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Study on Contamination by Heavy Metals in the Cotaxtla-Jamapa Basin with Influence in the Central Zone of the Gulf of Mexico

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Abstract Surface waters are exposed during their journey to various types of pollutants plus the contribution they receive from different effluents. The objective of this investigation was to evaluate the concentration of Pb, Cd, and Cu in surface waters of the Cotaxtla-Jamapa basin in Veracruz, Mexico. Analyzes were carried out in triplicate in six sampling sites, during three seasons, in morning, and night hours. At the sampling sites, Bocana and Arroyo Moreno, concentrations higher than the maximum permissible international limits of Pb and Cd were reported. The Pb, by time of sampling, presented significant statistical differences ($p < 0.05$) in three seasons of the year, in contrast to Cd and Cu. The above results indicated a risk in the use of water from the Cotaxtla-Jamapa basin, despite the fact that the concentrations obtained according to the national limits for NOM-001-SEMARNAT were not exceeded. It is necessary to update the national legislation to ensure the reduction of risk from exposure to heavy metals and to ensure conservation in terms of environmental quality.

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1 Introduction

A hydrological basin is a basic physical unit difficult to delimit of agricultural and environmental activities, due to its relationship with the environment where it is located (Valdovinos and Parra 2006; Torres-Beristáin et al. 2013). In particular, the coastal basin of the Jamapa River, since it is distributed totally within the state of Veracruz, Mexico (Fig. 1). This basin is born in the Sierra Madre Oriental, on the slopes of the Pico de Orizaba, joined by the Cotaxtla, Huatusco, and Totolapan Rivers (Maldonado-González et al. 2017). The final channel of this tributary has its mouth in the central zone of the Gulf of Mexico, southeast of the Port of Veracruz, in the municipality of Boca del Río, Veracruz, Mexico (Landeros-Sánchez et al. 2011; Salas-Monreal et al. 2013).

The Cotaxtla-Jamapa coastal basin has eight different uses identified with the concession title for the use of surface water, which corresponds mainly to agricultural, industrial, livestock, public-urban, services, domestic, aquaculture, and other different uses (REPDA 2014). Of the different managements, the agricultural is the one of greater volume of demand covering the 88.1%, followed by the industrial with 6.1% and the third place corresponds to the public-urban with 5.3%. The Cotaxtla-Jamapa basin supplies water to important cities

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in its territory such as Veracruz, Boca del Rio, Córdoba, Huatusco, and Coscomatepec, and more than a thousand rural locations (PAMIC 2017). The wide use of water in the basin is impacted by the incorporation of chemical contaminants of diverse nature.

Heavy metals are among the main pollutants in aquatic ecosystems, because they are present throughout the ecosystem and have been identified in high concentrations mg L^{-1} (Authman et al. 2015). Most heavy metals such as Pb, Cd, and Cu are widely used in various industrial areas in the coastal region of the Gulf of Mexico, including oil refining, and fertilizer production. These activities contribute to significantly increase the levels of these heavy metals (Páez-Osuna 2005; Villanueva and Botello 1992), in addition to the contributions for untreated domestic wastewater discharges. Heavy metals are mobilized towards ground and surface waters by a lixiviation process (Mahurpawar 2015; Malik and Khan 2016; Vetrimurugan et al. 2017; Modupe-Adesiyan et al. 2018). This process occurs via run off to surface waters such as rivers, which generate an environmental risk when causing harmful effects to the ecosystem, effects that depend on the dose that is absorbed and the exposure route in organisms (Baidya and Suryawanshi 2018; Modupe-Adesiyan et al. 2018). The main damages of the use of water in different domestic activities, due to its contents of heavy metal concentrations, have been associated with pathologies of hepathotoxic, immunotoxic, nefrotoic, and neurotoxy. However, there is an influence of factors that affect the toxicity of metals, like a chemical speciation in aquatic systems. Analyses of different chemical species facilitate to know what will be their behavior in the ecosystem, and so develop remediation measures in case of contamination (De Paiva Magalhaes et al. 2015).

Heavy metals in aquatic bodies tend to be deposited in its bottom with the sediments, where they are eliminated or transferred from the water column, adhering by their high affinity to particles of organic matter (Leyva-Cardoso et al. 2003). Several investigations on heavy metals have been carried out; however, these have focused mostly on coastal lagoon systems (Lango-Reynoso et al. 2013; Castañeda-Chávez et al. 2014), on sediments (Aguilar et al. 2012; Zamudio-Alemán et al. 2015; Castañeda-Chávez et al. 2017), and in aquatic biota such as molluscs and crustaceans (Aguilar-Ucán et al. 2014; Horta-Puga et al. 2016). All this due to the diverse sources of contamination, those are located in the coastal zone of the state of Veracruz, since they have become emitters of pollutants, with influence in the central zone of the Gulf of Mexico. The objective of this investigation was to study the contamination by heavy metals in surface waters of the Cotaxtla-Jamapa basin, which has influence in the central zone of the Gulf of Mexico.

2 Materials and Methods

2.1 Study Area

The coastal basin of the Jamapa River also known as the Cotaxtla-Jamapa basin is located in Veracruz Mexico, between 18°45′ and 19°14′ north latitude (Fig. 1), and between 95°56′ and 97°17′ east longitude (CONAGUA 2005). This has an approximate area of 3912 km^2 that is distributed totally within the state of Veracruz (98%) and the state of Puebla (2%) (Pereyra-Díaz and Pérez-Sesma 2005; Pereyra-Díaz et al. 2010; PAMIC 2017). It is estimated that the Cotaxtla aquifer dimension corresponds to an area of 3246.81 Km^2 (PRONACOSE 2017). This tributary supplies the Mandinga lagoon and travels the state of Veracruz for 150 km^2; two very important currents form this river, whose confluence is known as Cotaxtla-Jamapa (PAMIC 2017).

2.2 Selection of Sampling Sites

A prospective visit was made in the Cotaxtla-Jamapa basin to identify potential sources of contamination in the area. Next, six sampling sites were selected and identified using a GARMIN geolocator (GARMIN International Inc., Olathe, Kansas, USA). This selection was carried out according to the following characteristics: important discharge areas such as human settlements and production activities, discharges of aquaculture production units and of a thermoelectric power plant (Fig. 1). As well as the discharge of the Arroyo Moreno that receives the municipal effluents from the cities of Veracruz-Boca del Río and the Bocana of the Jamapa River, in Boca del Río, as an area of influx of the estuary that has a connection to the sea and the channel that feeds the Mandinga lagoon system (Table 1).

2.3 Collection and Sampling Periodicity

The surface water samples were collected in triplicate at the selected sampling sites during a morning and night

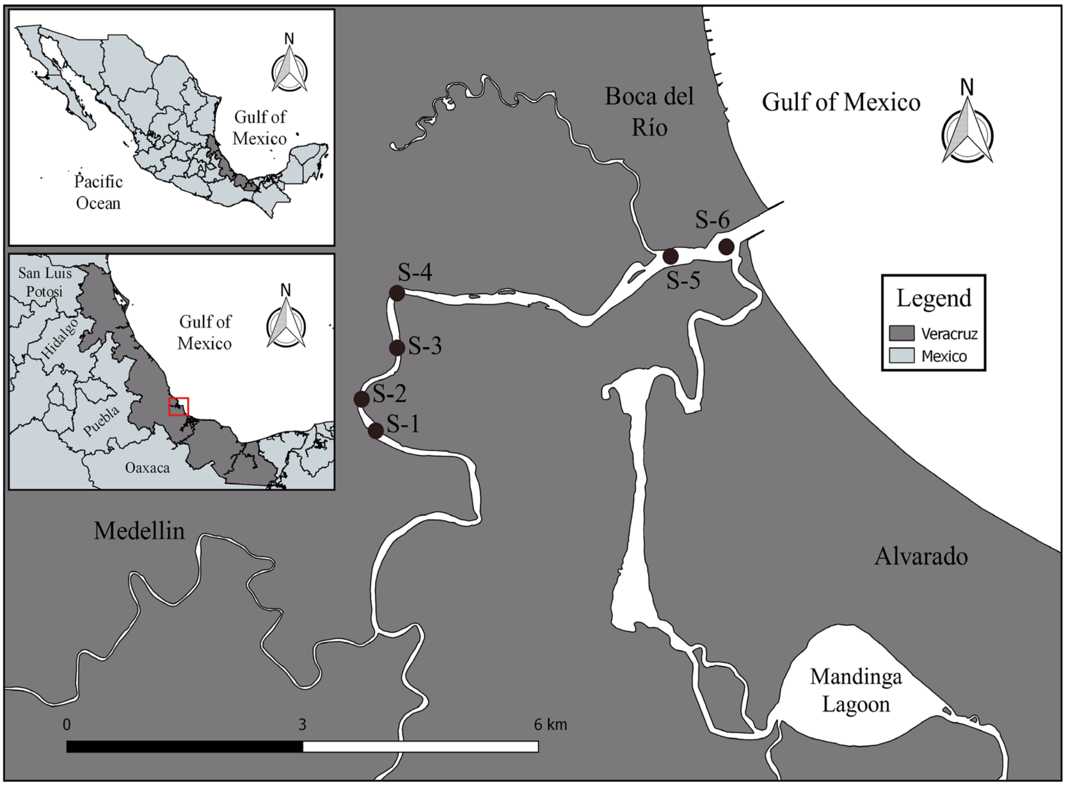

Fig. 1 Location of the study area and sampling sites in the Cotaxtla-Jamapa basin, Veracruz, Mexico

period, the collection was made at a depth of 40 cm from the surface, using a volume of 500 ml per sampling site, during three climatic seasons. The periods included for each climatic period were: north winds (NW) (November–February), dry (D) (March–June), and rainy (R) (July–October) (Farías and Padilla 1991).

The containers used in the collection of samples were previously washed according to the specifications of the NMX-051-SCFI-2016 (Diario Oficial 2016). After the collection, samples acidification was performed with HNO_3, concentrated at 70%, until pH < 4 was achieved.

Table 1 Location of sampling sites in the Cotaxtla-Jamapa basin, Veracruz, Mexico

Sampling site	Longitude W	Latitude N
S-1 Dos Bocas 1	96°13′51.10”	19°07′73.36”
S-2 Dos Bocas 2	96°14′40.66”	19°08′15.40”
S-3 La Rayana	96°14′ 05.92”	19°08′ 65.20”
S-4 Las Gualdras	96°14′08.43”	19°09′42.37”
S-5 Arroyo Moreno	96°11′09.32”	19°09′94.51”
S-6 La Bocana	96°10′40.48”	19°09′97.25”

With the aim of ensuring their good condition, they were maintained at 4 °C until laboratory processing.

2.4 Preparation of Material

In the cleaning of the material used in the digestion and processing of the samples, 10% phosphate-free neutral soap was used to avoid ionic interferences in the reading of the spectrophotometer, in accordance with NOM-117-SSA1–1994 (Diario Oficial 1994). Afterwards, the material was rinsed with tap water and then immersed in distilled water solution with 20% nitric acid HNO_3 for 24 h. After this washing period, the material was immersed in deionized water for 24 h to ensure complete removal of the acid. Subsequently, the clean material was dried in a forced air oven, Riossa CF-102, at 100 °C for 24 h and stored in hermetic bags to avoid possible contamination.

2.5 Microwave-Assisted Acid Digestion

A microwave CEM Mars 5 (CEM, Corporation Mathews, NC, USA) was used in the digestion of samples for the determination of heavy metals. After lyophilizing the sample, 0.5 g was taken for digestion with 9 ml of nitric acid (HNO_3) suprapur grade (JTBaker®). The microwave was programmed with two ramp times, the first with 5 min, 120 PSI pressure and a temperature of 150 °C, the second with 10 min, 100 PSI pressure, and 190 °C.

To process the samples, the acid digestion was performed per batch of samples; these were grouped in the same way as the samples for analysis, with a negative control prepared with deionized water (Milli-Q®) and a positive control sample prepared with sterile sediment. Once the samples were digested, filtration was carried out on 0.45 μm Millipore® nitrocellulose membranes and the solution obtained was adjusted to a volume of 25 ml with deionized water (Milli-Q®) and the final extract was deposited in amber polyethylene vial for storage at 4 °C, and for quantification by atomic absorption.

The quantification of heavy metals was performed on a Thermo Scientific iCE 3500 AAS spectrophotometer (Thermo Scientific®, China). Using certified high purity standards, High Purity Standards® (Charleston, SC), with a concentration of 1000 μg ml^{-1} in 2% HNO_3 for the preparation of the calibration curve. The spectrophotometer was adjusted with a wavelength of 217 nm for Pb, Cd, and 324.8 nm for Cu. The preparation of the calibration curve with certified standards was carried out with an adjusted range of a lower to higher concentration near the analyte, in order to obtain a correlation coefficient greater than 0.95. The precision and accuracy of the results were evaluated through the recovery of 10 samples of known concentration for each metal.

2.6 Quantification of Heavy Metals

The identification and quantification of Pb, Cd, and Cu was carried out in accordance with the specifications of the Official Mexican Standard NOM-117-SSA1–1994 (Diario Oficial 1994) using a Thermo Scientific Atomic Absorption Kit, Ice 3500 AA (Thermo Scientific®, China), which uses flame spectrophotometry with Praxair®. The wavelength for lead (Pb) reading was with a lamp of 217 nm; while for Cd and Cu it was performed at a length of 324.8 nm. The equipment was stabilized according to instrumental specifications of: air flow, acetylene gas, and wavelength, for each metal and burner height. In the quantification of metals, the calibration curve preparation was carried out with certified High Purity Standards®. In addition, a correlation coefficient of 0.96 was obtained, for which standards developed at known concentrations were used, with an adjusted range of a lower to higher concentration close to the analyte. The quantification of heavy metals was evaluated by reading the absorbency of analyzed samples, expressing them in mg L^{-1}.

2.7 Statistical Analysis

The analysis of heavy metal concentrations for Pb, Cd, and Cu in surface water by sampling site and time of year was performed with Statistica 7.0 software (StatSoft, Inc. Tulsa, USA), once fulfilled the assumptions of normality, homogeneity of variance, a one-way analysis of variance (ANOVA) was carried out with a test of Tukey's multiple comparisons ($p < 0.05$) for heavy metal concentrations analyzed. While the Factorial ANOVA analysis was used for sampling site-sampling collection schedule, also with a Tukey test.

3 Results and Discussions

3.1 Heavy Metals in the Cotaxtla-Jamapa Basin

The presence of Pb 0.0103 ± 0.0076, Cd 0.0068 ± 0.0046, and Cu 0.006891 ± 0.004602 mg L^{-1} in surface water from the Cotaxtla-Jamapa basin was detected in 100% of the sites analyzed during the three seasons of the year mentioned previously (Table 2). The above represents a risk to public and environmental health due to chronic exposure to sub-lethal concentrations of these elements (Morais et al. 2012; Malik and Khan 2016; Rodríguez-Heredia 2017; ATSDR 2017a, b, c; Engwa et al. 2019; Baghaie and Fereydoni 2019); due to the use of water along the Cotaxtla-Jamapa basin for human, agricultural, livestock, and fishing consumption. This is where chronic exposure to these metals occurs, which may generate sublethal effects in the exposed individuals. The bioaccumulation of heavy metals in aquatic organisms is a public health risk because its consumption can cause cancer and kidney damage in humans (Malik and Khan 2016; Chiziwa-Kaonga et al. 2017).

In the Cotaxtla-Jamapa basin, in the six sites analyzed, by time of year, the concentration pattern of the metals was: Pb $0.010307 \pm 0.007618 >$ Cd $0.006882 \pm$

Table 2 Concentrations of heavy metals (mg L^{-1}) per sampling site in surface waters of the Cotaxtla-Jamapa basin, Mexico

Sampling sites	Pb	Cd	Cu
Dos Bocas 1	0.003644 ± 0.002069	0.003501 ± 0.001239	0.003533 ± 0.001295
Dos Bocas 2	0.008793 ± 0.005708	0.004252 ± 0.001173	0.004313 ± 0.001169
La Rayana	0.008892 ± 0.006123	0.003427 ± 0.002171	0.003476 ± 0.002142
Las Gualdras	0.009939 ± 0.002914	0.004506 ± 0.001398	0.004640 ± 0.001364
Arroyo Moreno	0.014817 ± 0.008893	0.013964 ± 0.002372	0.013852 ± 0.002377
La Bocana	0.015754 ± 0.009543	0.011642 ± 0.002697	0.011535 ± 0.002700
Total	0.010307 ± 0.007618	0.006882 ± 0.004676	0.006891 ± 0.004602

0.004676 > Cu 0.006891 ± 0.004602 mg L^{-1}. The concentration of this pattern coincided partially with the concentration of Pb with regard to Cd reported by Hameed et al. (2014) in surface water of the Mahrut River: Cr > Pb > Fe > Ni > Mn > Cu > Cd > Zn in summer, whereas the concentration pattern totally differed from the results obtained in the present investigation in winter: Cr > Fe > Ni > Mn > Cu > Pb > Cd > Zn. The concentration of metals in surface waters of both rivers is mainly influenced by anthropogenic activities that download directly without prior treatment. In this investigation, concentrations of heavy metals in analyzed sites were identified mainly in the final portion of the Jamapa River basin, where the Arroyo Moreno and the mouth of the Jamapa River are located. According to the results of this study, the increases of urban settlements and infrastructure in the metropolitan area of Veracruz have transformed the Jamapa River basin. In addition to the increase of tourist activities, downloads of residual waters, temporary agriculture with crops such as sugar, corn, and shadow coffee cultivation in transition to be in the sun, plus extensive livestock (Alfaro-Gómez et al. 2014; INECC-FGM 2018). All these activities depend on the water of this basin and also provide pollutants as heavy metals and pesticides traces.

The importance in the evaluation of the presence of heavy metals in surface waters is due to the fact that the degradation of water resources by these elements compromises the sustainability of water bodies and vital aquatic ecosystems, in addition to negatively affecting the management of these water resources (Chiziwa-Kaonga et al. 2017). Chemical compounds containing water-soluble metals are considered bio-available and are more toxic for organisms that are exposed to them (Morais et al. 2012; De Paiva Magalhaes et al. 2015; Bhattacharjee and Goswami 2018).

3.2 Transfer of Metals to Environmental Matrices

The concentrations of the three metals in the six sites analyzed at the aforementioned times of the year represent in turn a source of transfer of pollutants to other environmental matrices in the aquatic systems of the basin such as sediments and subsequently biota. Pintilie et al. (2007a, b) also indicated that rivers that flow through areas with industrial pollution in the form of solution and adhered to suspended solids could transport heavy metals. Where, this transport contributes to its accumulation in sediments and other aquatic bodies such as lakes and lagoons, generating significant negative effects on wildlife, and public health upon entering the food chain.

According to recent research, it has been documented that water can contribute to the transfer of pollutants to the soil at higher concentrations, indicating that the levels of metals in soils and organisms were much higher than in the water samples analyzed, confirming its possible accumulation and damage to public health (Chiziwa-Kaonga et al. 2017).

3.3 Pb

The analysis of Pb concentrations allowed to identify the site of the mouth of the river as the point with the highest concentration with 0.0157 ± 0.0095 mg L^{-1}, followed by Arroyo Moreno with 0.0148 ± 0.0088 mg L^{-1}. This metal also had the highest concentration compared to Cd and Cu (Table 2). The Arroyo Moreno and the Bocana sampling sites located at the end of the basin presented the greatest concentrations for the three metals analyzed. In contrast to the present study, Akaahan et al. (2015) did not report significant differences in metal concentrations at the analyzed sites of the Benue River, Nigeria.

The concentrations obtained in the Bocana and Arroyo Moreno exceeded the maximum level of the pollutant and action of Pb with 0.015 mg L^{-1} (EPA 2012), the presence of higher concentrations Pb, Cd and Cu in these two sampling sites indicate its constant income and its accumulation in the final portion of the Jamapa River basin (Fig. 2). This is explained by simulating the transport of heavy metals in the water column and sediment at the bottom of an aquatic system; where there are input and output currents that reflect a dynamic behavior with a tendency to reach a steady state, which depends on volumetric flows, and in a smaller proportion of the metal concentration during the flow of incoming water (Pintilie et al. 2007a, b). Radakovitch et al. (2007) reported that the temporal and spatial variations in river flows of particulate metals such as Cr, Co, Ni, Cu, Pb, Cd, and Zn, were a consequence of the discharge of water and the incorporation of suspended particles in river flows. The foregoing highlights the central role of the river discharge areas, in the mobilization of heavy metals in a system towards nearby coastal environments; as well as the constant contribution of these chemical pollutants in river surface waters. The aforementioned, in turn implies chronic exposure representing a risk to public health and to the aquatic environment. It also exceeded the drinking water quality limit reported by WHO (2004) as the maximum value of Pb allowed of 0.01 mg L^{-1}. The population in general that uses surface waters for various purposes, as in the kitchen and basic hygiene, in addition to agricultural and industrial activities, are exposed through heavy metals (Ali et al. 2019). In the basin of the Jamapa River such as initially indicated, a large variety of agricultural, pecuniary, and tourism activities is performed. Its population in general has more probabilities when exposed to these metals and that these same bio-accumulate in different organs of the human body (Vetrimurugan et al. 2017; Jamshaid et al. 2018; Hussain et al. 2019). This exposure may have long-term effects, exposure to Pb is accumulative and these high concentrations in the body can cause permanent damage to the central nervous system and to the kidney (Abdeldayem 2020). In accordance with the International Cancer Research Agency (ICRA) inorganic Pb is considered carcinogenic in human beings (ATSDR 2017a; Jamshaid et al. 2018).

The presence of concentrations of Pb, higher or close to the limits established in the national regulations, represents a risk to public health. ATSDR (2017a) noted that after a period of several weeks of exposure occur the most of the Pb accumulation in bones and teeth of people exposed to this element. In addition, the International Agency for Research on Cancer (IARC) has determined that inorganic lead is probably carcinogenic in humans (ATSDR 2017a).

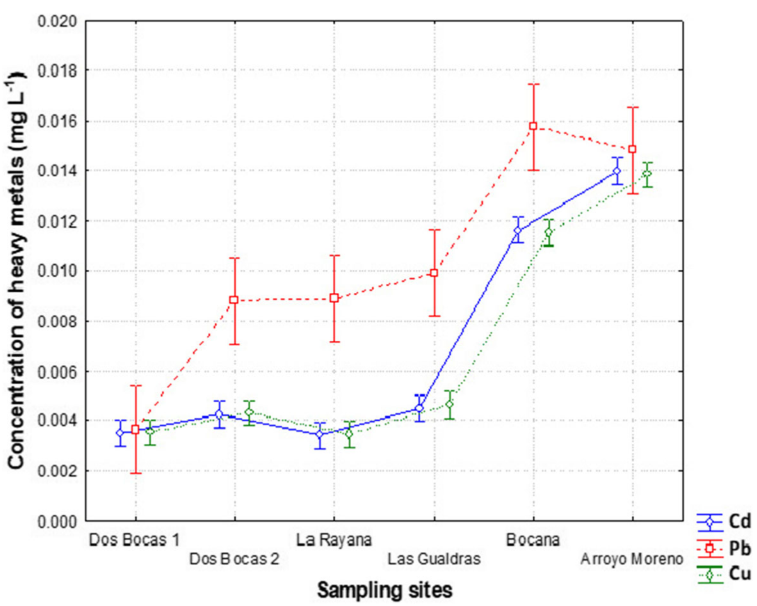

Fig. 2 Heavy metal concentration in surface waters by sampling sites in the Cotaxtla-Jamapa basin in Veracruz, Mexico

Regarding the permissible limits, also Chiziwa-Kaonga et al. (2017) indicated for the Pb a criterion between 0.01–0.05 mg L^{-1} as standard of the Malawi Bureau of Standards (MBS 2005) in drinking water for trace elements and heavy metals. Therefore, the values obtained at the sites Bocana and Arroyo Moreno also exceeded this reference criterion, representing a risk to public health. Regarding the source of this element in the environment, Hameed et al. (2014) indicated that a high concentration of Pb in river water might be related to anthropogenic activities such as vehicle emissions.

The concentrations of Pb in the three seasons in the Cotaxtla-Jamapa basin showed significant statistical differences ($p < 0.05$) in comparison with Cd and Cu. By season, the maximum concentration was obtained during rains, followed by north winds and finally dry season with a minimum concentration of 0.0037 ± 0.0026 mg L^{-1} (Table 4). Coinciding with that reported by Akaahan et al. (2015) who obtained significant difference ($p < 0.05$) in Pb concentration during the rainy and dry seasons.

In contrast, Hameed et al. (2014) reported in the Mahrut River, Diyala in Iraq a concentration range of Pb, which varied from 218.0 (0.218 mg L^{-1}) to 330.0 μg L^{-1}, and from 10.0 (0.01 mg L^{-1}) to 79.0 μg L^{-1} in the summer and winter season, respectively. It should also be noted, the discrepancies with respect to the period with the highest level of Pb, that the previous concentrations were higher than the maximum values obtained in the Cotaxtla-Jamapa basin. Likewise, Hameed et al. (2014) indicated that all surface water sources analyzed had a higher Pb content in the dry season compared to the rainy season. The presence of concentrations higher than the recommended Pb in waters according to the standard can be harmful to the consumer's health. However, this element is usually found in water naturally, but not in high concentrations (Akaahan et al. 2015).

3.4 Cd

The Cd concentrations did not show significant statistical differences ($p < 0.05$) between the seasons (Fig. 3). By sampling site, the Bocana and Arroyo Moreno presented significant statistical differences ($p < 0.05$) with mean concentrations of 0.011642 ± 0.002697 and 0.013964 ± 0.002372 mg L^{-1}, respectively (Fig. 2). Meanwhile, the Cd concentrations in the rest of the sites did not show significant statistical differences (Table 2).

All the sampling sites in this investigation presented a value close to the value referred by Chiziwa-Kaonga et al. (2017), where they indicated a criterion for the Cd in drinking water of 0.003–0.005 mg L^{-1} according to MBS 2005 (Table 3). The foregoing indicates a potential risk and damage to public health, as well as to the environment due to chronic exposure to this element through water. Cd adheres strongly to organic matters, in which it remains immobile and could be bioaccumulated by plants, and with it, enters to the trophic chain (ATSDR 2017b). Cd in freshwater fish can alter reproductive and physiological behaviors, affecting the environmental permanence and biodiversity of the ecosystem in question (Perera et al. 2015). With regard to

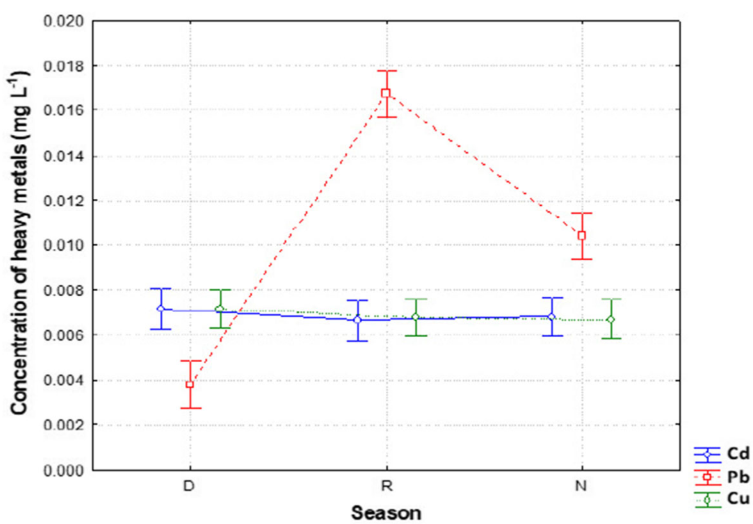

Fig. 3 Heavy metal concentration by season in surface waters of the Cotaxtla-Jamapa basin in Veracruz, Mexico. Dry (D), Rainy (R), North winds (N)

the effect on health, most of the Cd that enters the body accumulates in kidney and liver, and this element can remain in these organs for many years (Singh and Kalamdhad 2011; ATSDR 2017b). The accumulation of this metal in kidneys reaches high enough concentrations causing kidney damage and weakening of the bones that make them more vulnerable to fractures, and in accordance with the International Cancer Research Agency (ICRA) it was determined that Cd and the compounds derived from this, are carcinogenic in human beings (Wu et al. 2016; ATSDR 2017b).

However, according to the criterion for this element, the EPA (2012), only two sites, the Bocana (0.011642 ± 0.002697) and Arroyo Moreno (0.013964 ± 0.002372 mg L^{-1}) presented a value higher than the allowable limit of 0.005 mg L^{-1} for Cd (Table 3). It coincides with this increase in the concentration of surface water of rivers, according to the WHO (2010). It was indicated that human activities significantly increase the concentration of this element in the aquatic ecosystem. They indicated and pointed out the capacity of this element to move long distances from the source of emission by atmospheric transport.

3.5 Heavy Metal Concentration and Sampling Times

The relationship between the concentrations between sampling sites and the collection schedule showed significant differences ($p < 0.05$), mainly for the Bocana and Arroyo Moreno sites, both for morning and night sampling (Fig. 4). Pb presented the highest concentrations at night time at the Arroyo Moreno and the Bocana sites with 15.356 (0.015356) ± 9.776 (0.009776) and 14.076 (0.014076) ± 8.2 (0.008200 mg) μg L^{-1}, respectively. Regarding the influence of the collection schedule, in contrast Márquez et al. (2008) reported in the Unare lagoon in Venezuela, that the values of heavy metals in terms of suspension were higher during the

Table 3 Permissible limits of heavy metals (mg L^{-1}) in national and international surface water

Heavy metal	Criterion	Permissible limits	Source
Pb	River water: use in agricultural irrigation	0.5 (m.a); 1 mg L^{-1} (d.a)	NOM-001-SEMARNAT-2018. Mexico
	River water: urban public	0.2 (m.a); 0.4 mg L^{-1} (d.a)	
	River water: protection of aquatic life	0.2 (m.a); 0.4 mg L^{-1} (d.a)	
	Maximum level of contaminant and action of Pb	0.015	EPA (2012)
	Water quality guidelines for the protection of aquatic life	0.007	CCME (2007)
Cd	River water: use in agricultural irrigation	0.2 (m.a); 0.4 mg L^{-1} (d.a)	NOM-001-SEMARNAT-2018. Mexico
	River water: urban public	0.1 (m.a); 0.2 mg L^{-1} (d.a)	
	River water: protection of aquatic life	0.1 (m.a); 0.2 mg L^{-1} (d.a)	
	Maximum level of contaminant	0.005	EPA (2012)
	Water quality guidelines for the protection of aquatic life	0.000017	CCME (2007)
Cu	River water: use in agricultural irrigation	4.0 (m.a); 6.0 mg L^{-1} (d.a)	NOM-001-SEMARNAT-2018. Mexico
	River water: urban public	4.0 (m.a); 6.0 mg L^{-1} (d.a)	
	River water: protection of aquatic life	4.0 (m.a); 6.0 mg L^{-1} (d.a)	
	Maximum level of contaminant	1.3	EPA (2012)
	Dermal effect (skin discoloration or teeth) esthetic (taste, smell or color).	1.0	
	Water quality guidelines for the protection of aquatic life	0.004	CCME (2007)

m.a (monthly average); d.a. (daily average)

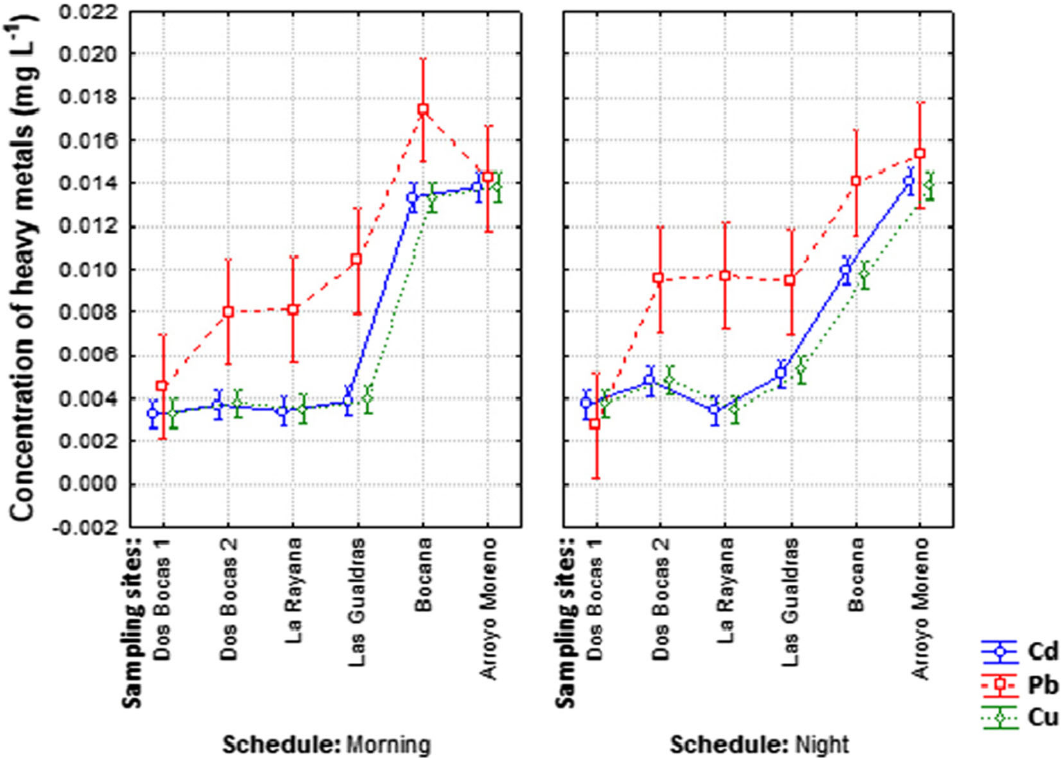

Fig. 4 Concentration of heavy metals by sampling site and time in surface waters of the Cotaxtla-Jamapa basin in Veracruz, Mexico

night hours. Likewise, they related these results to the degradation of the organic matter of the sediment during the night, and therefore it releases the metals to the water column. Also, Fermín (2002) pointed out that during the night dissolved oxygen concentrations decrease in water, because this is used in the oxidation of organic matter and therefore can be related to the variations of heavy metals in that time.

Regarding the presence of a greater concentration of metals in the Arroyo Moreno and the Bocana sites, located in the final portion of the basin, these can be associated with the transport of pollutants like metals to the mouth of the river, coinciding with the aforementioned Rodríguez et al. (2012) indicated that in the Manzanares River in Venezuela, the sites located in the mouth and in the spillway of the river represent the area of high influence due to high concentrations of Cr and Zn, as well as low concentrations of Pb and Co. In addition, they indicated a continuous contribution of Zn and Co in the study area as a result of the discharges of the Manzanares River through its mouth and spillway to the adjacent coastal area.

The presence of Cd in the aquatic environment represents a risk for the aquatic and terrestrial biota, for which the limits in their water concentrations are stricter to the Canadian Council of Ministers of the Environment (CCME 2007) guidelines for the protection of aquatic life of 0.017 μg L^{-1}, compared to a Pb value of 7 and Cu of 4 μg L^{-1}. According to the Canadian Council of Ministers of the Environment (CCME 2007) in the water quality guidelines for the protection of aquatic life, the concentration of Cd should not exceed 0.000017 mg L^{-1}. While for Pb the limit considered is 0.007 mg L^{-1} (Table 3).

3.6 Cu

The concentrations of Cu did not show significant statistical differences ($p > 0.05$) between the seasons, the dry season had the highest concentration with 0.0071 ± 0.0035 mg L^{-1} (Table 4). In contrast, Rubio-Arias et al. (2010) indicated that in the Conchos River in Chihuahua, they detected statistical differences in concentrations of Cu per year and time of sampling. They also pointed out that the concentration peaks detected could be associated with the fact that Cu-containing fungicides are commonly used at the beginning of the year in nut production and other crops.

Table 4 Concentrations of heavy metals (μg L^{-1}) by season in surface waters of the Cotaxtla-Jamapa basin, Veracruz, Mexico

Season	Pb	Cd	Cu
Dry	3.774 ± 2.601	7.164 ± 3.585	7.172 ± 3.584
Rainy	16.743 ± 7.546	6.665 ± 5.473	6.789 ± 5.389
North winds	10.402 ± 5.157	6.817 ± 4.803	6.714 ± 4.683
Total	10.307 ± 7.618	6.882 ± 4.676	6.891 ± 4.602

In the case of the sampling sites, the Bocana and Arroyo Moreno, in the Jamapa River basin, the maximum concentrations obtained were 0.0115 ± 0.0027 and 0.0138 ± 0.0023 mg L^{-1}. In contrast, the previous values were lower than those reported by Rubio-Arias et al. (2010) who indicated 2.50 mg L^{-1} as maximum value of Cu, while in the concentration range in two sampling sites were 0.37 mg L^{-1} in site 4 and 0.50 mg L^{-1} in site 3. Also, Hameed et al. (2014) in the Mahrut River indicated concentrations of Cu with a range of: not detected at 62.0 μg L^{-1} (0.062 mg L^{-1}) and 29.9 μg L^{-1} (0.0299) to 47.2 μg L^{-1} during summer and winter season, respectively.

Cu concentrations obtained by sampling site and season in the Cotaxtla-Jamapa basin were low compared to other investigations as indicated above. This coincides with what was reported by the ATSDR (2017b), which pointed out that Cu occurs naturally in low concentrations in rocks, water, sediments, and air. Concentrations in the Cotaxtla-Jamapa basin were within the permissible limits, Chiziwa-Kaonga et al. (2017) indicated for a value of 0.5–1.0 mg L^{-1} of Cd in drinking water. Also, Hameed et al. (2014) indicated a Cu value for the river maintenance system of 50 μg L^{-1} or 0.05 mg L^{-1} (IOG 1967). In contrast, according to the CCME (2007), the limit for the protection of aquatic life corresponds to 0.004 mg L^{-1}, therefore, Cu concentrations in the Jamapa River were higher than this reference value during the three seasons and at the sites of sampling (Dos Bocas 2, Las Gualdras, La Bocana, and Arroyo Moreno).

Rubio-Arias et al. (2010) indicated that knowing when there are high concentrations of heavy metals such as Cu can help prevent health risks by suggesting to establish a recommendation on the time of direct exposure in communities located along the river basin that use this resource for recreational activities, such as swimming and fishing. Likewise, Londoño-Franco et al. (2016) indicated that constant monitoring programs are required due to the risk for both health and ecosystems. This is related to the potential hazard to public health, since ATSDR (2017c) indicated that intentional ingestion of high levels of Cu could cause damage to liver, kidneys, and in some cases even death. Therefore, the analysis of the presence of heavy metals in river waters and sediment constitutes a contribution to the provision of environmental information in these aquatic ecosystems, which will eventually contribute to the diagnosis of their watersheds. Likewise, the information provided by such heavy metal analysis will be useful to develop effective management strategies for the control of pollution in rivers with similar conditions and to contribute to decision-making, especially of a governmental nature (Contreras-Pérez et al. 2004; Tang et al. 2016).

4 Conclusions

Heavy metals in surface waters of the Cotaxtla-Jamapa basin are an indicator of their use and the route of these compounds at some sites in this basin. The highest concentration of these elements was evident in endpoints of the river basin. Nevertheless, it was observed that only the values obtained for Pb exceeded the permissible limits considered safe for public health and for aquatic environments. However, the presence of Cd and Cu represents a risk from chronic exposure, which implies the presence of sub-lethal effects in exposed organisms.

Carrying out heavy metal monitoring in the final portion of a basin is a useful tool for managing water resources, which would contribute to the generation of scientific knowledge, and strengthen the ability to propose strategies that reduce and mitigate exposure to these pollutants. Among these are: the generation of a greater number of research in the area, as well as the implementation of plans to reduce or replace the use of compounds with traces of heavy metals, thus reducing the risk they imply for public health and for ecosystems. In this way, international agreements in which Mexico participates are fulfilled, to reduce and avoid the impact on the environment, specifically in the Gulf of Mexico.

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