

Evaluation of Physicochemical Parameters and Heavy Metals in Water and Surface Sediment in the Ilusiones Lagoon, Tabasco, Mexico

Evaluación de parámetros fisicoquímicos y metales pesados en agua y sedimento superficial de la Laguna de las Ilusiones, Tabasco, México

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Abstract

This work was done in the Ilusiones Lagoon located in Villahermosa, Tabasco. It analyzed some of the physicochemical parameters and

the concentrations of heavy metals in surface sediments and water. Water samples and surface sediments (0-10 cm) were randomly separated into three different zones for an exploratory analysis. Water parameters were measured *in situ* with a multiparametric method to determine pH, temperature, electrical conductivity (EC, dS/m), redox potential (ORP), dissolved oxygen (DO %), cation exchange capacity (CIC C mo(+)/kg) and total salts (TDS mg/kg). In addition, the chemical oxygen demand (COD mg/L) was determined based on the NMX-AA-030-SCFI-2001 standard and organic matter content (OM). Sediment samples were taken according to the NOM-021-Semarnat-2000 (Semarnat 2001a, 2001b). Digestion of the samples were performed according to EPA 3050B and NOM-147-Semarnat/SSA1-2004 guidelines. The NMX-AA-132-SCFI-2006 standard was used to determine heavy metal concentrations using an atomic absorption spectrophotometer. The values of pH in water ranged between 8.9 and 9.6, which were alkaline and above the limits (6.5 - 9.0). The pH of the sediment ranged from 5.9 (slightly acidic) to 8.4 (slightly alkaline) (NOM-021-Semarnat-2000). In the water, the heavy metals Cd, Ni, Cr, Mn, Zn, Al and Pb were all below the NOM-001-Semarnat-1996. The concentrations of Cd, Ni, Cu, Mn, Zn, Pb and Al in the sediments exceeded the criteria for heavy metals established by Canadian and American standards. We conclude that the lake is polluted by illegal discharges of sewage from nearby houses, hospital waste, and infiltration from other polluted lakes.

Keywords: Heavy metal, sediment, pollution water, lagoon of Ilusiones.

Resumen

Este trabajo se realizó en la Laguna de las Ilusiones, ubicada en Villahermosa, Tabasco, México. Se analizaron algunos parámetros fisicoquímicos y las concentraciones de metales pesados en agua y sedimentos superficiales. Las muestras de agua y sedimento superficial (0-10 cm) se tomaron al azar en tres zonas diferentes para un análisis exploratorio. Los parámetros del agua se midieron *in situ* con un equipo multiparamétrico para determinar pH, temperatura, conductividad eléctrica (CE, dS/m), potencial redox (ORP), oxígeno disuelto (DO%), capacidad de intercambio catiónico (CIC Cmol⁽⁺⁾/kg) y sales totales (SDT mg/kg). Además, se determinó la demanda química de oxígeno (DQO mg/l), empleando la norma NMX-AA-030-SCFI-2001 (SCFI, 2001a) y el contenido de materia orgánica (MO). Las muestras de sedimentos fueron tratadas de acuerdo con la norma NOM-021-Semarnat-2000 (Semarnat, 2000a), normas EPA 3050B (EPA, 2000) y NOM-147-Semarnat/SSA1-2004. La norma NMX-AA-132-SCFI-2006 se

utilizó para determinar las concentraciones de metales pesados, utilizando el espectrofotómetro de absorción atómica. Los valores de pH en agua oscilaron entre 8.9 y 9.6; se encuentran por arriba de los límites (6.5-9.0). En los sedimentos, el pH osciló en valores desde 5.9, moderadamente ácido, hasta 8.4, medianamente alcalino (NOM-021-Semarnat-2000b). Los metales pesados determinados en el agua, Cd, Ni, Cr, Mn, Zn, Al y Pb, se encuentran todos por debajo de la NOM-001-Semarnat-1996 (NOM-001-ECOL-1996; Semarnat, 1996b). La concentración de Cd, Ni, Cr, Mn, Zn, Pb y Al en los sedimentos sobrepasan los criterios de metales pesados establecidos en las normas canadienses y estadounidenses. Se concluye que la laguna está contaminada por descargas ilícitas de aguas negras procedentes de las viviendas cercanas, desechos de hospitales y por la infiltración de otras lagunas contaminadas.

Palabras clave: metales pesados, sedimento, contaminación del agua, laguna de las Ilusiones.

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Introduction

Industrialization produces effluents that contain toxic compounds such as metals, whose discharges into water bodies are the major source of pollution and various diseases (ATSDR, 2012). The water and the sediments in lakes and lagoons become receivers of various pollutant, which enter the food chains (Theoneste, Gang, Jing, Xu, & Lei, 2013; Lemus, Castañeda, & Chung, 2014). This poses a risk to biota because of bioaccumulation and biomagnification in the organs and tissues of many aquatic and terrestrial species (Sobrino, Cáceres, & Rosas, 2007). Other equally important sources include municipal discharges and agricultural and particle emission. Forty-two percent of the substances discharged into surface water bodies are metals that end up in sediments. Sediments are matrices composed of organic matter in

various stages of decomposition and organic and inorganic particulate material of biological and anthropogenic origin (Chen & White, 2004).

Heavy metals are pollutants that, due to their persistence and long-range transport, easily reach surface water bodies, posing a potential risk to biota. These pollutants can come from various sources such as: oil activities, agriculture, metallurgy, and sugar, as well as urban and sanitary (herbicides and insecticides). The high toxicity of metals bioaccumulate in biota and magnify up the food chain in higher organisms, including humans (Herrera, Rodríguez, Coto, Salgado, & Borbón, 2012).

Rivers receive waste generated by human activities through effluents that introduce hazardous substances, especially metals such as lead, cadmium, chromium, mercury, and manganese, among others. These tend to settle in the sediment, become suspended, or dissolve in the water column (Rodríguez, Ruíz, & Vertiz, 1994). These rivers carry pollutants along their courses, and when they overflow they may be deposited in water bodies such as lakes and springs. The Ilusiones Lagoon in Villahermosa is surrounded by two large rivers (Grijalva and Usumacinta) in an area with high rates of rainfall, which have caused these rivers to flood. Weather conditions also contribute to the potential transfer of pollutants from the atmosphere to the lagoon in particular, and other bodies of water in general (Palma, Cisneros, Moreno, & Rincón, 2007).

Next are some examples that illustrate the extent of metal pollution in the country. Arsenic and lead concentrations in surface sediments in the Zahuapan-Atoyac hydrologic system ranged from 1.3 to 127.7 mg kg⁻¹ and 27.3 to 89.5 mg kg⁻¹, respectively (García-Nieto *et al.*, 2011). Rosales-Hoz and Carranza-Edwards (1998) detected levels of metals in sediment in the Coatzacoalcos River ranging from 21.2 – 53.5 mg kg⁻¹ for total lead, 2.1 - 2.7 mg kg⁻¹ for total cadmium and 21.6 – 152.7 mg kg⁻¹ for total chromium. González-Mille *et al.* (2010) found Pb (4 – 22 mg kg⁻¹), Cr⁺⁶ (9 – 93 mg kg⁻¹) and manganese (76.7 – 2129 µg kg⁻¹) in the same river.

Heavy metals bioaccumulate in aquatic species such as oysters, clams, shrimp, and some fish species. Lango-Reynoso, Landeros-Sánchez and Castañeda-Chávez (2010) determined the bioaccumulation of arsenic, cadmium, and lead in oysters in the Tamiahua Lagoon in Veracruz, with mean values of 4.02 mg kg⁻¹ for arsenic, 11.7 mg kg⁻¹ for cadmium and 0.48 mg kg⁻¹ for lead. The cadmium exceeded the maximum permissible limits stipulated by consumer health rules for bivalves and pose a risk to human health. The pollution in water and sediment in the Ilusiones

Lagoon can change the balance of populations, especially those that are most susceptible. Gamboa, Gamboa, Saldívar and Espejel (2007) quantified lead in the blood of crocodile (*Cocodylus moreletti*), finding values ($6.55 - 15.34 \mu\text{g dL}^{-1}$) that were higher than permissible limits for aquatic life.

No recent studies have been published to assess the environmental and ecotoxicological conditions of the Ilusiones Lagoon. The few studies that have been reported include one from 1992 to 1994 of phosphorous (10.6 mg L^{-1}) and total nitrogen (4.1 mg L^{-1}) present in the lagoon, in which it was categorized as hypertrophic with a dendritic morphology and low hydraulic mixture, preventing water changes that favor the persistence of conservative and non-conservative substances (Rodríguez *et al.*, 1994). In general, the content of pollutants in water bodies increases over time. For example, in 1994, 30% of Mexican rivers were polluted by mercury and lead, whereas currently 95% are reported to be polluted. In 1992, the concentration of lead in surface sediments in the Ilusiones Lagoon was $158.68 \mu\text{g g}^{-1}$ (Villanueva & Botello, 1992).

The Ilusiones Lagoon is important to the city of Villahermosa, Tabasco. Because of its great diversity of aquatic and terrestrial species, it was declared a nature reserve in 1995 (Semarnat-Conanp, 2014). However, for several years it has been subjected to stress from human activities that have directly and indirectly deposited agricultural, urban, and industrial waste, degrading its ecological value (Semarnat-Conanp, 2014). While there are practically no studies addressing pollution in the Ilusiones Lagoon, particularly of heavy metals, there are many examples of metal contamination in many rivers in Mexico, suggesting that a body of water with the conditions of the Ilusiones Lagoon can be considered as a potentially polluted site. The aim of this study was to determine the physical and chemical parameters and metals (Pb, Cd, Mn, Zn, Cr, Al and Ni) in water and surface sediment in the Ilusiones Lagoon, and whether they pose a risk of adverse effects to aquatic life.

Material and methods

Study location

The state of Tabasco is located in southeast Mexico, it measures 24 738 km² and has a warm humid climate with rains in the summer. The mean annual temperature ranges from 24 to 28 °C and annual precipitation ranges between 1500 to 2000 mm (Palma *et al.*, 2007). The Ilusiones Lagoon is located in hydrologic region RH30, in the Grijalva – Usumacinta Basin. It is located in the urban area of Villahermosa (17° 59' 22" to 18° 01' 22" N and 92° 55' 20" to 92° 56' 40" O), in the physiographic province of the coastal plain of the Gulf of Mexico, and covers an area of 160 ha. It is surrounded by the Mezcalapa and Carrizal rivers at an average altitude of 10 masl (Figure 1). In 1995, the state proclaimed it to be protected area, as an ecological reserve for the preservation of the water, flora, and fauna. The area occupied by the lagoon has decreased an average of 30 ha over a period of 10 years because of the development of the city of Villahermosa (Semarnat-Conanp, 2014; Sernapam, 2014).



Figure 1. The Ilusiones Lagoon study site.

Collection of environmental arrays

The Ilusiones Lagoon was divided into three zones, each defined based on the methodology proposed by Ilizaliturri *et al.* 2009, with six sampling sites (Figure 2). Six water samples were collected in each, in polyethylene containers. Surface sediments were collected in glass bottles. For the determination of metals in water, polyethylene bottles were used containing 1 mL of concentrated nitric acid to prevent volatilization losses. For the sediment sample, 2-liter amber containers were used. The samples were transported and stored at 4 °C until analysis (NOM-001-Semarnat-1996). Two samplings of water were collected, one in April 2013 and the other in September 2014.

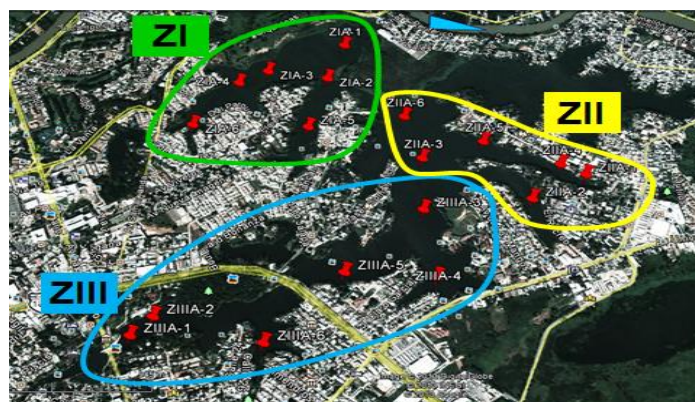


Figure 2. Ilusiones Lagoon sampling sites.

Physicochemical characterization

Water

The determination of the physicochemical parameters of the water was performed in situ with a multiparameter bench photometer (HANNA) model HI 9828, which recorded pH, temperature ($^{\circ}\text{C}$), electrical conductivity (EC , $\mu\text{S cm}^{-1}$), oxidation – reduction potential (ORP, mV), dissolved oxygen (DO , mg L^{-1}), and total dissolved solids (TDS , mg L^{-1}). Chemical oxygen demand (COD , mg L^{-1}) was determined in the laboratory using the closed reflux method with potassium dichromate.

Sediment

The sediment samples were collected with a plastic dredger in 2-liter amber containers which were transported and kept at 4°C until analysis. These were dried in an oven at 60°C for 72 hours; they were then mechanically homogenized in an agate mortar and filtered with a $600\ \mu\text{m}$ mesh. The sediments were characterized by determining the texture using the Bouyoucos method. Organic matter contents (OM) were determined by the Walkley and Black method, and pH by the electrometric method using a Denver Instruments brand potentiometer, model 215. Electrical conductivity was calculated based on the saturation extract (NOM-021-Semarnat-2000).

Quantification of metals in water and sediment

Before quantifying the metals, the water samples and sediment were digested in a Microwave oven 907, 501 through 3050 and 3052 according to EPA methods. Quantification of metals was carried out with an Analyst 300 model atomic absorption spectrophotometer equipped with flame ionization detector, previously calibrated according to certified reference materials from the National Institute of Standards (NIST) (Benavides *et al.*, 2007; SCFI,-2001a, 2001b). The average

values for each of the measured parameters were subjected to analysis of variance (ANOVA) con $p < 0.05$.

Results and discussion

Figure 3 shows the physicochemical properties determined based on water samples collected from the three areas of the lake. The pH values in water, ranging between 8.9 and 9.6, were alkaline and above the limits (6.5 – 9.0) permitted by the Guidelines for Canadian Water Quality, and the lower limit (8.9) was greater than that which is allowed (5.5) by NOM-002-Semarnat-1996. The highest value (9.6) was present in Zone 3 and the lowest value (8.9) in Zone 1, presumably due to the presence of carbonate and hydroxide ions that can come from anthropogenic waste and soluble natural minerals.

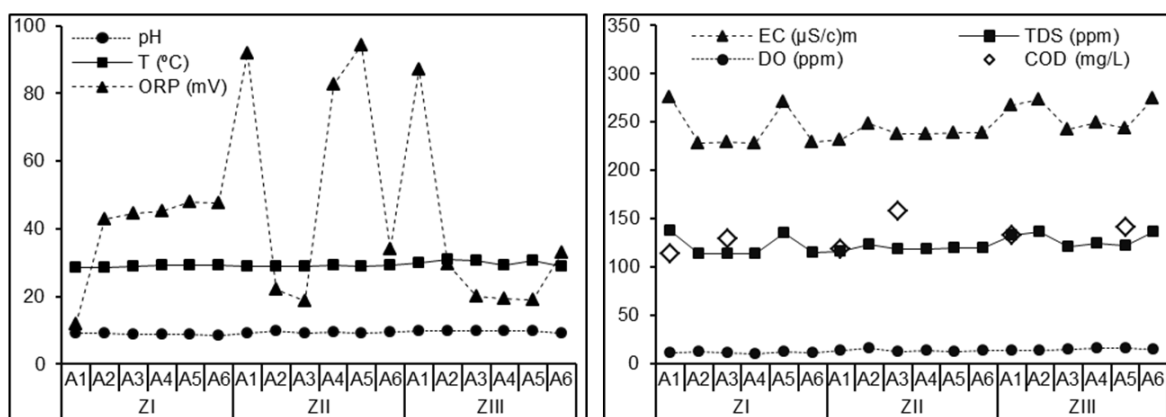


Figure 3. Physicochemical properties determined in water samples.

The water temperature ranged from 28.8 to 29.9 °C, which was below the limit allowed by Mexican regulations (40 °C). The ORP varied in the three areas, from 5 mV in zone 1 to as much as 80 mV in Zone 2. With regard to the DO, this ranged from 7 to 11 mg L⁻¹, similar to the limits proposed by the EPA (not less than 5 mg L⁻¹) and the Guidelines for

Canadian Water Quality (9.5 mg L^{-1}). The EC values ranged from 225 to $275 \mu\text{S cm}^{-1}$ which were below ($2500 \mu\text{S cm}^{-1}$) the NOM- 069- ECOL- 1994 for freshwater bodies. The COD ranged from 105 to $155 \text{ mg O}_2 \text{ L}^{-1}$, which was within the range classified as polluted by Conagua in 2012 ($40 < \text{CO} < 200$). TDS ($114 - 137 \text{ mg L}^{-1}$) was similar to values reported by the Secretaria de Energía Recursos Naturales y Protección Ambiental (SERNAPAM) in 2012 and 2013 (Table 1). The physicochemical parameters are shown in (Figure 4).

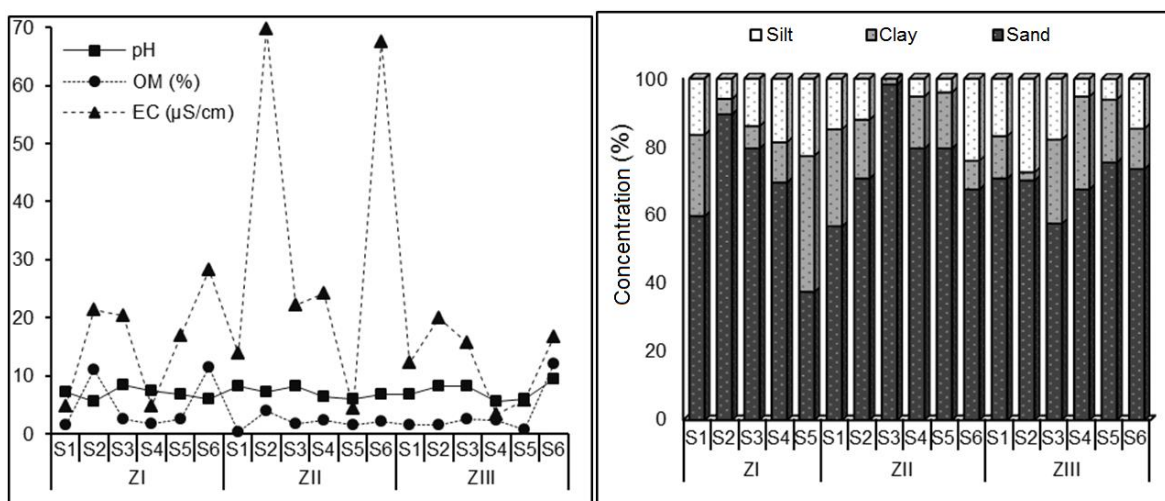


Figure 4. Physicochemical parameters.

In sediments, the pH ranged from 5.9 (mildly acidic) to 8.4 (mildly alkaline) (NOM- 021 Semarnat 2000). Values of 1 to 11% of OM indicate volcanic origin, and the EC had negligible effects of salinity because it ranged from 4 to $28 \mu\text{S cm}^{-1}$. The particle size was, on average, 67.2% sand, 17.2% clay and 15.4% silt for Zone 1; 75.4% sand, 14.5% clay and 10% silt for Zone 2; and 69.2% sand, 16.1% clay and 14.6% silt for Zone 3. In terms of the texture triangle used by the U.S. Department of Agriculture, the results from the three zones corresponded to a textural classification that ranges from sandy to moderately thick sandy loam.

Table 1. Sernapam parameters (NOM-021-Semarnat-2000).

Period	Sampling points	pH	T (°C)	EC (µS/cm)	OD (ppm)	TDS (ppm)	COD (mg/L)
2011	Cencali (n = 1)	6.7 ± 0.4	26.9 ± 1.6	249 ± 54.0	5.2 ± 1.7	180.8 ± 64	48.4 ± 8.2
	Ilusiones (n = 6)	8.5 ± 0.7	27.6 ± 0.6	233.1 ± 25.3	8.13 ± 2.48	166.1 ± 36.9	47.5 ± 6.4
2012	Cencali (n = 1)	6.9 ± 0.4	28.8 ± 2.7	197.8 ± 4.2	8.1 ± 2.9	181.3 ± 29.2	67 ± 9.0
	Ilusiones (n = 6)	8.3 ± 0.9	28.3 ± 2.9	223.2 ± 52.0	8.0 ± 2.3	165.6 ± 40.6	59.5 ± 8.7
2013	Cencali (n = 1)	7.7 ± 1.2	27 ± 1.7	246.6 ± 27.7	8.8 ± 2.1	216 ± 40.3	34 ± 9.3
	Ilusiones (n = 6)	8.4 ± 0.7	28.8 ± 1.5	264.5 ± 41.1	9.5 ± 2.0	170.2 ± 19.9	66 ± 9.2

Table 2 shows the concentrations of the metals quantified in the water (Cd, 2.2 – 5.6 µg L⁻¹), (Ni, 2.2 – 7.8 µg L⁻¹), (Cr, 28 – 64.4 µg L⁻¹), (Mn, 38.9 – 112.2 µg L⁻¹), (Zn, 12.2 – 79.2 µg L⁻¹), (Al, 218 – 1385 µg L⁻¹) and (Pb, ND a 0.1 µg L⁻¹), all below the NOM-001-Semarnat-1996. However, the Cr and Cd hazard ratio (reference concentration / mean) was greater than one. Table 3 shows the concentrations of metals found in sediments (Cd, 1.1 – 4.0 mg/kg), (Ni, 21.4 – 75.3 mg/kg), (Cr, 23.1 – 99.5 mg/kg), (Mn, 42.4 – 341.9 mg/kg), (Zn, 13.8 – 193.2 mg/kg), (Pb, ND - 204 mg/kg) and (Al, 4404.9 – 73593.6 mg/kg). Here the hazard ratio was greater than one for all metals found except Zn and Mn. According to the legislation of Canada and the United States, when

the hazard ratio is greater than unity, there is already a potential risk to aquatic life.

Table 2. Heavy metals in surface water.

Zone	Mn	Ni	Cd	Pb	Cr	Zn	Al
Z1A1	96.7	<5.6	3.3	<55.6	49.9	21.7	894.4
Z1A2	101.1	4.4	4.4	<44.4	46.8	28.1	634.4
Z1A3	Microwave oven 907	2.2	2.2	<44.4	55.0	28.0	1385.6
Z1A4	108.9	7.8	4.4	<11.1	50.2	28.3	175.6
Z1A5	75.6	2.2	3.3	<33.3	59.8	53.7	584.4
Z1A6	112.2	<3.3	4.4	<55.6	49.1	32.7	484.4
ZIIA1	63.3	6.7	4.4	<22.2	64.4	23.6	541.1
ZIIA2	53.3	7.8	3.3	<55.6	58.6	79.2	351.1
ZIIA3	65.6	<1.1	4.4	<22.2	61.9	26.3	621.1
ZIIA4	51.1	<3.3	4.4	<44.4	64.4	20.2	696.7
ZIIA5	72.2	7.8	5.6	<44.4	63.3	26.1	790.0
ZIIA6	53.3	<3.3	2.2	<66.7	49.9	58.7	1155.6
ZIIIA1	51.7	6.7	3.9	<27.8	59.3	23.7	472.2
ZIIIA2	45.6	<3.3	5.6	<44.4	33.9	24.6	598.9
ZIIIA3	43.3	5.6	4.4	<33.3	28.0	43.6	374.4
ZIIIA4	46.7	<2.2	4.4	<55.6	30.7	18.8	764.4
ZIIIA5	45.0	0.0	3.9	<50.0	45.1	24.9	311.7

ZIIIA6	38.9	3.3	4.4	<44.4	30.4	65.9	184.4
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< : Low detection limit. All concentrations are in $\mu\text{g L}^{-1}$.

Table 3. Heavy metals in surface sediments.

Concentration (mg/kg)	Mn	Ni	Cd	Pb	Cr	Zn	Al (%)
Z I S1	75.3	18.6	1.9	9.0	91.2	33.6	5257 (0.5)
Z I S2	42.4	41.3	1.7	24.4	71.9	300.3	42753 (4.3)
Z I S3	114.4	30.9	1.6	7.5	61.2	66.9	17433 (1.7)
Z I S4	53.2	21.4	1.1	ND	37.9	42.3	30020 (3.0)
Z I S5	57.4	24.7	2.2	21.2	24.4	80.9	12322 (1.2)
Z I S6	92.1	28.3	3.2	204.7	38.0	193.2	19404 (1.9)
Z II S1	102.7	21.7	2.6	17.0	23.1	26.9	2563 (0.3)
Z II S2	47.7	24.8	2.9	57.5	34.7	84.3	19227 (1.9)
Z II S3	124.6	30.3	3.3	37.4	50.8	35.5	21887 (2.2)
Z II S4	123.0	26.1	3.2	40.3	66.4	13.8	17752 (1.8)
Z II S5	158.1	28.7	3.4	38.5	70.6	44.2	15629 (1.6)
Z II S6	47.3	33.9	2.9	23.8	58.7	52.1	20353

							(2.0)
Z III S1	114.3	29.1	2.2	44.8	78.1	45.5	20584 (2.1)
Z III S2	152.7	23.8	2.7	22.2	44.0	43.8	4405 (0.4)
Z III S3	82.3	42.1	3.1	35.7	63.2	80.3	66074 (6.6)
Z III S4	341.9	26.3	2.7	29.4	99.5	34.1	32673 (3.3)
Z III S5	44.7	33.2	3.0	24.1	71.9	86.1	73811 (7.4)
Z III S6	75.8	52.1	4.0	137.9	74.0	47.3	73594 (7.4)
Average $\pm$ DE	102.8 $\pm$ 70.1	29.9 $\pm$ 8.4	2.6 $\pm$ 0.7	42.8 $\pm$ 50.3	58.9 $\pm$ 21.8	72.8 $\pm$ 69.1	2.8 $\pm$ 2.2
*LEL (NJ-DEP)	630	16	0.6	31	26	120	2.55
ISQG (CSQG)	-	-	0.6	35	37.3	123	-
*CP (Average/LEL)	0.2	1.9	4.3	1.4	2.3	0.6	1.1

Conclusions

In this study site, the pH values in water ranged between 8.9 and 9.6, which were alkaline and above the limits (6.5 - 9.0) permitted by the Guidelines for Canadian Water Quality. The water temperature (28.8 - 29.9 °C) was below the limit allowed by Mexican regulations (40 °C). The dissolved oxygen was similar to values established by the EPA and the Guidelines for Canadian Water Quality. The COD value of the water

body was classified as polluted by Conagua in 2012 ($40 < \text{COD} < 200 \text{ mg L}^{-1}$). The EC and TDS values were within the parameters set by the SERNAPAM, while the heavy metals in the water (Cd, Ni, Cr, Mn, Zn, Al and Pb) were all below the NOM-001-Semarnat 1996.

In the sediment, the pH ranged from 5.9 (moderately acidic) to 8.4 (moderately alkaline), which was within permissible limits stipulated by NOM-021 Semarnat 2000. The percentage of organic matter indicated volcanic origin and the electric conductivity showed negligible effects from salinity. The particle size in the three sampling areas corresponded to a textural classification that ranged from sandy to moderately thick sandy loam. The concentrations of Cd, Ni, Cu, Mn, Zn, Pb and Al in sediment were within the Mexican norms, however when compared to the values corresponding to Canadian and United States standards, they exceeded the criteria established for heavy metals in freshwater bodies. This indicates that the biota was affected in terms of accumulating high concentrations of these metals in the system studied. Therefore, the authorities should be aware of the imminent dangers that to which nearby towns may be exposed.

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