activities (Lera, 2016). The last water sampling site, SM4, is outside the urban area and receives tertiary-treated effluent from the Municipal Wastewater Treatment Plant; the discharge point is located 10 m upstream of the sampling site.

2.3. Sampling procedure and analyses

Samples for water quality and risk assessment were collected on May 2015 (=spring), July 2015 (=summer), September 2015 (=autumn) and February 2016 (=winter). Two samples were collected at each site, 5 min apart, into 3.5-L plastic bottles that had been previously washed and rinsed with 10 % HCl. For microbiological analyses of fecal coliforms (FC), previously washed and sterilized 1-L plastic bottles were used. All water samples were preserved in ice for their transport to the laboratory and refrigeration (4 °C) until analyzed. Temperature, pH, conductivity, salinity and total dissolved solids (TDS) were measured in situ using a pre-calibrated Hach® sensION 156 multiparameter probe (Hach Company, Loveland, Colorado, USA). Dissolved oxygen (DO) was read with a pre-calibrated YSI® OD/Temperature meter (YSI Incorporated, Yellow Springs, OH, USA).

In the laboratory, water samples were analyzed for alkalinity, Chemical Oxygen Demand (COD), ionized ammonia nitrogen (NH_4^+), cyanide (CN^-), Cd, Cu and Pb using test kits with a Merck Spectroquant® SQ-118 photometer (Merck, Darmstadt, Germany); the Spectroquant® methods used are equivalent according to the standard methods for the water assessment (APHA, 1999). Total phosphorus (TP) and sulphates (SO_4^{2-}) were quantified according to the standard methods (APHA, 1999). Fecal coliforms analysis was done using the colony-forming unit (CFU) counting method of the Health Public State Laboratory of Tamaulipas, according to the Mexican Official Norm NOM-210 (Secretaría de Salud (SSA), 2014).

2.4. Surface water quality and ecological risk assessment

We evaluated overall water quality according to the Water Quality Index (WQI) of the Canadian Council of Ministers of the Environment (CCME) (2001). For this purpose, water quality parameters for each river water site (SM1-SM4) and season (Spring 2015-Winter 2016) were compared to recommended international and national water quality criteria (WQC) for aquatic life protection. To identify potential sources of contamination into the river, wastewater values were also compared to the Mexican Official Norm NOM-001 for permissible maximum limits (PML) for wastewater (Secretaría de Medio Ambiente, Recursos Naturales y Pesca (SEMARNAT), 1996).

We also made an ecological risk assessment based on the mean seasonal values for each river site and season. For this purpose, the risk quotients (RQ) were calculated for each river site and season according the method of Lemly (1996), which consist of dividing the exposure environmental concentration of each parameter by its WQC.

2.5. Statistical analysis

Statistical analyses were done using STATISTICA® 8.0 (StatSoft, 2007) with a confidence interval of 95 % and statistical significance level (α) of 0.05. We assessed normality and homoscedasticity of data using the Kolmogorov-Smirnov and Bartlett tests, respectively. To fulfill the assumption of homoscedasticity, some parameters were square or square-root transformed; once transformed, significant differences of parameters between sampling sites were assessed with ANOVAs followed by Tukey's HSD post-hoc tests. Transformed data that did not accomplish homoscedasticity were analyzed by non-parametric ANOVAs Kruskal-Wallis tests.

To correct for or improve linearity for analyses based on correlations, normal scores were obtained for all variables using the method of Blom (1958). This data transformation was done using the RANK procedure in SAS version 9.4 (SAS Institute Inc., Cary, NC, USA). The overall association of all variables from all sites between each other, as well as the association between sampling sites and wastewater for CN^- and heavy metals, were evaluated with Pearson correlation analyses.

The type 1 error rates introduced by conducting numerous hypothesis tests were controlled with the False Discovery Rate (FDR) method. For this purpose, all *p*-values generated from parametric and non-parametric ANOVAs and correlations analyses were used to calculate *q*-values (interpreted in similar fashion as *p*-values) while maintaining the percentage of false discoveries at 5 % according to the adaptive method of Benjamini et al. (2006). *Q*-values were obtained using GraphPad Prism® 8.1.1 (GraphPad Software, 2019).

To examine geographic and seasonal patterns of river water quality in our study area, principal component analysis (PCA) based on correlations was applied to normal scores using STATISTICA® 8.0 (StatSoft, 2007). The criterion of eigenvalues ≥ 1.0 was used to select principal components (PCs) for interpretation. The importance of the contribution of each variable to individual PCs was assessed by their loading factors with a value $\geq |0.6|$. To facilitate identification of patterns in data distribution, 95 % confidence ellipses (standard error [SE]) were drawn around selected data groups in PC biplots. Grouping variables for this analysis were site and season.

3. Results

3.1. Surface water quality and ecological risk assessment

The annual mean concentrations of DO, NH_4^+, TP, COD, Cd and Pb parameters in the river sampling sites (SM1-SM4) were outside of the international and national recommended levels of WQC for aquatic life protection (Table 1). In regard to pH, conductivity, FC and Cu, their annual mean concentrations were outside of the recommended levels of WQC in the following sites: pH and Cu in SM2 and SM4; conductivity in SM1; FC in SM1, SM2 and SM3. In the wastewater (WW) site, the annual mean concentrations ($n = 16$) of Cd and Pb exceeded the PML for aquatic life protection (Secretaría de Medio Ambiente, Recursos Naturales y Pesca (SEMARNAT), 1996) (Table 1).

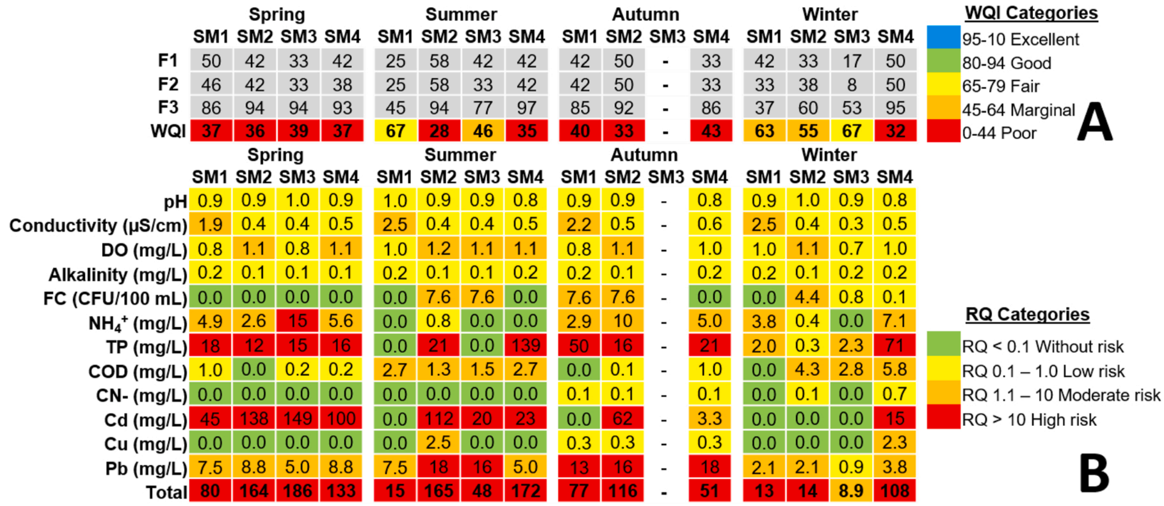
According to the CCMEWQI method (CCME, 2001), the annual average for water quality was classified as "poor", the worst category, for all sites (Fig. 2A). The severity of impairment by site was SM2 > SM4 > SM3 > SM1. By season, the best/worst water quality was registered in winter/spring, coinciding with the outside/inside period of raining, respectively; while in summer, SM1 and SM3 were classified as

Table 1

Annual concentrations of physicochemical parameters in surface water (SM1-SM4) and wastewater (WW). For each site, data for all sampling dates were combined and reported as means ± standard deviation. Values in parenthesis indicate range (minimum-maximum). All the San Marcos River Sub-basin sites were sampled on 2015 (May, July, September) and 2016 (February). In bold: values outside the range of recommended limits.

Parameter	SM1 (n = 8)		SM2 (n = 8)		SM3 (n = 6)		SM4 (n = 8)		WW (n = 8)		WQC (surface water)	PML (wastewater)
Physicochemical												
Temperature (°C)	22.9 ± 2.5	(20–26.4)	23.5 ± 2.8	(19.5–26.6)	24.5 ± 3.0	(21–27.2)	26.5 ± 2.4	(23.1–29.1)	25.6 ± 3.6	(20.4–28.5)	NE	NE
pH (Standard units)	7.2 ± 0.2	(7.1–7.6)	7.5 ± 0.5	(6.9–**8.2**)	7.6 ± 0.3	(7.2–7.9)	6.7 ± 0.3	(**6.2**–6.9)	7.7 ± 0.5	(7.2–8.5)	6.5–8 (Water Quality Management Strategy (NWQMS), 2000)	NE
Conductivity (μS/cm)	**800** ± 82	**(670–881)**	973 ± 149	(823–1182)	793 ± 102	(671–909)	1170 ± 77	(1082–1272)	1634 ± 123	(1451–1774)	30–350/125–2200 * (Water Quality Management Strategy (NWQMS), 2000)	NE
Salinity (%)	0.4 ± 0.1	(0.3–0.5)	0.4 ± 0.1	(0.4–0.5)	0.3 ± 0.1	(0.3–0.4)	0.5 ± 0.0	(0.5–0.5)	0.8 ± 0.1	(0.7–0.9)	NE	NE
TDS (mg/L)	396 ± 52	(339–470)	482 ± 54	(445–567)	377 ± 25	(357–408)	548 ± 18	(521–565)	804 ± 42	(739–875)	NE	NE
DO (mg/L)	5.6 ± 0.6	(**4.8**–6.4)	**4.5** ± 0.4	(**3.92**–5)	6 ± 1.2	(**4.5**–7.5)	**4.8** ± 0.4	(**4.4** – 5.4)	0.2 ± 0.2	(0–0.5)	≥ 5 ** European Commission (EC) (2006)	NE
Alkalinity (mg/L)	162 ± 24	(125–220)	281 ± 21	(260–305)	198 ± 37	(125–250)	178 ± 24	(160–225)	453 ± 55	(410–575)	> 20 (US Environmental Protection Agency (USEPA), 1985)	NE
Microbiological												
Fecal Coliforms (CFU/100 mL)	**409** ± 774	(2–**1600**)	**1031** ± 609	(4–**1600**)	**593** ± 816	(9–**1600**)	4.8 ± 7.0	(2–21)	na		< 210 (Secretaría de Desarrollo Urbano y Ecología (SDUE), 1989)	NE
Nutrients												
NH_4^+ (mg/L)	**0.1** ± 0.1	(0–**0.29**)	**0.13** ± 0.2	(0–**0.47**)	**0.18** ± 0.4	(0–**0.8**)	**0.16** ± 0.1	(0–**0.4**)	0.37 ± 0.2	(0.13–0.9)	< 0.036 *** (Environment and Sustainable Resource Development (ESRD), 2014)	25
Total Phosphorus (mg/L)	**0.4** ± 0.5	(0–**1.0**)	**0.6** ± 0.5	(0.01–**1.3**)	**0.3** ± 0.3	(0–**0.8**)	**3.1** ± 2.8	**(0.8–8.3)**	6.38 ± 2.2	(3.9–10)	< 0.02 / < 0.05 * (Water Quality Management Strategy (NWQMS), 2000)	10
Chemical												
COD (mg/L)	2.8 ± 3.8	(0–8)	**14** ± 19.1	(0–**43**)	**15** ± 22.9	(0–**56**)	**24** ± 27.0	(0–**82**)	51 ± 16.3	(33–77)	< 3 **** (1994 United Nations Economic Commission for Europe (UNECE), 1994)	NE
CN^- (mg/L)	0.0 ± 0.0	(0–0.002)	0.0 ± 0.0	(0–0.003)	0.0 ± 0.0	(0–0.001)	0 ± 0.01	(0–0.014)	0.04 ± 0.02	(0.014–0.079)	< 0.022 (US Environmental Protection Agency (USEPA), 1985)	2
SO_4 (mg/L)	143 ± 39.3	(83–202)	110 ± 28.7	(82–155)	98 ± 23.3	(83–130)	123 ± 23.6	(56–167)	122 ± 17	(76–151)	NE	NE
Heavy metals												
Cd (mg/L)	**0.02** ± 0.05	(0–**0.13**)	**0.14** ± 0.09	(0–**0.39**)	**0.1** ± 0.17	(0–**0.4**)	**0.06** ± 0.04	(0–**0.25**)	**0.4** ± 0.24	**(0.09–1.02)**	< 0.0018 ***** (Environmental Protection Agency (EPA), 2016)	0.2
Cu (mg/L)	0.0 ± 0.0	(0–0.01)	0.03 ± 0.05	(0–**0.1**)	0 ± 0	(0-0)	0.03 ± 0.04	(0–**0.11**)	0.59 ± 0.27	(0.27–1.1)	< 0.04 ***** European Commission (EC) (2006)	6
Pb (mg/L)	**0.3** ± 0.17	**(0.08–0.5)**	**0.45** ± 0.34	**(0.8–1)**	**0.3** ± 0.32	(0.03–**0.7**)	**0.35** ± 0.27	**(0.15–0.9)**	**2.98** ± 1.52	**(0.94–4.7)**	**< 0.04** ****** (Water Quality Management Strategy (NWQMS), 2000)	0.4

Notes: WQC: Water Quality Criteria. PML: Permissible Maximum Limit in wastewater discharged to national waterbodies, for the protection of aquatic life Secretaría de Medio Ambiente, Recursos Naturales y Pesca (SEMARNAT), 1996). NE: not established. (*) Upstream/Downstream; (**) cyprinids waters (waters in which fish belonging to the cyprinids live or could live (Cyprinidae), or to other species such as the pike (Esox lucius), perch (Perca fluviatilis) and eel (Anguilla anguilla); (***) Calculated according to a temperature of 20°C and pH of 7. (****) Best ecological class. (*****) Dissolved in water with a hardness of 100 mg CaCO3/L. (******) Dissolved in water with a hardness of 210 mg CaCO3/L·.



	Spring				Summer				Autumn				Winter			
	SM1	SM2	SM3	SM4	SM1	SM2	SM3	SM4	SM1	SM2	SM3	SM4	SM1	SM2	SM3	SM4
F1	50	42	33	42	25	58	42	42	42	50	-	33	42	33	17	50
F2	46	42	33	38	25	58	33	42	42	50	-	33	33	38	8	50
F3	86	94	94	93	45	94	77	97	85	92	-	86	37	60	53	95
WQI	37	36	39	37	67	28	46	35	40	33	-	43	63	55	67	32

	Spring				Summer				Autumn				Winter			
	SM1	SM2	SM3	SM4	SM1	SM2	SM3	SM4	SM1	SM2	SM3	SM4	SM1	SM2	SM3	SM4
pH	0.9	0.9	1.0	0.9	1.0	0.9	0.9	0.8	0.9	0.9	-	0.8	0.9	1.0	0.9	0.8
Conductivity (μS/cm)	1.9	0.4	0.4	0.5	2.5	0.4	0.4	0.5	2.2	0.5	-	0.6	2.5	0.4	0.3	0.5
DO (mg/L)	0.8	1.1	0.8	1.1	1.0	1.2	1.1	1.1	0.8	1.1	-	1.0	1.0	1.1	0.7	1.0
Alkalinity (mg/L)	0.2	0.1	0.1	0.1	0.2	0.1	0.1	0.2	0.2	0.1	-	0.2	0.2	0.1	0.2	0.2
FC (CFU/100 mL)	0.0	0.0	0.0	0.0	0.0	7.6	7.6	0.0	7.6	7.6	-	0.0	0.0	4.4	0.8	0.1
NH_4^+ (mg/L)	4.9	2.6	15	5.6	0.0	0.8	0.0	0.0	2.9	10	-	5.0	3.8	0.4	0.0	7.1
TP (mg/L)	18	12	15	16	0.0	21	0.0	139	50	16	-	21	2.0	0.3	2.3	71
COD (mg/L)	1.0	0.0	0.2	0.2	2.7	1.3	1.5	2.7	0.0	0.1	-	1.0	0.0	4.3	2.8	5.8
CN- (mg/L)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	-	0.1	0.0	0.1	0.0	0.7
Cd (mg/L)	45	138	149	100	0.0	112	20	23	0.0	62	-	3.3	0.0	0.0	0.0	15
Cu (mg/L)	0.0	0.0	0.0	0.0	0.0	2.5	0.0	0.0	0.3	0.3	-	0.3	0.0	0.0	0.0	2.3
Pb (mg/L)	7.5	8.8	5.0	8.8	7.5	18	16	5.0	13	16	-	18	2.1	2.1	0.9	3.8
Total	80	164	186	133	15	165	48	172	77	116	-	51	13	14	8.9	108

Fig. 2. A: Water Quality Index Factors: F1 (scope): percentage of variables that do not meet their objectives; F2 (Frequency): percentage of individual tests that do not meet objectives; F3 (Amplitude): amount by which failed test values do not meet their objectives. Water Quality Index (WQI) and category in each water sampling site (SM1-SM4) and season, along the San Marcos River sub-basin, according CCMCEWQI (CCME, 2001). B: Ecological categories of risk calculated from risk quotients in each season and water site (SM1-SM4) from the San Marcos River sub-basin.

fair and marginal quality, respectively.

The results of the ecological risk assessment for each sampling site and parameter separated by season are provided in Fig. 2B. Alkalinity, conductivity, pH, DO, CN^-, FC and Cu did not reach the high-risk category in any site or season. Fecal coliforms, CN^-, and Cu classified as "without risk" in all sites in spring; $NH_4^+$and Cu also classified in this category in summer in all sites except SM2. Total phosphorus, Cd, Pb and NH_4^+ fell in the highest-risk category on several sites and seasons (Fig. 2B); Pb had the worst category in SM2 and SM3 in summer, and SM1, SM2 and SM4 in autumn. Winter only showed two high-risk categories, for TP and Cd, in SM4.

3.2. Water quality variation between sampling sites

Mean values (± Standard Deviation) and their pairwise differences (n = 2) between sampling sites for each parameter, separated by season are shown on Supplemental figures S2-S4. Parameter values in wastewater were significantly (q <0.05) higher than those in surface water in all seasons for the following: alkalinity, conductivity, TDS, TP, salinity, CN^-, Cu and Pb (Supplemental Figs. S2-S4). There were no significant (q >0.05) differences between wastewater and surface water in the following seasons/parameters: spring/temperature, NH_4 and SO_4^{2-}; summer/pH and temperature; autumn/pH, COD; and winter/NH_4, COD and temperature.

In the San Marcos River sub-basin, temperature was the only parameter that registered a significant (q <0.05) increase in a downstream direction (SM1 < SM2 < SM3 < SM4) in all seasons (Supplemental Fig. S2). The following parameters also registered a downstream increase compared to SM1, but in different ways: for TP and COD only in spring and summer, respectively; TDS except in site SM3 where the values were similar to SM1 in summer (Supplemental Figs. S2 and S3). It also must be noted that, for the largest significant differences observed, a discontinuous spatial and temporal pattern was observed for the following parameters (Supplemental Figs. S2-S4): alkalinity, pH, TP, FC and Cd in SM2; pH, DO, FC, TP, COD in SM3; and COD, TP, salinity, CN^- and Pb in SM4. Lastly, NH_4^+ and Cu did not vary (q >0.05) among surface water sampling sites; while the highest values for DO were observed in winter.

3.3. Geographic and seasonal patterns in water quality

The first four principal components explained the 73 % of the variance in the data (Supplemental Table S5). Conductivity, Cd, Temperature, Pb, TP and DO dominated PC1, and were positively associated with each other and negatively with DO (Supplemental Table S5). The highest loading factors in PC2 were for CN, Cu, SO_4 and pH, and were positively associated with each other and negatively with pH (Supplemental Table S5). In PC3 and PC4, the highest loading factors were for FC/alkalinity and COD/NH_4, respectively and FC and alkalinity were positively associated, whereas COD and NH_4 were inversely associated with each other, respectively (Supplemental Table S5).

The PC1-PC2 biplots show a clear separation between sites/seasons; along the PC1 axis, streamflow at SM4-SM2 generally had the highest/lowest conductivity, Cd, temperature, Pb, TP at autumn/winter, respectively; and the lowest/highest DO occurred at autumn/winter, respectively (Fig. 3A). Samples taken from SM3 and some SM1 generally had intermediate values. The PC2 axis clearly separated water quality data according to sites/season; for PC2, the highest CN, Cu and SO_4 and lowest pH were observed in SM4 at autumn and winter, and the reverse conditions occurred in SM3 at summer and spring (Fig. 3A).

The PC3-PC4 biplots (Fig. 3B) also seemed to indicate spatial and seasonal separation of water quality data but in a more specific manner than the PC1-PC2 biplots (Fig. 3A). The 95 % confidence ellipses of water data grouped by site suggested that SM2 had higher FC and alkalinity (PC3) than SM4 in all seasons, while COD/NH_4 was highest/lowest in summer/spring, respectively (Fig. 3B).

3.4. Correlation of physicochemical, microbiological and heavy metals parameters

The global correlation matrix made of physicochemical, microbiological and heavy metals in samples from all seasons and sites indicated several significant (q < 0.05) correlations (Fig. 4A). Namely, significant correlations were observed for physicochemical versus cyanide/Cd/Cu/Pb (r = 0.4-0.7); SO_4 versus Cd (r = -0.6); CN^-/Cd versus Cu/Pb (r = 0.4-0.8); Cu versus Pb (r = 0.8) (Fig. 4A).

Cyanide and heavy metal concentrations indicated several correlations between WW and surface water quality at several of the sampling sites (Fig. 4B). No significant correlations (q > 0.05) were observed between WW and surface water from SM1, except for Cd. The other streamflow sites did register significant correlations with WW (q < 0.05) although in different ways: for CN^- with SM2 to SM4; for Cu with SM2; for Cd with SM3; and for Pb with SM2 and SM3.

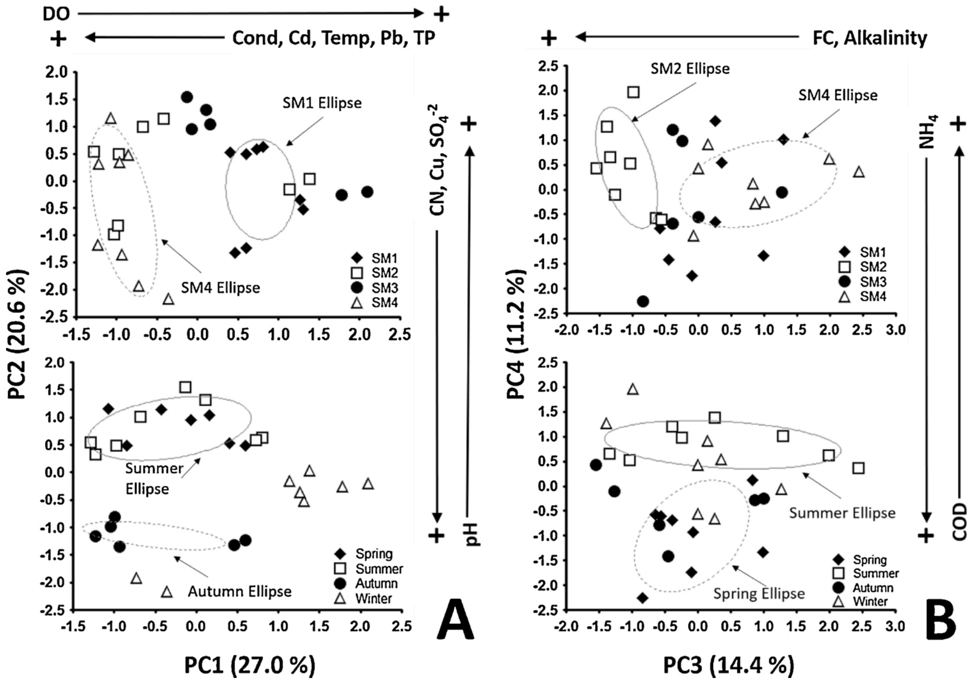


Fig. 3. Biplots of the four principal components (PC) factor scores from PCA of water quality parameters in San Marcos River sub-basin, Mexico. A: PC 1 and 2. B: PC 3 and 4. To facilitate visual identification of patterns, 95 % confidence ellipses were constructed around the groups showing the greatest or clearest separation. The direction of factor loadings with a correlation coefficient ≥ |0.6| for each PC are shown on the top and right margins of each biplot set.

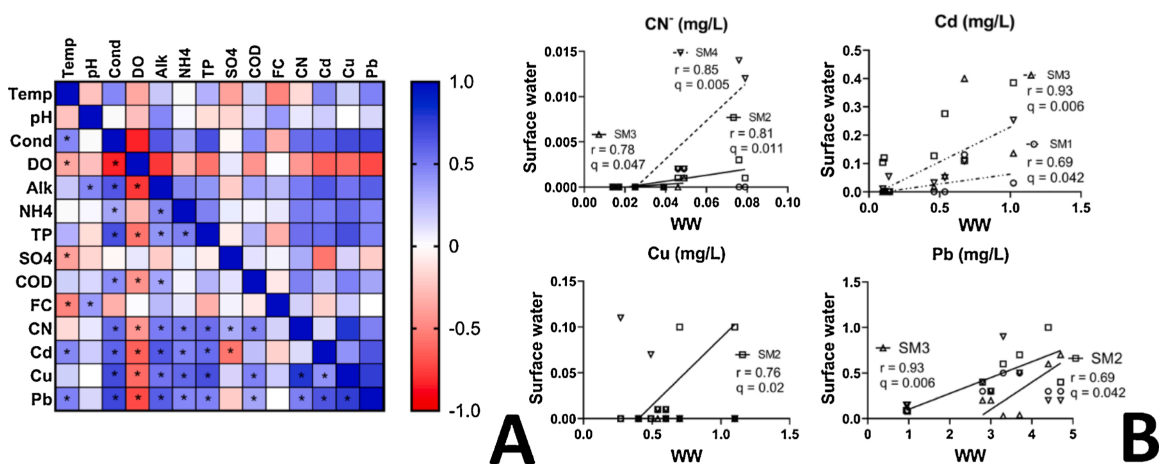


Fig. 4. A: Pearson correlation Heatmap of rank-transformed water parameters from the San Marcos River sub-basin. *, significant association at $q < 0.05$. B: Pearson correlation scatterplots of cyanide and heavy metals concentrations in surface water (SM1-SM4) against wastewater (WW) along the San Marcos River sub-basin. Data were pool for all seasons (n = 8), except for SM3 in autumn when this site was dry (n = 6). For each site, a regression line was superimposed on the respective scatterplot when the association was significant.

4. Discussion

4.1. Water quality indices and ecological risk

The lack of effective water management plans coupled with population growth, estimated in Mexico to be 1.41 % average annual growth rate for 2010–2015 (UN, 2017), can lead to steep increases in human demands for water withdrawals. According to Hudson et al. (2005), this scenario becomes more unfavorable when considering that the hydrology, geomorphology, biodiversity and ecology of rivers in Mexico is insufficiently studied and, therefore, the impacts of anthropogenic activities are largely unknown. Concerning wastewater impacts on rivers, proper maintenance of the sanitation network becomes key to guaranteeing ecological protection from potential sources of pollution. The challenge for studies such as the present one is that reference (unimpacted) sites are rarely available for comparison purposes, but this does not undermine the conclusions of the study regarding spatiotemporal patterns in water quality.

In the present study, estimates of poor water quality and high ecological risk for El Novillo and San Marcos rivers were based on annual averages of water quality parameters that exceeded recommended levels for the protection of aquatic life. At one or more sites, the parameters of DO, pH, conductivity, COD, NH_4^+, TP, FC, Cd, Cu and Pb exceeded the recommended standards. The upstream-most site of this study, SM1, is in a rural area where mining activity takes place. Recommended values for conductivity (< 350 µs/cm for headwaters), TP (< 0.02 mg/L for headwaters), NH_4^+ (< 0.036 mg/L) and FC (<210 CFU/100 mL) were exceeded at this site. The reason for the high levels of these parameters at this site are likely due to pollution sources not examined in this study, such as the organic decomposition, geological deposits, soil erosion and fertilizer runoff (Wang et al., 2013). Despite NH_4^+ exceeding the recommended value, however, the annual average concentration (0.1 mg/L) is typical of surface waters (range, 0.1 to 0.2 mg/L; Meybeck et al., 1996). According to Meybeck et al. (1996), the anthropogenic increase of phosphorus may lead to the acceleration of eutrophication processes in river water, due to overproduction of primary producers. The annual average of Cd and Pb (0.02 and 0.3 mg/L, respectively) also exceeded the recommended values at SM1. Vehicular traffic at off-road river crossings may be the source of Cd and Pb in this area; this suggestion is consistent with the heavy metals and TP found in other studies carried out in water closer to the traffic and road areas (Czemiel Berndtsson, 2014). According to Van Bohemen and Van de Laak. (2003) the transported products (e.g. waste, extraction materials) from trucks can fall and pollute the environment. The Pb exceedance also coincides with the proximity of this site to lead deposits and serpentine rocks in El Novillo mining-region (Servicio Geológico Mexicano (SGM), 2014). High concentrations of other potentially toxic elements (Co, Cr, Cu, Fe, Ni) have been found in serpentine soils and plants (Bini et al., 2017). Regarding the ecosystem services derived from ANPAC (Periódico Oficial., 2015), the exceedance levels of these contaminants have the potential to impact surface waters and cause damage to the health of aquatic species and human health (e.g. transmission of infectious diseases).

Urban and post-urban areas showed lower (poorer) WQI than site SM1, which coincided with high ecological risk categories for nutrients, Cd and Pb (RQ > 10) and moderate risk for COD and FC (RQ = 1–10). The low WQI value in SM2 coincided with the highest and significant ($q < 0.05$) levels for conductivity, pH, COD, DO, TDS, temperature, TP, SO_4^{2-}, FC and Cd observed at this site. These levels of contamination at SM2 are likely due to leakage from the wastewater pipeline located a short distance (100 m) upstream of the sampling site, a conclusion also supported by the significant ($q < 0.05$) correlation of Cu and Pb versus CN- observed at this site. Other authors elsewhere have reported similar values and types of pollutants associated with municipal wastewater effluents (Avakul and Jutagate., 2012; Wang et al., 2013). The FC concentrations found in urban area (highest 1600 CFU/100 mL) present a risk to public health, as these pathogenic microorganisms can cause gastroenteritis and other diseases (Ashbolt, 2004). These observations are consistent with those of Sandoval Villasana et al. (2009), who showed that municipal wastewater is the main pollution source of fecal bacteria in surface waters elsewhere in Mexico. In summer and autumn, the highest FC concentration in pre and urban areas occurred in summer and autumn during the rainy season, a finding consistent with the study of Sanders et al. (2013), who reported higher levels of this parameter during periods of rain in Santa Cruz basin (South Arizona, USA).

In the downstream-most site of this study, SM4, the low WQI value was associated with significantly ($q < 0.05$) higher levels (compared to SM1) of alkalinity, CN^-, Pb (in winter), conductivity, TDS (all seasons), COD (summer), TP, SO_4^{2-} (summer and winter), and Cd (spring). The maximum CN- levels registered in this site (0.014 mg/L) are higher than those reported by Zheng et al. (2003) in unchlorinated (0.002 mg/L) and chlorinated (0.004 mg/L) secondary municipal effluents.

In the wastewater seepage site (WW), Cd/Pb concentrations were above the PML (>0.2/>0.4 mg/L). Effluent at this site leaking through the subsoil into the stream had not undergone treatment process. The maximum levels of Cd/Pb (1/4.7 mg/L) are of concern because if these are released to surface water, they can bioaccumulate in the trophic chain (Yamaguchi et al., 2003). Elevated concentrations of Pb in ecosystems have been associated to urbanization, population densities and vehicular traffic (Lohani et al., 2008; Czemiel Berndtsson, 2014). Cadmium and lead in surface water are of concern because they are harmful to aquatic organisms as well as humans, as it can affect the nervous system and internal organs (Mazet et al., 2005). The high CN^- concentrations (0.079 mg CN^-/L) at the WW site also are of ecological concern because of the lethality of cyanide to fishes; this value is above the median lethal concentration (LC50) for rainbow trout (0.049 mg CN^-/L) reported by Barber et al. (2003).

4.2. Geographic and seasonal patterns in water quality

The PC1-PC2 biplots indicated that SM1 and SM4/SM2 clearly separate from each other by their concentrations of DO (higher in SM1, especially in winter) and conductivity, temperature, Pb, Cd and TP (higher in SM4, especially in autumn and summer). This observation was expected due to the upstream/midstream position of these sites and their pre/post-urban location, as well as natural phenomena related to the geographic position in rivers reported by Margalef (1983). The inverse association between temperature and DO in a seasonal manner observed in this study agrees with the observations of Dawson et al. (2015) in Texas surface waters. While the generally higher levels of TP observed in summer disagree with the observations of Dawson et al. (2015), the latter study focused on reservoirs and not on flowing waters as the present study. The PC3-PC4 biplots indicated that the highest/lowest FC were observed in SM2/SM4, respectively. The location of these sites within (SM2) and downstream (SM4) the urban area suggests a degree of microbiological processing as the water flows downstream as well as the effect of discharge of chlorinated effluent of municipal effluent just upstream of the SM4 site.

4.3. Correlations

The significant ($q < 0.05$) correlations of chemical parameters (conductivity/NH_4/TP/COD/SO_4) versus CN^- and heavy metals (Cd/Cu/Pb) between each other in our study are similar to those reported in other urban and mining areas (Kar et al., 2008; Ning et al., 2011). According to Ning et al. (2011), metallic ions such as the Cd/Cu/Pb can react with cyanide and form heavy metals cyanide in water, which usually precipitate in water.

The lack of significant ($q > 0.05$) correlations registered for CN^-/Cu/Pb between WW and SM1 is consistent with its geographical upstream location of the SM1 site. The significant correlation ($q < 0.05$) between WW and SM1 for Cd was unexpected; the reason for this finding is uncertain but could be due to mining-rural inputs of this metal at the SM1 site, as reported in other mining-urban areas (Kar et al., 2008; Ning et al., 2011). Within the urban area (SM2/SM3), significant correlations for CN^-/Cd/Cu/Pb were observed between WW and the surface water sites; these observations support the findings of poor water quality and high ecological risk registered at these sites as well as the spatial separation between sites in PC1-PC2 biplots (section 4.1 and 4.2). Other studies have reported similar heavy metal contamination in urban streams receiving partially-treated or untreated wastewater discharges (Principi et al., 2006; Reza and Singh., 2010). Heavy metals from urban and municipal wastewater sources represent a threat to aquatic biota, as they can accumulate in fish and affect their health and reproductive condition (Patiño et al., 2012). Inadequate water management practices are common in developing countries as the consequence of insufficient financial resources, low prioritization of water and sanitation, lack of accountability and inefficient management (Montgomery and Elimelech., 2007).

5. Conclusions

Results of this study indicated that anthropogenic activities have influenced water quality in the San Marcos River sub-basin. Positive correlations of cyanide and heavy metals between wastewater and streamflow within the urban area suggest that wastewater leakages are contributing to the poor water quality condition of river streamflow. Other human activities could also be affecting water quality, such as runoff and wastes from the vehicular traffic at off-road river crossings (mining and post-urban area), the lack of a pluvial draining in urban areas, and suboptimal wastewater management practices in urban and post-urban areas. Judicious management of waste (liquid and solid) discharges into the river would likely improve water quality and consequently reduce the risk to ecosystem integrity and health of the local population.

The lack of adequate aquatic life protection measures can impair biodiversity and ecosystem integrity (Arthington et al., 2014). Specifically, in the case of temporary rivers impacted by wastewater discharges, concentrations of pollutants may increase during low or no-flow conditions (David et al., 2013). Regarding the high concentrations of nutrients observed downstream from sewage inputs, these lead to eutrophication and reduce biodiversity (David et al., 2013). According to Arthington et al. (2014), there is a need for better monitoring, management and conservation of freshwater biota in intermittent streams and rivers, where increasing pressure from human activities and environmental change is expected. Options to address some of these issues may include the establishment of a land management program to prevent or reduce potential sources of pollution, such as the activities carried out on the banks of the river. Beneficial outcomes may also result from waste reduction programs, improvements in soil conservation practices and in fertilizer and pesticide use and management, a monitoring program for mining activities as well as repairs and improvements of sanitary drainage pipes that cross the riverbed. Implementation of these options may need to take into account sustainability criteria of socially inclusive planning programs.

Author contributions

E.L. made the water collection and analysis, statistical analysis, interpretation of data and wrote the article. M.L.V.S., L.H. and L.U.A.M. contributed to the study design. R.V., M.L.V.S. and L.H. contributed to the collection of data. M.L.V.S., R.P.C., R.P. and R.V. contributed to the interpretation of data. R.P. and R.P.C. contributed to the statistical analysis of the data. R.P. contributed to the editing of English. All authors contributed in the decision to submit the article for publication and have approved the final article.

Author Statement

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All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing, or revision of the manuscript. Furthermore, each author certifies that this material or similar material has not been and will not be submitted to or published in any other publication before its appearance in the *Environmental Nanotechnology, Monitoring and Management.*

Authorship contributions

Category 1

Conception and design of study: L. Heyer, M.L. Vázquez-Sauceda, L. U. Arellano-Méndez;

Acquisition of data: E. López, R. Ventura, M.L. Vázquez-Sauceda, L. Heyer;

Analysis and/or interpretation of data: E. López, R. Patiño, M.L. Vázquez-Sauceda, R. Pérez-Castañeda, R. Ventura.

Category 2

Drafting the manuscript: E. López, R. Patiño, R. Pérez-Castañeda, R. Ventura;

Revising the manuscript critically for important intellectual content: E. López, R. Patiño, R. Pérez-Castañeda, M.L. Vázquez-Sauceda, R. Ventura, L. Heyer.

Editing the english: R. Patiño, R. Pérez-Castañeda.

Category 3

Approval of the version of the manuscript to be published:

E. López, R. Patiño, M.L. Vázquez-Sauceda, R. Pérez-Castañeda, L.U. Arellano-Méndez, R. Ventura, L. Heyer.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.enmm.2020.100369.

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