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Articles

Sediments contamination from a meander of the Lerma River, Mexico

Contaminación de sedimentos de un meandro del río Lerma, México

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Abstract

The aim of this work was to determine the degree of sediment contamination of the isolated part of the Lerma River that crosses the La Piedad and Pénjamo interstate metropolitan area to support the decision-making that must be undertaken with respect to this body of water that interacts with an urban environment. Physicochemical, microbiological, heavy metal, and microscopic particle parameters of sediment samples collected at seven sites in the study area were evaluated. On average, the sediments had a sandy loam texture, with neutral pH (7.6) and electrical conductivity of 868 $\mu\text{S}/\text{cm}$, they were moderately rich in organic matter (2.7 %), with a slight load of fecal coliforms (753 NMP/100 g) and they are being enriched with Zn, Cr and Cu. Plankton particles were observed, but also particles with heavy metals. Considering that the urban sites (5 and 6) showed more indicators outside the established criteria, it is likely that the sediments are receiving contaminants derived from the anthropogenic activities of the place and not those generated upstream. In general, the contamination of the sediments was moderate, however, it is imperative to limit the accumulation of organic matter, pathogenic microorganisms and toxic metals such as Cr in the sediment and avoid reaching a critical point. Due to the above and with the application of some strategies, it will be possible to recover and conserve this area of the river as an isolated body of water independent of the original riverbed.

Keywords: Pollution, fecal coliforms, La Piedad, X-ray fluorescence (XRF), scanning electron microscope (SEM).

Resumen

El objetivo de este trabajo fue determinar el grado de contaminación de sedimentos del cauce aislado del río Lerma que atraviesa la zona metropolitana interestatal La Piedad y Pénjamo, para sustentar la toma de decisiones que haya que emprender con respecto a este cuerpo de agua que interactúa con un ambiente urbano. Se evaluaron parámetros fisicoquímicos, microbiológicos, metales pesados y partículas microscópicas de muestras de sedimentos recolectados en siete sitios del área de estudio. En promedio, los sedimentos tuvieron textura franco arenosa, con pH (7.6) neutro y conductividad eléctrica de 868 $\mu\text{S}/\text{cm}$; mostraron ser medianamente ricos en materia orgánica (2.7 %), con ligera carga de coliformes fecales (753 NMP/100 g), y presentaron un factor de enriquecimiento moderado para Zn, Cr y Cu. Se observaron partículas de plancton, pero también partículas con metales pesados. Considerando que los sitios urbanos (5 y 6) mostraron más indicadores fuera de los criterios establecidos es probable que los sedimentos están recibiendo contaminantes derivados de las actividades antrópicas propias del lugar y no los generados río arriba. En general, la contaminación de los sedimentos fue moderada; no obstante, es imperante limitar que la materia orgánica, microorganismos patógenos y metales tóxicos como el Cr se sigan acumulando en el sedimento y evitar que lleguen a un punto crítico. Por lo anterior y con la aplicación de algunas estrategias será posible recuperar y conservar esta área del río como un cuerpo de agua aislado e independiente del cauce original.

Palabras clave: contaminación, coliformes fecales, La Piedad, fluorescencia de rayos X (FRX), microscopio electrónico de barrido (MEB).

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Introduction

The Lerma River is 708 km long and drains a basin of 47,116 km². It begins at the natural springs of Almoloya del Río, State of Mexico, flows northwest through Querétaro, Guanajuato, Michoacán and drains into Lake Chapala in Jalisco (Hansen, León, & Bravo, 1995). In these regions, the Lerma River has always been a basic natural resource for human activities; however, the continuous and diverse industrial, urban, agricultural, and livestock discharges it receives have classified it as one of the most polluted inland rivers in Mexico. It has been reported that in certain stretches the maximum permitted limits of some pollutants in the water are exceeded (López-Hernández, Ramos-Espinosa, & Carranza-Fraser, 2007; Carreño, Zarazúa, Fall, Ávila-Pérez, & Tejeda, 2018; Conagua, 2018; Hernández-Mendoza, Ríos-Lugo, Romero-Guzmán, Reyes-Gutiérrez, & Ketterer, 2018).

A section of the Lerma River (12.5 km) called “La Piedad-Pénjamo meander”, located on the border between Michoacán and Guanajuato was isolated from the natural channel in the late 1970s with a drain approximately 2.8 km long due to the problem of flooding suffered by urban areas during the flooding of the Lerma River. Being isolated, this meander is constantly silting up, thus decreasing its natural width, and

most of the year it only has stagnant water that, in addition to considerably affecting the ecosystem of the place, produces bad odors, the presence of mosquitoes and a considerable load of open-air pollutants that have strongly influenced public health problems in the region (Ayala-Ortiz, & Abarca-Guzmán, 2014). This is exacerbated considering that in the last 50 years, the population has doubled in this metropolitan nucleus, comprised of the interstate municipalities of La Piedad and Pénjamo, reaching 261,450 inhabitants in 2020 (INEGI, 2020).

The National Water Commission (Conagua) has reported that between 2011 and 2018, the water quality of the meander has declined due to parameters such as total suspended solids, fecal coliforms (FC), and *Escherichia coli* (*E. coli*) being outside the standards established for surface water (Conagua, 2018). In 2009, it was reported that the concentrations of Pb, Cd, and Cr in the water exceeded the limits established by NOM-001-SEMARNAT-1996 (Semarnat, 1996) at clear points in the meander. In addition, the pesticides Dichlorophenyl Dichloroethylene (DDE), endrin, and dieldrin were detected. DDE is a metabolite of the toxic dichlorodiphenyltrichloroethane (DDT), while the other two are used as household insecticides, although dieldrin is banned as a possible carcinogen (Rueda *et al.*, 2011). In addition, sediments were reported to be slightly contaminated with Pb and Ni, moderately to heavily contaminated with Cu and Cr, and heavily contaminated with Zn. The most contaminated sites are located near urban areas, so it was suggested that these metals came from anthropogenic activities (Villalobos-Castañeda *et al.*, 2016). The discharges from the main activity in the area, pig farming, could be the leading source of pollutants (Hansen *et al.*, 1995; Pérez, 2006), although industrial wastewater (some of it

from the metal-mechanical, brick-making, among others) and untreated municipal wastewater that is dumped into the meander, mainly from the municipality of Pénjamo, have also had a considerable impact (IMTA, 2009).

The concentration of heavy metals and pesticides used in agriculture and to combat pests caused by river pollution have been associated with an increase in cancer cases, specifically childhood leukemia (Ayala-Ortiz, & Abarca-Guzmán, 2014). Additionally, the presence of parasites in the water of the meander contributes to the high percentage of minors with gastrointestinal and bronchopulmonary conditions, along with various parasitosis (Rueda *et al.*, 2011).

So far, two plans have been proposed to provide a solution: to channel the meander or consider it a body of water independent of the river bed and view it as a linear park (Rueda *et al.*, 2011; Aguirre, 2019). The river waters are an indispensable part of the ecosystemic base of the region, as well as being a significant part of the history and daily life of the surrounding municipalities (García-Sánchez, 2019; Aguirre, 2019); therefore, the priority in the selection of the most appropriate option was aimed at protecting its integrity and recovery. To have elements that facilitated decision-making, this study seeks to understand the situation of the isolated river bed through the characterization of its sediment, since they are transporters and potential sources of pollutants in aquatic systems (García-Aragón, Díaz-Delgado, & Morales-Reyes, 2003). To this end, the degree of contamination of the sediments was assessed by determining physicochemical and microbiological parameters, the concentration of heavy metals, and the type of microscopic particles.

Materials and methods

Study Field

The study area is a part of the Lerma River, which has a wide curvature known as the “La Piedad-Pénjamo Lerma River meander.” The meander is located between the municipality of La Piedad, northeast of Michoacán, and the Santa Ana Pacueco delegation belonging to the community of Pénjamo, northwest of Guanajuato, at an approximate altitude of 1,675 meters above sea level. The temperature range is commonly 3 to 38 °C. Its semi-warm climate, with hot summers, permanent rains from June to September, and a poorly defined winter season (Téllez, 2019). The Lerma River belongs to the Lerma-Chapala-Santiago hydrological region of the Angulo-Briseñas River sub-basin (Alberto-Villavicencio, 2019). The meander is isolated from the natural channel of the Lerma River due to a relief drain. The meander is fed by the Zináparo, Cinco de Oros, and Hondo streams, as well as treated and untreated municipal water from the surrounding municipalities, as well as water from the Lerma River tributary when the drain gates are opened, mainly to support irrigated agriculture established on the sides of various areas of the meander (Téllez, 2019). Therefore, the amount of water in the meander varies throughout the year. During the rainy season, it is more likely to observe a column of water throughout the meander, while during the dry season, the amount of water decreases considerably to the point that it has sometimes been observed to be completely dry.

Sediment sampling

Sediment sampling was carried out from January to May 2018, when the meander had no water. The seven sampling sites were established at an approximate distance of 1.78 km from each other (Figure 1). At each sampling site, three sediment subsamples were obtained at a depth of 20 cm. Two of them were taken from each bank, and the third from the center of the river. These subsamples were mixed to form a composite sample from each site (Table 1). The sediment was spread on a tray and left to dry in a ventilated room. The final sediment moisture was 8 %.

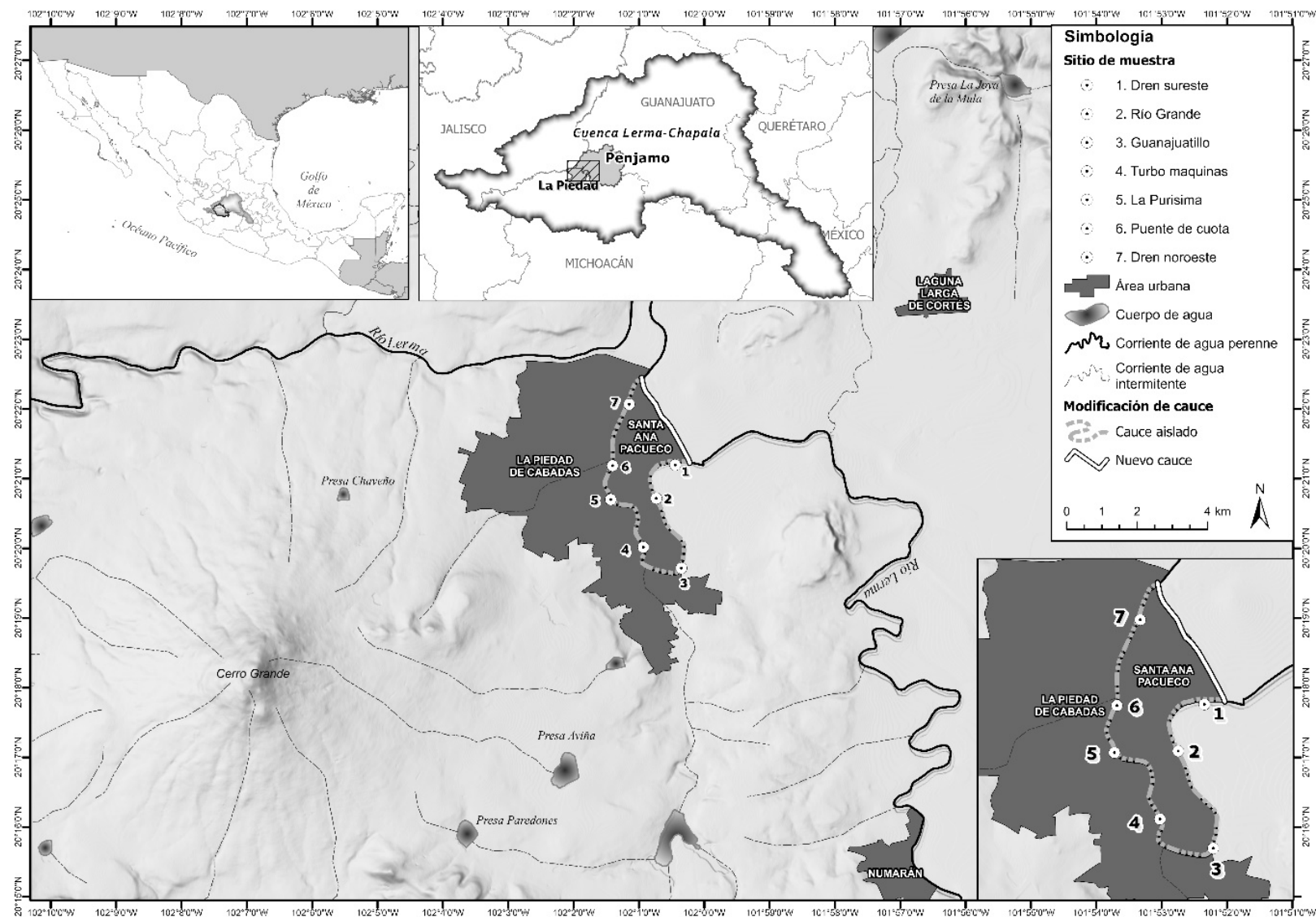


Figure 1. Location of sediment sampling sites in the Lerma River meander. Map prepared by Marco Antonio Hernández-Andrade (2018).

Format: Portable Network Graphics.

Table 1. Location coordinates of sediment sampling sites, location reference and area characteristics.

Site	Reference of the location	Coordinates Latitude N Length O	Sampling site characteristic
1	Southeast drain	20° 21' 11.8", 102° 00' 26.8"	Agricultural area
2	Río Grande	20° 20' 43", 102° 00' 44"	Urban and agricultural area
3	Zináparo stream	20° 19' 43", 102° 00' 21"	Agricultural area
4	Turbo machines	20° 20' 01", 102° 00' 56"	Urban and agricultural area
5	La Purísima	20° 20' 42", 102° 01' 26"	Urban area
6	Toll bridge	20° 21' 11.13", 102° 01' 24.33"	Urban and agricultural area
7	Northwest drain	20° 22' 04", 102° 01' 09"	Agricultural area

Determination of physicochemical parameters

Temperature was measured *in situ* by inserting a 20 cm thermometer into the sediment and reported in °C. Apparent density (AD) was assessed using the test tube method (Semarnat, 2000). The texture class was determined by the Bouyoucos hydrometer method using a 5 % Na₂CO₃ dispersing solution. These results are reported as % sand, % silt, and % clay (Semarnat, 2000). For pH and electrical conductivity (EC) determination, the potentiometric method was used with 20 g of dry sample dispersed in 40 ml of distilled water and homogenized for 30 minutes. Measurements were made after 1 hour (Semarnat, 2000; ASTM, 2000) with a Thermo Scientific potentiometer, mod. Orion A215. Organic

matter (OM) was determined by the Walkley and Black method. To 0.10 g of sample, 5 ml of $K_2Cr_2O_7$ (1 N), 10 ml of 98 % H_2SO_4 , 100 ml of distilled H_2O , and 10 drops of 0.5 % diphenylamine indicator were added. This solution was titrated with 14 % $FeSO_4$ until it turned green (ASTM, 2000; Semarnat, 2000).

Determination of microbiological parameters

10 g of sediment was dispersed in 90 ml of peptone water, then serial dilutions were made of the supernatant (SSA, 1994a) and the most probable number (MPN) procedure was continued (SSA, 1994b) for the quantification of fecal coliforms (FC) and the plate count with nutrient agar for the quantification of aerobic mesophiles (AM). The determination was carried out in triplicate.

Determination of heavy metals

The total heavy metal concentration was determined using the X-ray fluorescence (XRF) method. Each sample was oven-dried at 40 °C, manually disaggregated, pulverized with a mallet, micro-ground, and placed in an aluminum mold to which 20 tons of pressure were applied for 1 minute using a hydraulic press to form a pellet. The pellet was introduced into the chamber of a Thermo Scientific Niton XL3t model, programmed to "Test All Geo" for 240 seconds out of 60-second cycles. XRF measurements were empirically calibrated using two standard soil reference materials with certified metal concentrations. These included the National Institute of Standards and Technology (NIST) standard NIST-

SRM-2709a and the CCRMP Till-4 standard. The average of three measurements in mg/kg is reported, the results are compared with the Maximum Permissible Limits (MPL) for agricultural soils of NOM-147-SEMARNAT/SSA1-2004 (Semarnat, 2004) and with the Lowest Effect Levels (LEL) and Severe Effect Level (SEL) of the Sediment Quality Guide adopted by the National Oceanic and Atmospheric Administration of the United States for freshwater sediments (Buchman, 2008).

Heavy metal enrichment factor

The enrichment factors (EF) were estimated using equation 1, where the sample Me/Fe ratio refers to the concentration obtained for each metal (Me) concerning the Fe concentration. For the background Me/Fe ratio the data reported by the Quality Guide adopted by the National Oceanic and Atmospheric Administration of the United States (NOAA) (Buchman, 2008) were taken:

$$EF = \frac{\frac{Me}{Fe}_{sample}}{\frac{Me}{Fe}_{background}} \quad (1)$$

For interpretation, the values reported by Villalobos-Castañeda *et al.* (2016) were used: $EF < 1$ indicates no enrichment; $1 < EF < 3$ indicates minor enrichment; $3 < EF < 5$ indicates moderate enrichment; $5 < EF < 10$ high enrichment; $10 < EF < 25$ severe, and $25 < EF < 50$ indicates extremely severe enrichment.

Particle analysis in Scanning Electron Microscope (SEM)

A portion of each sample was placed on an aluminum support and introduced into a Scanning Electron Microscope (SEM) (JEOL-JSM-6390LV/LGS). Ten micrographs of different areas of the sample were taken at magnifications ranging from 1000x to 5000x and 20kV. Elemental chemical analysis of the selected particles was performed with an Energy Dispersive X-ray (EDS) coupled to the SEM.

Statistical analysis

The values obtained for each parameter were analyzed using ANOVA with a $p < 0.5$ using Microsoft® Excel® software version 2016. Pearson correlation analysis and principal component analysis (PCA) were performed using Origin software from the Origin Lab 2009 Corporation.

Results and discussion

Physicochemical parameters of sediments

On average, the sediment texture class of the meander is “sandy loam” (Table 2); however, it is a combination of clay, silt, and, to a greater extent, sand. However, in 2009, Villalobos-Castañeda *et al.* (2016) reported that the sediments, sampled at a depth of 10 cm, contained more clay and silt than sand. This is important because it has been established that many of the contaminants, mainly metals, are associated with the clay and silt fraction. Probably, the decrease in the water column, which has prevailed in recent years, causes the fine fraction to be more

susceptible to drag, in addition to the fact that there is less contribution of materials from the river slopes, and therefore the proportion of coarse materials in the substrate increases (Herrera-Núñez, Rodríguez-Corrales, Coto-Campos, Salgado-Silva, & Borbón-Alpizar, 2013).

Table 2. Percentages of sand, silt, and clay and textural class of sediment sample.

Site	% sand	% silt	% clay	Sediment texture
1	52.9 ^a	19.3 ^a	27.8 ^a	Sandy clay loam
2	68.2 ^a	15.3 ^b	16.5 ^a	Sandy loam
3	63.5 ^a	24.0 ^a	12.5 ^a	Sandy loam
4	43.5 ^b	20.0 ^a	36.5 ^b	Clay loam
5	65.5 ^a	19.3 ^a	15.2 ^a	Sandy loam
6	68.4 ^a	21.3 ^a	10.4 ^a	Sandy loam
7	53.3 ^a	42.0 ^c	4.7 ^c	Sandy loam

Different letters per column represent significant differences between sites ($p < 0.5$).

The values of the physicochemical parameters are presented in Table 3. The *in situ* temperatures of the sediments were statistically equal at all sites except for the temperature of site 6 (Puente de cuota) which was four degrees lower than the average. This temperature is probably because the sampling site is under a bridge and does not receive direct sunlight. In general, temperature is an aspect that has an impact on the

growth and type of microorganisms present, and although it is not part of this study, it is also related to the adsorption and desorption capacity of some organic chemical compounds and the diffusion of water flow (Robador *et al.*, 2016; Cornelissen, Van Noort, Parsons, & Govers, 1997; Silliman, Ramirez, & McCabe, 1995).

Table 3. Chemical and physical parameters of the sediments.

Site	T (°C)	AD (g/cm ³)	OM (%)	pH (pH unit)	EC (μS/cm)
1	19.0 ± 0.1 ^a	1.09 ± 0.0 ^a	2.47 ± 2.7 ^a	7.14 ± 0.0 ^a	1 320.0 ± 103.7 ^a
2	20.6 ± 0.2 ^a	0.99 ± 0.0 ^b	2.92 ± 0.0 ^a	7.90 ± 0.1 ^b	585.0 ± 10.3 ^b
3	20.1 ± 0.1 ^a	1.13 ± 0.0 ^c	0.92 ± 0.0 ^b	7.83 ± 0.1 ^b	1 441.0 ± 348.2 ^a
4	21.5 ± 0.0 ^a	1.07 ± 0.0 ^a	2.27 ± 1.3 ^a	7.26 ± 0.0 ^c	247.16 ± 3.1 ^c
5	21.9 ± 0.1 ^a	1.08 ± 0.0 ^a	3.81 ± 1.3 ^c	7.86 ± 0.1 ^b	430.9 ± 3.6 ^b
6	15.0 ± 0.0 ^b	0.99 ± 0.0 ^b	3.25 ± 0.7 ^d	7.97 ± 0.0 ^b	1 771.0 ± 243.9 ^a
7	19.3 ± 0.3 ^a	1.07 ± 0.0 ^a	3.31 ± 0.6 ^d	7.24 ± 0.0 ^c	286.86 ± 0.8 ^c
Average	19.6 ± 2.0	1.06 ± 0.0	2.71 ± 8.8	7.60 ± 0.3	868.85 ± 578.5

T: Temperature

AD: Apparent density

OM: Organic matter

EC: Electrical conductivity

The average of the three measurements is shown. Different superscript letters indicate that there is a significant difference between sampling sites (Tukey, $p < 0.05$).

The AD of the sediments ranges between 0.99 and 1.13 g/cm³, indicating that the sediment allows for adequate air exchange and good nutrient absorption (Vela, Vázquez, Rodríguez, & Domínguez, 2007). At sites 2 and 6 the AD was shown to be significantly equal but lower compared to the other sites.

Site 4 had the lowest EC (247.16 μ S/cm), while the highest was recorded at site 6 (1 771.00 μ S/cm). None of the sites exceeded 2 000 μ S/cm, the maximum permissible limit (MPL) indicated by the USDA Soil Taxonomy (USDA, 1999) which considers that from that value the morphological and physicochemical properties of the profile (and therefore the genesis) are strongly influenced by the saline character.

The pH of the sediments showed values considered neutral (between 7.14 and 7.97) while, in 2009, in sediments from the same area, slightly lower values were recorded (between 6.46 and 7.17) (Villalobos-Castañeda *et al.*, 2016). Neutral to alkaline pH values were also reported in sediments from the upper course of the Lerma River and Lake Chapala (7.1-8.5) (Badillo-Camacho, Murillo-Delgado, Barcelo-Quintal, & Zarate, 2016; Carreño *et al.*, 2018) and in sediments from the San Pedro River in the Aguascalientes region, Mexico (Guzmán-Colis *et al.*, 2011).

On average, the sediment was moderately rich in OM according to the official Mexican standard NOM-021-SEMARNAT-2000 (Semarnat, 2000). Similar results were reported by Juárez, De-la-Fuente and Vaca-Paulín (2005) in soils from the upper basin of the Lerma River with OM percentages of 2.41 %. In sediments from the Pirro River, they found percentages within the same range (2.11-2.71) (Herrera-Núñez *et al.*, 2013), while Márquez, García, Senior, Martínez and González (2012) reported results with a wider range from 0.51 to 5.18 in the middle

Orinoco River. The sediment from site 5, where the main urban settlements are located on both sides of the riverbank, had the highest OM content (3.8 %), while the sediment from site 3, surrounded exclusively by agricultural land, had the lowest content (0.92 %). The above suggests that urban activities influence the accumulation of OM in sediments.

Microbiological results of sediments

The FC content in the sediments varied from 4 to 4,300 MPN per 100 g (Table 4). Other studies have identified very varied concentrations ranging from 1 to 500,000 MPN/100 g in sediments sampled at different depths (Pachepsky, & Shelton, 2011). In sediments from Lake Pátzcuaro, 13 000 MPN/100 g were quantified (Barrera-Escorcia, Fernández-Rendón, Wong-Chang, & Ramírez-Romero, 2013), with concentrations much higher than those found in the sediments of the Lerma River meander.

Table 4. The concentration of mesophiles and fecal coliforms in sediments from the La Piedad-Pénjamo meander.

Site	Aerobic mesophiles (CFU/g)	Fecal coliforms (MPN/100 g)
1	300 ± 20 ^a	400 ± 50 ^a
2	310 ± 10 ^a	230 ± 40 ^a
3	158 ± 10 ^a	4 ± 0.50 ^b
4	340 ± 40 ^a	93 ± 15 ^a
5	1 400 ± 140 ^b	90 ± 10 ^a
6	470 ± 12 ^a	4 300 ± 700 ^c
7	260 ± 40 ^a	150 ± 30 ^a
Average	462.57	752.43

CFU: Colony Forming Units. Different letters per column represent significant differences between sites (Tukey, $p < 0.5$).

The highest concentrations of FC were detected in the sediments of sites 5 and 6, which coincides with what Conagua reports for the water sampled between 2012 and 2018, whose FC concentrations exceeded the LMP established by Mexican regulations by two orders of magnitude (Semarnat, 1996). For example, at site 6, called Puente de cuota, FC was reported in 2018 at 895,252 MPN/100 ml (Conagua, 2018). Several pig farms are located there, so these bacteria probably come from untreated wastewater of municipal and livestock origin, which is dumped into the

meander, whose sediment represents a reservoir of these microorganisms at its interface with the water (Rivera *et al.*, 2007). These microorganisms, which are associated with pathogens, can be resuspended from the sediment into the tributary and represent health risks for the fauna, flora, and inhabitants of the region. In addition, factors such as the OM content and waste dumped into the meander are conducive to the proliferation of microorganisms.

Amount of heavy metals

In the absence of Mexican regulations on sediments, the concentrations of the analyzed metals (Table 5) were compared with the criteria established by the Mexican Official Standard NOM-147-SEMARNAT/SSA1-2004 (Semarnat, 2004) to determine the remediation concentrations of soils contaminated with metals and with the convention for the protection of freshwater sediments, severe effect level and low effect level (SEL and LEL), indicated by NOAA (Buchman, 2008). Regarding the Mexican official standard, the metal concentrations obtained are below the total reference concentrations, considering agricultural/residential/commercial land use. It should be noted that these limits indicated by the Mexican standard are much laxer than those proposed by the NOAA sediment quality guide. According to the latter, site 5 was the one with the highest concentration of metals (Cr, Cu, Ni, and Zn) above the low effect level (LEL). This is the only place, of all those studied, that is urban and where the largest population of the two settled municipalities is concentrated. The next site is site 2, with concentrations of Zn, Cu, and Cr that exceed the LEL, in addition to being the only site that showed significant amounts of Cd. At

this site, there is urban activity on one side of the riverbank and agricultural activity on the other side, so part of the Cd could come from phosphate fertilizers (Márquez *et al.*, 2012). During sampling, a sewage drain was observed right next to the collector, which probably reinforces the increase in metal concentration.

Table 5. The concentration of total metals in sediments of the La Piedad-Pénjamo meander.

Element mg/kg	Sampling site*							TRL NOM 147**	LEL/SEL NOAA***
	1	2	3	4	5	6	7		
Cd	<4 ^a	5.9 ± 3.4 ^b	<4 ^a	<4 ^a	<4 ^a	<4 ^a	<4 ^a	37	0.6/10
Cr	87.2 ± 14.3 ^{ab}	101.5 ± 13.5 ^a	101.1 ± 12.9 ^a	101.3 ± 15.1 ^a	82.1 ± 11.6 ^{ab}	71.6 ± 13.6 ^b	67.7 ± 14.6 ^b	280	26/110
Cu	28.7 ± 8.1 ^{de}	58.8 ± 8.4 ^b	14.8 ± 2.7 ^f	27.2 ± 7.9 ^{ef}	81.3 ± 6.4 ^a	41.3 ± 7.9 ^{cd}	51.5 ± 8.2 ^{bc}	-	16/110
Fe (%)	3.9 ± 0.03 ^b	3.3 ± 0.03 ^e	3.1 ± 0.03 ^f	4.2 ± 0.03 ^a	3.5 ± 0.02 ^d	3.5 ± 0.03 ^c	3.9 ± 0.03 ^b	-	2/4
Ni	<4 ^a	<4 ^a	<4 ^a	<4 ^a	21.1 ± 10.4 ^b	<4 ^a	<4 ^a	1600	16/75
Pb	17.3 ± 3.5 ^b	15.8 ± 3.3 ^b	<4 ^c	13.2 ± 3.3 ^b	29.7 ± 2.6 ^b	26.5 ± 3.6 ^b	<4 ^c	400	31/250
Zn	147.5 ± 7.4 ^e	236.2 ± 8.6 ^b	76.3 ± 5.2 ^g	96.8 ± 6.3 ^f	272.1 ± 6.6 ^a	179.1 ± 7.8 ^d	206.9 ± 7.4 ^c	-	120/820

*The result of the average concentration ± standard deviation performed in duplicate is shown. Different letters in each row indicate sites with significant differences ($p < 0.5$)

**Total reference limits (TRL) for agricultural-residential soils of the official Mexican standard NOM-147-SEMARNAT/SSA1-2004 (Semarnat, 2004)

***Sediment Quality Guide adopted by the National Oceanic and Atmospheric Administration of the United States, for freshwater sediments. Lowest Effect Level (LEL), Severe Effect Level (SEL) (Buchman, 2008)

At all sites except site 3, Cu and Zn exceeded the LEL but did not exceed the severe effect level (SEL). These metals can occur at significant levels naturally in aquatic environments or come from fertilizers,

fungicides, and garbage leachates, and in the case of Zn, coming out of animal and human excrement (Moreno, 2003). The high correlation between them ($r = 0.96$) and with OM ($r = 0.86$ for Cu and $r = 0.88$ for Zn) suggests that they come from the same source, which is probably the wastewater dumped into the river from pig farms, the main activity in the study area, since it has been reported that they contain Cu (1.68 ppm) and Zn (43 ppm). Since the 1990s, it had been reported that Cu, used as a growth promoter in pigs, and Zn, used to prevent enterotoxemia by *E. coli*, were enriched in the sediments of the meander. In other areas of the Lerma River similar to Salamanca, Ibarra, and Laja, where industrial activity contributes a greater amount of these metals, the sediments do not retain as much of these elements as the sediments of La Piedad do (Hansen *et al.*, 1995; Pérez, 2006). The concentrations of Cu and Zn were higher in the study carried out in 2016 by Villalobos-Castañeda *et al.* (2016) so it is possible that these metals are being reincorporated into the water column, as these authors had already suggested at that time. In sediments from other rivers with similar conditions to the Lerma River such as the San Pedro River (Guzmán-Colis *et al.*, 2011), Grijalva basin (Laino-Guanes *et al.*, 2015) and the Orinoco River (Márquez *et al.*, 2012) lower amounts of Cu (0.93-17.64 mg/kg) and Zn (42.56-181.45 mg/kg) were reported than those found in the present investigation, although in rivers of Kosovo the amount of Cu was higher than 100 mg/kg (Gashi, Franciskovic-Bilinski, & Bilinski, 2009).

The amount of Cr (67-101 mg/kg) exceeded the LEL at all sites. This metal may come mainly from leather tanning and oil refining, among other industrial sources established in Salamanca, a city located 100 km upstream from the study area. However, it has been reported that Cr

precipitates and sediments rapidly due to its low mobility, which is independent of acidity and redox conditions (Hansen et al., 1995), so Cr may come from the few local industries and municipal waters, which precipitate and sediment thanks to this very fact and the barrier created by *Eichornia crassipes* present along the meander, present even in the dry months because the meander continues to receive untreated municipal wastewater, allowing this plant to survive. However, it is more likely that Cr may have a geogenic origin because its distribution in the meander is homogeneous, so it could not be associated with any anthropogenic source. The Cr concentrations are concerning, as they are very close to the SEL and are higher than those found in sediments from other rivers, which do not exceed 89 mg/kg (Guzmán-Colis et al., 2011; Laino-Guanes et al., 2015; Márquez et al., 2012).

The concentration of Ni (21 mg/kg) only exceeded the LEL at site 5. It had previously been reported that industries in Querétaro, Salamanca and León contribute high amounts of this metal to the Lerma River. However, its mobility is low considering the slightly alkaline conditions of the river. Therefore, the sediment is surely being enriched with this metal from local waste from the urban area that is dumped into the river, such as batteries, household appliances, and the transportation of liquid products from urban areas to the river, such as oils, paints and lubricants (Hansen et al., 1995). However, another source that also has a high mesophile content should also be considered, given its high significant correlation ($r = 0.97$). In general, the amount of Ni is much lower than that found in other sediments (Márquez et al., 2012).

The amount of Pb in all sites was below the LEL and although its origin has been related to natural sources (Villalobos-Castañeda et al.,

2016), the highest levels were found in urban areas, so the contribution may also be through anthropogenic sources. In rivers with urban contributions, such as the San Pedro River, Pb concentrations were up to 126 mg/kg (Guzmán-Colis *et al.*, 2011).

Over the last 30 years, the concentrations of heavy metals in sediments from different parts of the Lerma River have been evaluated from its source, upper course of the river, middle course, and up to its mouth, so it is possible to compare these results with those obtained in the meander. The sediments near the source of the river contain concentrations of heavy metals much lower than those found in the bend, but this is not the case in the sediments sampled 20 km further on, where the industrial zone of Lerma and Toluca is located, whose concentrations of Cu, Zn, Cr and Pb in 1999 (Ávila-Pérez, Balcázar, Zarazúa-Ortega, Quintal, & Díaz-Delgado, 1999) and 2006 (Tejeda *et al.*, 2006) were four times higher than those identified in the bend, although in more recent studies higher quantities were observed, reaching values up to 10 times above the LEL for Cr (105-421 mg/kg), Pb (147-312 mg/kg) and Ni (564-1 559 mg/kg), where the presence of *Eichornia crassipes*, has also been reported in the river bed, which favors their sedimentation (Zarazúa *et al.*, 2011; Hernández-Mendoza *et al.*, 2018). That is a consequence of the discharges of wastewater from 30 cities that are much more populated than those located in the meander, such as Toluca, Lerma, and San Mateo Atenco, as well as discharges from industrial areas and treatment plants. Further ahead, approximately 10 km (Villa Cuauhtémoc) and up to the Alzate dam, the concentrations of heavy metals are lower, possibly due to dilution by the contributions of natural tributaries that are incorporated (Ávila-Pérez *et al.*, 1999; Tejeda *et al.*, 2006; Zarazúa *et al.*, 2011).

Following the course of the Lerma River, it has been reported that the sediments of Laja and Salamanca, sites located upstream of the study area, were more enriched with Cd, Zn, Pb, and Cu (Hansen *et al.*, 1995) than what was observed in the meander. This is relevant because, under certain conditions, these metals could migrate freely to the study area if the relief drain did not prevent it.

In a study carried out in 2009 in three (sites 2, 5, and 6) out of the seven sites evaluated in the present study (Villalobos-Castañeda *et al.*, 2016), the concentrations of Cu, Cr, Ni, and Zn, as well as Pb, the latter only for site 5, exceeded the LEL (Table 6). These concentrations, except Cr, were higher than those found in this research. The above suggests the mobility of these metals in sediments and the water column, of course when the latter is present.

Table 6. Heavy metals in 2009 and 2018 for sediments of the Lerma River.

Element (mg/kg)	Sampling site						
	2		5		6		LEL/SEL
	2009*	2018**	2009*	2018**	2009*	2018**	NOAA***
Cr	73.0	101.5	70.0	82.0	59.0	71.0	26/110
Cu	52.0	58.8	138.0	81.0	66.0	41.0	16/110
Ni	28.0	<4	32.0	21.0	32.0	<4	16/75
Pb	22.0	15.8	50.0	29.0	41.0	26.5	31/250
Zn	217.0	236.0	497.0	272.0	246.0	179.0	120/820

*Data reported for February 2009 are shown (Villalobos-Castañeda *et al.*, 2016).

**Data reported in the present study.

*** Sediment Quality Guideline adopted by the US National Oceanic and Atmospheric Administration. Lowest Effect Levels (LEL) for freshwater sediments, Severe Effect Levels (SEL) (Buchman, 2008).

At the Ibarra and Lake Chapala sites, in the final part of the Lerma River, enrichment for Zn and Cu was only observed in 1995 (Hansen *et al.*, 1995), although in 2016, unlike the meander, more Pb, Ni, and Fe were found, but less Mn, Cu and Zn and similar concentrations of Cr according to Badillo-Camacho *et al.* (2016). These authors established that heavy metals, especially those from anthropogenic activities that are concentrated in the exchangeable fraction and the carbonates of the sediments, are mobilized or sedimented depending on the contributions of each site. Thus, the untreated wastewater that is dumped by nearby settlements on the periphery of Lake Chapala contributed to increasing the amounts of Pb and Cr.

The enrichment factors (EF) calculated for each metal and each site (Table 7) indicate that Cd is the only metal that showed a high EF (10.8), although only for site 2; this metal probably comes from the fertilizers used in that agricultural area. In 1995, much decreasing EF was reported for this metal (2); this situation should be closely monitored since Cd at neutral and alkaline pH presents high mobility; hence, it can migrate to the water and represent a source of poisoning (Hansen *et al.*, 1995). Zn has maintained a moderate EF with a value of 7 in the 1995 study and values from 1.8 to 6.5 both in 2009 and in the present study. The EF of Cr has remained at values around 4. Although the enrichment is moderate, the accumulation concerning time is evident, as previously mentioned above. Cu had been reported with a highly EF (20) in 1995; however, in 2009, it now showed much lower values (0.3-1.8). Something similar happened with Pb, which went from an EF of 5.7 in 1995 to values less than 2 in 2009 and this study, so there is practically no enrichment of the sediment with this metal. On the contrary, the EF of Ni has

remained in the same range (0.9-3), so it is considered not enriched (Hansen *et al.*, 1995. Villalobos-Castañeda *et al.*, 2016). Site 5 is the place where all the elements, except Cd, have a moderate to severe enrichment factor, which is consistent with the values of the concentrations found; hence, the contribution can be attributed to anthropogenic activities in the urban area. Additionally, the presence of *E. crassipes* can act as a physical barrier and favor their sedimentation (Zarazúa *et al.*, 2011).

Table 7. Metal enrichment factors in sediments of the Lerma River meander.

Element	Enrichment factor per sampling site						
	1	2	3	4	5	6	7
Cd	-	10.8	-	-	-	-	-
Cr	3.7	4.3	4.3	4.3	3.5	3	2.9
Cu	0.6	1.3	0.3	0.6	1.8	0.9	1.1
Ni	-	-	-	-	1.2	-	-
Pb	0.6	0.5	-	0.4	1.0	0.9	-
Zn	3.5	5.7	1.8	2.3	6.5	4.3	5.0

Microscopic particles of sediment

Most of the particles observed by SEM at all sites contained Fe and Al (20 %) or Fe and Ti (21 %) (Figure 2g), and these results are similar to those reported in sediments from the upper course of the Lerma River (Zarazúa *et al.*, 2011). Orthogonal particles composed of Fe and S (Figure 2f) were

found to a lesser extent (11 %) at sites 2, 4, 5, and 7, which have been associated with anaerobic bacterial processes caused by the high content of organic matter that promotes the precipitation of FeS compounds (Tejeda *et al.*, 2006), although they can also be produced by phytoplankton or aquatic plants (Zarazúa *et al.*, 2011). At most sites, except for sites 2 and 5, remains of plankton organisms were observed (Figure 2c), which are characteristic of bodies of water with aquatic life. However, particles containing Ba, Cr, Zr, Mn (Figure 2a, b, d, h) and other metals in their composition were also identified, probably originating from residual discharges (Tejeda *et al.*, 2006). In addition, there were particles containing P and Ca (Fig. 2e) at sites 5, 6, and 7, which are characteristic of the inorganic form of P (Zarazúa *et al.*, 2011).

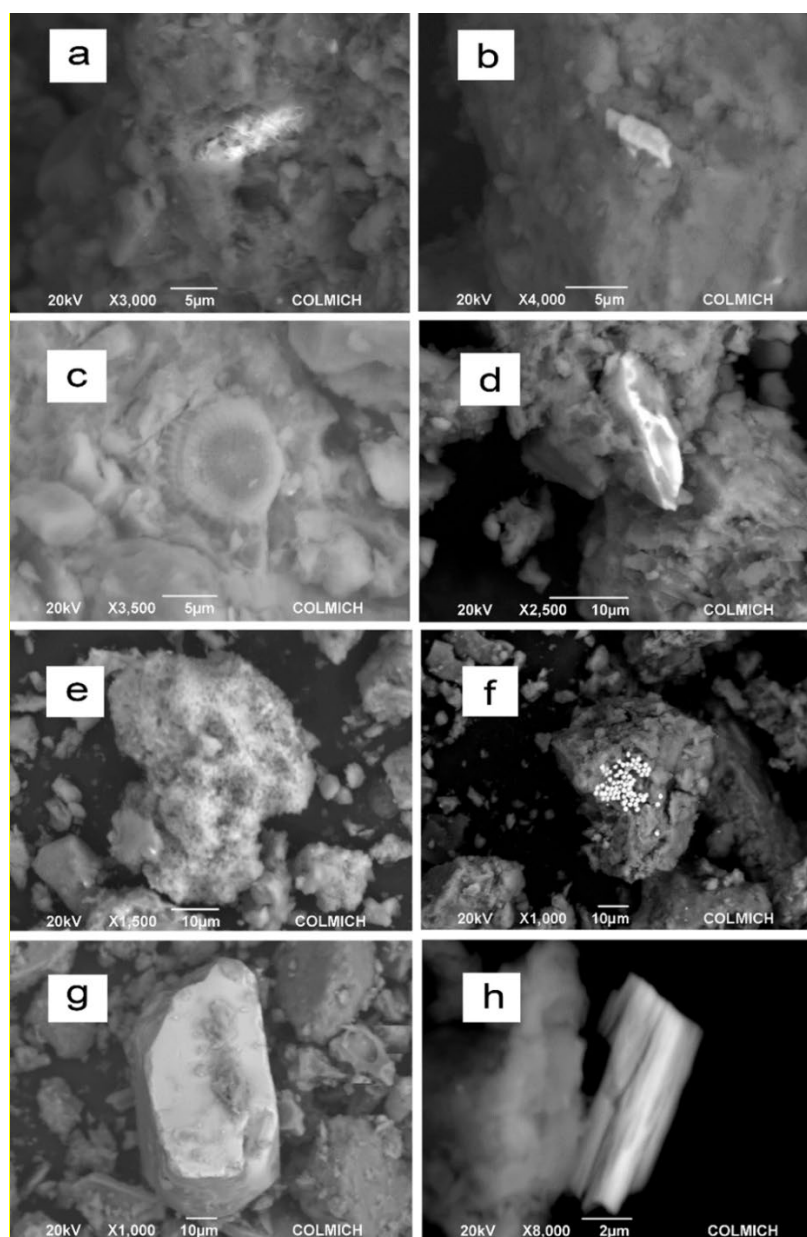


Figure 2. a) Particle composed of O, C, Si and Ba from site 1; b) Particle composed of O, Fe, C, Si and Cr from site 2; c) Plankton particle from site 3; d) Particle with O, Si, Zr from site 4; e) Particle composed of O, C, Ca and P from site 5; f) Particles composed of O, C, S and Fe from site 5; g) Particle composed of O, Fe and Ti from site 6; h) Particle with O, C, Mn from site 7.

On the other hand, given the importance of the sediment-water interaction, the concentrations of total heavy metals in water reported by Conagua (2018) were correlated with those of the sediment. Although the concentrations in water of Cr (Site 3 = 0.0107 mg/l, Site 4 = 0.0136 mg/l and Site 6 = 0.0082 mg/l) and Pb (Site 3 = 0.013 mg/l, Site 4 = 0.0136 mg/l, Site 6 = 0.0023 mg/l) evaluated in January, March and April 2018 did not exceed the reference values indicated in the Mexican official standard for aquatic life (SEMARNAT, 1996), these presented a significant correlation with the concentrations found in the sediments ($r = 0.847$ for Cr and $r = 0.905$ for Pb), which suggests that these metals could be passing from the sediment to the water or vice versa, in any case their presence represents a risk for both aquatic life and people given that the river water is used to irrigate crops located on the slopes of the same. As already discussed above, it seems that only Cr has increased steadily in the sediment and this may be due to its high affinity with Fe oxides. The latter was evidenced by the characterization of particles where Cr was found together with O and Fe (Figure 2b) unlike Zarazúa *et al.* (2011), who found Cr associated with steel particles.

Principal component analysis of the meander sediments

In the principal component analysis (PCA), it is observed how the individual parameters are correlated with each site (Figure 3). The first principal component is defined mainly by the % of sand, pH, FC, and Zn, and the second principal component by Temperature, Mesophiles, Ni, and Cu. The first group is made up of sites 1, 7, 3, and 4. The first two sites are located at the beginning and end of the meander, where the drain

gates are located, which are opened at the discretion of the water concessionaires. At site 3, the Zináparo stream converges, and at site 4, there is a dam belonging to the Hacienda La Quinta de Guadalupe. These sites presented low concentrations of microorganisms and heavy metals except for Cr, which is, they are the least contaminated sites; this is certain because there are few human settlements, they have larger hydrodynamics, and there is even a contribution from tributaries that dilute the contaminants. On the other hand, without grouping, there are sites 2, 5, and 6; these are the most contaminated sites. Site 2 was characterized by the presence of Cd, while sites 5 and 6 presented both microbiological and heavy metal contaminants. These last sites are located in the middle part of the meander, where the main cities in the study area are concentrated. This suggests that the pollutants do not come from the water of the natural channel of the Lerma River, which eventually enters when the floodgates are opened (near sites 1 and 7), but are probably generated, discharged, and sedimented in the same place.

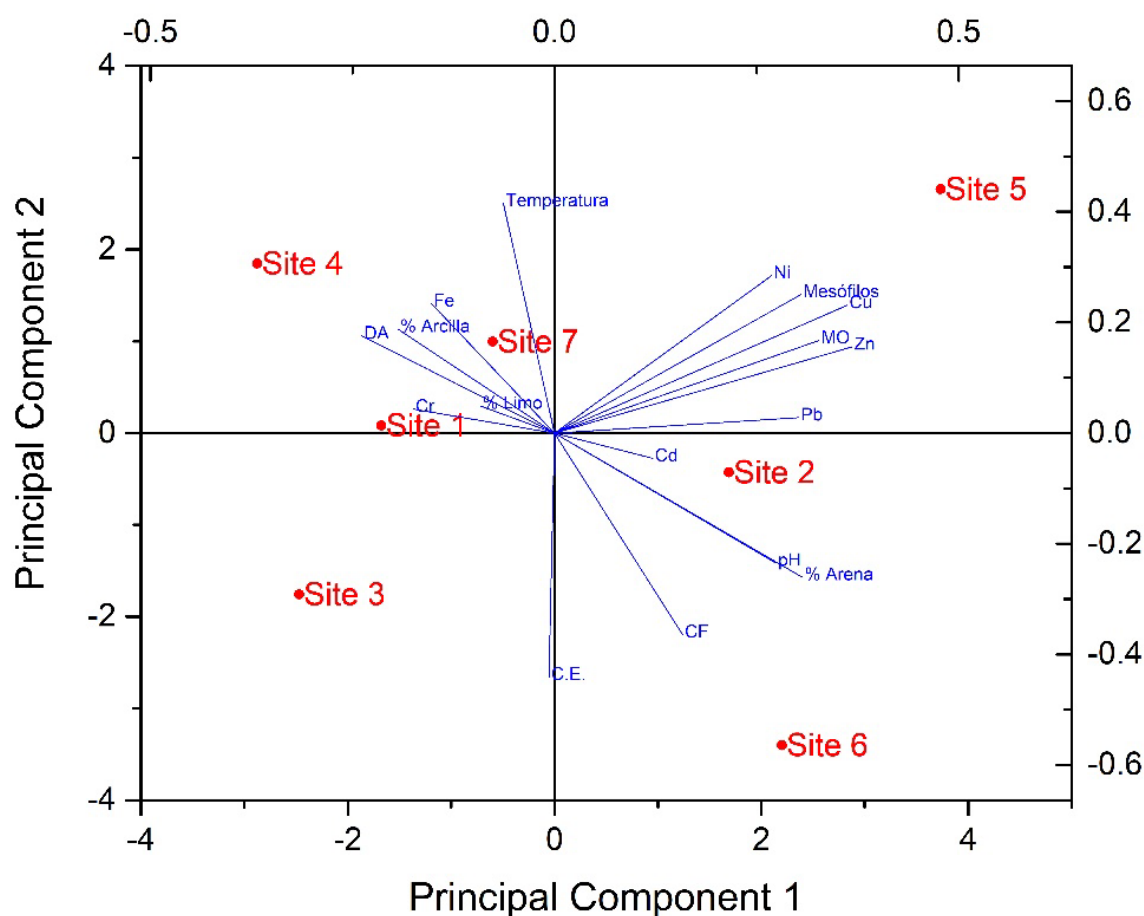


Figure 3. Principal component analysis (PCA) of the physicochemical and microbiological parameters evaluated in sediments from the La Piedad-Pénjamo meander.

In general, the amount of contaminants in the sediments has not reached alarming levels, however, it is necessary to prevent all the components of the meander from continuing to be enriched with toxic substances.

Conclusions

The sediments of the La Piedad-Pénjamo meander, an isolated channel, had a neutral pH with an EC that indicates appropriate salinity for this type of water body. Although its texture is sandy loam, it presents significant amounts of silt and clay that, together with the moderate amount of OM could serve as a reservoir for contaminants. According to the enrichment factor, the sediments of the meander were moderately enriched with Zn, Cr, and Cu, which exceeded the minimum effect level in almost all sites but did not exceed the severe effect level according to NOAA criteria. Sites 5, 6, and 2, on whose banks the main cities of the area are located, were those that presented the highest concentration values, between the lowest and most severe effect level criteria, which suggests that the contaminants are generated by local anthropogenic activities, being the fundamental sources urban and industrial wastewater discharged into the meander without treatment, pig farming waste and urban garbage.

In general, the sediments of the meander are moderately contaminated, with the OM, U, and the amount of Cr, Zn, and Cu being the most significant parameters, both for their concentration and because of their unfavorable potential effect on the environment and health. The fact that microscopic plankton particles were found indicates that aquatic life continues to develop; however, aquatic lilies were found covering several areas of the meander, which is evidence of eutrophication. It is necessary to reduce the sources of contamination to prevent the sediments from continuing to be enriched with toxic contaminants. As well as to establish targeted strategies for removing these contaminants in

case of they may be re-suspended in the water column. Additionally, municipal agreements must be established so that the meander is only fed with clean water from the natural tributaries within the micro-basin or treated water as long as it complies with the quality parameters. For all the above reasons, it seems feasible to recover and maintain the meander as a body of water isolated from the original channel so that, instead of representing a source of infection, it is seen as a living natural heritage and a space with socio-cultural potential for the population of the metropolitan area settled on its sides.

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