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ORIGINAL ARTICLE

Water quality and heavy metal levels in the Sinú River, a drinking water source in the Colombian Caribbean

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Abstract

The objective of this work was to evaluate water quality in the Sinú River in northern Colombia, during its dry and rainy seasons. The water quality index (WQI), the heavy metal pollution index (HPI), the heavy metal evaluation index (HEI), the heavy metal toxicity load (HMTL), and the degree of contamination (Cd) were calculated based on analyses of water samples taken along the entire length of the river at sixteen sampling sites. Comprehensive and in some cases punctual samplings were performed depending on the morphology of the current. Five samplings were carried out in the dry and rainy periods from March 2008 to April 2009. All samples were taken in triplicate at each sampling site. For the determination of metals, a Thermo electron atomic absorption spectrometer, model S4AA System was used. Of the metals monitored, only zinc, iron, and manganese were identified at quantifiable levels, with average values of $8.5\times10^{-5}\,\mathrm{kg\,m^{-3}}$, $0.004\,424\,\mathrm{kg\,m^{-3}}$ and $8.5\times10^{-5}\,\mathrm{kg\,m^{-3}}$, respectively in the rainy season. The obtained index values altogether (WQI $= 63.5$, HPI $= 145$, HEI $= 24$, HMTL $= 0.1329$, and $C_d = 20.8$) revealed the presence of contamination by heavy metals in the Sinú River, although the observed toxicity level does not imply a hazard to human health.

Keywords: contamination, spectroscopy, water quality, iron, zinc, manganese, Sinú River.

1. Introduction

The Sinú River flows through northwestern Colombia along 415 km to its mouth in the Caribbean Sea. Its source is located in the Paramillo Massif, within the department of Antioquia, and as it flows northward, it crosses the department of Cordoba before reaching the sea. The river course covers an area of $13\,700\,\mathrm{km^2}$, and its average flow rate at the Urrá site is $342\,\mathrm{m^3\,s^{-1}}$, with a water depth, ahead of this dam, of 7 m. This river system hosts important fish species, such as bocachico (*Prochilodusmagdalenae*), white catfish (*Pimelodus albicans*), liseta (*Leporinusmuyscorum*), among others, which are sold in local, regional and national markets. The Sinú River supplies water to the fifteen municipalities along its course within the department of Córdoba, and it is also an income source for fishermen of the region, thus contributing to the economic development of the department of Córdoba (Corporación Autónoma de los Valles del Sinú y San Jorge, 1998).

The department of Córdoba is chiefly devoted to agricultural activities with a low level of industrialization. Their waste is directly poured into the Sinú River without efficient treatment, and pollution in this water stream is mounting. Heavy metal pollution is currently a global problem (Al-Ani *et al.*, 1987; Tiwari and Singh, 2014; Tiwari *et al.*, 2015; Marrugo-Negrete *et al.*, 2017; Mitra *et al.*, 2022), and there is a growing concern about heavy metal toxicity and accumulation in aquatic life (Tietze and Kettschau, 1997; Jordan *et al.*, 2014; Tscheikner-Gratl *et al.*, 2019). Heavy metals play a key ecotoxicological role due to their bioaccumulation, persistence, and biomagnification in food chains (Yin *et al.*, 2019). This type of pollution in different water sources has both natural and anthropogenic origins (Wei and Yang, 2010; Muhammad *et al.*, 2011; Qu *et al.*, 2018). Thus, a thorough evaluation of the quality of water streams, like the Sinú River, requires the use of different metrics.

The water quality index (WQI), indicative of the state of a particular water source, varies among countries, considering their unique geographies and water use. Currently, WQI is used to monitor water quality in rivers over time; if the water stream has a WQI from 91 to 100, its quality is good, a WQI from 71 to 90 reveals an acceptable water quality, values between 51 and 70 denote regular water quality, values from 26 to 50 imply a bad water quality, and values from 0 to 25 mark the lowest water quality levels (Rojas, 1991).

The heavy metal pollution index (HPI) reveals the combined effect of heavy metals on surface water quality (Sheykhi and Moore, 2012), and the heavy metal assessment index (HEI) provides information about the state of the body of water related to heavy metals. Surface water quality is assessed with this index; if HEI < 10, pollution is low; values between 10 and 20 reveal moderate pollution; and values > 20 indicate high pollution. The degree of contamination (C_d) measures HM impact on a water body. Heavy metal pollution categories according to C_d are as follows: $C_d < 1$ mark low pollution; C_d from 1 to 3 reveal moderate pollution; and $C_d > 3$ indicate high pollution in the body of surface water due to heavy metals (Backman *et al.*, 1998).

Some anthropogenic activities are associated with the type of contaminating metals. For instance, mining results in the liberation of As, Cd, Cu, Ni, Pb, and Zn; corrosion leads to an increase in Fe, Cu, Pb Cr, Ni, Co, Cd, and Zn levels; and agriculture and cattle farming result in the liberation of Cu, As, Mn, Pb, and Zn (Vink *et al.*, 1999; Domenech and Peral, 2006). Studies conducted in South America reveal that these metals are altogether responsible for the contamination of water sources linked to mining activities, conventional agriculture, involving the use of fertilizers and pesticides, the weathering of rocks and wastewater discharge (Zhou *et al.*, 2020). Moreover, it is necessary to assess the level of exposure of fish species to these metal contaminants (Anadon *et al.*, 1984). Since the divalent metal cations Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and $Zn^{2+}$are structurally similar to each other, they are likely to displace one another in their physiological functions within the cell, with harmful consequences (Navarro-Aviñó *et al.*, 2007). For example, if Zn^{2+} is replaced by Ni^{2+}, or Be for Mn^{2+} in enzymes, these become disabled and lose their function. Likewise, the substitution of Ca by other metals in membrane proteins causes functional disorders (Nies, 1999).

In Colombia in 2006, organizations such as IDEAM and CORMAGDALENA monitored water contamination at 120 points in the Magdalena River and at 101 points along the Cauca River (from their sources to their mouths). In the Magdalena River, the obtained WQI levels ranged in the categories of medium and good quality. Whereas in the Cauca River, WQI values ranged from the lowest to the best water qualities. Also, the determination of heavy metals in these rivers revealed the presence of Zinc with values below $0.001\,\mathrm{kg\,m^{-3}}$. Mercury was also detected, for instance at sampling point Puente Balseadero (municipality of Agrado – Huila) in the Magdalena River, and in the Cauca River, this metal was detected at several points, some related to mining activity, *e.g.*, at Quebrada Marmato, in the department of Caldas (IDEAM, 2007).

In the literature, there are no reports on the influx of heavy metals into the Sinú River in the department of Córdoba. Thus, it is necessary to assess the quality of its waters based on water quality indices and keep a record in time, providing information to determine water quality evolution and to inform environmental authorities' decisions to preserve this water body. The objective of this research is to measure the quality of the water of the Sinú River employing the quality indices WQI, HEI, Cd, HPI, and HMLT.

2. Materials and Methods

2.1. Study area

The studied area included the Sinú River basin in the department of Córdoba that covered the regions of upper, middle, and lower Sinú. Sampling stations were selected considering the sixteen control points established by the Corporación de los Valles del Sinú and San Jorge (**Figure 1**)

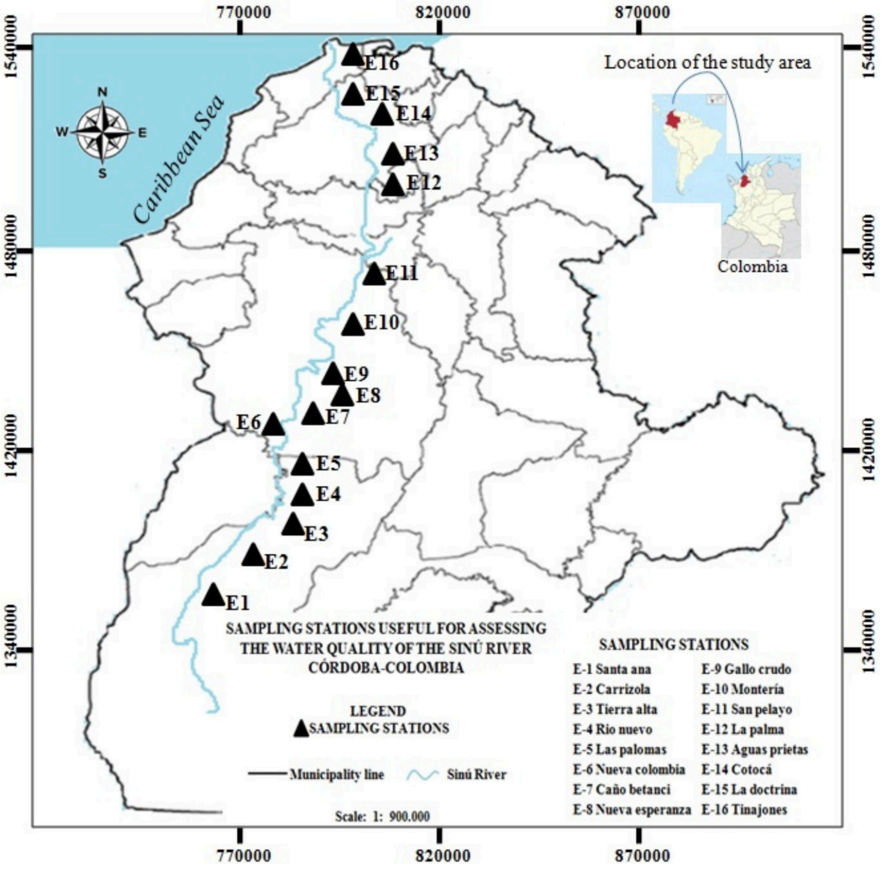

Figure 1. Sampling site locations in the Sinú River basin.

2.2. Sample collection

Water samples were collected over a year (from March 2008 to April 2009) at 16 stations along the Sinu River, covering dry and rainy periods, as marked in Figure 1. The sampling stations are: Santa Ana (E1), Carrizola (E2), Tierra Alta (E3), Río nuevo (E4), Las palomas (E5), Nueva Colombia (E6), Caño Betancí (E7), Nueva esperanza (E8), Gallo crudo (E9), Montería (E10), San Pelayo (E11), La palma (E12), Aguas prietas (E13), Cotocá (E14), La doctrina (E15), and Tinajones (E16).

Depending on the size and morphology of the current, point or integrated samples were taken. At sites where the current was well mixed and was less than 100 m wide, a single, or punctual, sample was taken. In stations where the breadth of the current was greater than 100 m wide, an integrated sample was taken; implying that subsamples of equal volume at one-fourth, one half, and three-fourths of the current's cross-section were collected and blend into a one-liter polyethylene bottle. All samples were taken in triplicate at each sampling site. These were acidified with concentrated HNO_3 up to a pH of 2.0, refrigerated and transported to the laboratory. (American Public Health Association, 2005).

2.3. Water pollution indices

2.3.1. Water Quality Index (WQI)

Each country adopts the WQI depending on its unique geographical conditions and pollutant load of rivers. Rojas (1991) adapted the WQI-NSF to the specific conditions of some rivers in Colombia, taking into account parameters of importance that reflect water from its source. In order to obtain the WQI - Rojas 1991 (Colombia) Index, the biochemical oxygen demand, fecal coliforms, turbidity, total dissolved solids, dissolved oxygen, and pH were determined. Whereby the last two parameters recorded *in situ.*

The WQI was calculated with the following equation:

$$\mathrm{WQI} = \sum_{i=1}^{n} C_i \cdot W_i, \tag{1}$$

where W_i is the weight or percentage assigned to the i-th parameter, ranging from 0 to 1, and n is the number of parameters, that in our case were six C_i. The quality graph obtained considered parameter concentration (Rojas, 1991). Water quality according to WQI (Rojas, 1991) and the weights assigned to each parameter.

2.3.2. Parameters and data:

OD: $W_i = 0.25; 0 \leq \mathrm{WQI} \leq 25$; Water quality = very bad.

pH: $W_i = 0.17; 26 \leq \mathrm{WQI} \leq 50$; Water quality = bad.

BOD: $W_i = 0.15; 51 \leq \mathrm{WQI} \leq 70$; Water quality = regular.

Coli.fecal: $W_i = 0.21; 71 \leq \mathrm{WQI} \leq 90$; Water quality = acceptable.

Turbidity: $W_i = 0.11; 91 \leq \mathrm{WQI} \leq 100$; Water quality = good. (SDT: $W_i = 0.11$).

2.3.3. Heavy metal Pollution Index (HPI)

This index takes into account the ratio of each heavy metal present, according to its relative importance and is inversely proportional to the recommended standard value for each heavy metal. This index was calculated with the following equation:

$$\mathrm{HPI} = \sum_{i=1}^{n} W_i \cdot Q_i \Bigg/ \sum_{i=1}^{n} W_i \ , \tag{2}$$

where, W_i is the weight unit of the i-th heavy metal; Q_i is the sub-index for the i-th heavy metal; and n is the number of metals under study, which in our case were 3.

The Q_i were calculated as follows:

$$Q_i = 100 \cdot \sum_{i=1}^{n} \frac{|M_i - I_i|}{S_i - I_i}, \tag{3}$$

where M_i (kg m^{-3}) is the value of i-th heavy metal, with S_i and I_i as the standard and ideal values for drinking water, respectively (WHO, 2017; Kumar *et al.*, 2019). For a given heavy metal concentration (kg m^{-3}), (S_i) refers to the maximum permitted concentration of heavy metal in the absence of an alternative source for drinking water. The maximum desirable value (I_i) indicates the standard limit of the same parameter for drinking water (Tiwari *et al.*, 2015). A HPI value below 100, reveals low heavy metal contamination, a value of 100 is regarded as a threshold posing the likelihood of health damage, and a HPI value above 100 indicates that the water is not suitable for consumption.

2.3.4. Heavy metal assessment index (HEI)

This index quantifies water health in general with respect to its heavy metal content (Ameh, 2013; Kumar *et al.*, 2019) and was calculated with the following formula:

$$\mathrm{HEI} = \sum_{i=1}^{n} \frac{M_i}{\mathrm{MAC}_i} \tag{4}$$

where MAC_i was the monitored value and maximum allowable concentration of the i-th heavy metal. Reference values were according to Siegel (2002).

2.3.5. Degree of pollution (C_d)

C_d indicates the collective heavy metal impact on water deterioration (Backman *et al.*, 1998) and was calculated as follows:

$$C_d = \sum_{i=1}^{n} \mathcal{C}_i, \tag{5}$$

with

$$\mathcal{C}_i := \frac{M_i}{\mathrm{MAC}_i} - 1. \tag{6}$$

Here, $\mathcal{C}_i$ was the i-th heavy metal factor. The heavy metal pollution categories, as defined by this index, are: $C_d < 1$, revealing low pollution; $1 \leq C_d \leq 3$, revealing moderate pollution, and $C_d > 3$ indicating high pollution in the body of surface water due to heavy metals.

2.3.6. Heavy metal toxicity load (HMTL)

The HMTL index assesses water heavy metal content and its effect on human health (Saha and Paul, 2018) and is calculated with the following equation:

$$\mathrm{HMTL} = \sum_{i=1}^{n} M_i \cdot \mathrm{HIS}_i \tag{7}$$

Here, HIS_i is the hazard intensity score of the i-th heavy metal, as established by ASTDR (2019). Each HIS was assigned based on heavy metal incidence as a harmful substance, established in the National Priority List (NPL), considering metals that entail a significant threat to human health due to their known or suspected toxicity. The maximum HMTL for a HM is 1800, where 600 points are assigned to each of the metals established in the NPL, taking into account their frequency, toxicity, and human contact perspective.

2.4. Total metal extraction

A volume of 50 ml of each unfiltered water sample was digested at 150 °C with 5 ml of HNO_3 at 68 % v/v and 1 ml of H_2O_2 at 30 % v/v for two hours. Then, a volume of 25 ml was measured with acidic water for analysis. To assess total Hg, 50 ml of the unfiltered samples were taken, previously acidified with HNO_3 at 68 % v/v. The respective digestion was then carried out by adding 10 ml of 68 % v/v HNO_3, 5 ml of 5 % w/v $KMnO_4$ solution and 3 ml of 5 % w/v $K_2S_2O_8$ solution in a water bath at a temperature of 95 °C for two hours.

2.5. Metal determination by atomic absorption spectroscopy

Standards of each of the metals under study were prepared, and the concentrations of heavy metals present in the samples were quantified using the calibration curve method. For the determination of metals, a *Thermoelectron*atomic absorption equipment, model S4AA *System* (Thermofisher Scientific, MA, USA) was used. All samples were analyzed in the laboratory of the Water, Pesticides and Heavy Metal research group at Universidad de Córdoba, Colombia.

2.6. Statistical Analysis

All statistical analyses were performed with the IBM SPSS 22.0 program. Results are shown as the arithmetic mean of the triplicate determinations, with a 95 % significance. To evaluate the normality of the data points, the Kolmogorov-Smirnov and Saphiro-Wilks tests were used. To evaluate the homogeneity of the variance of ANOVA, the Levene test was used. When the data did not behave as expected, the Kruskal-Wallis test was used. To establish the relationship between metal and seasonal periods, between the WQI and each parameter the Pearson correlation was used.

3. Results and Discussion

3.1. Statistical analysis of heavy metals

95 %tab:1 shows the measured heavy metal levels per season in the Sinú River. Such levels were the highest during the rainy season. Among the three measured heavy metals, iron revealed the highest concentrations in both seasonal periods: 0.004 424 $kg\,m^{-3}$ (rainy season) and 0.001 813 $kg\,m^{-3}$ (dry season). The highest values for each of the heavy metals occurred in the rainy season and the lowest values in the dry season. In the studied period the minimum heavy metal value was recorded for zinc (3.4×10^{-5} $kg\,m^{-3}$) and the maximum value was observed for iron (0.005 602 $kg\,m^{-3}$) in the rainy season.

Table 1. Statistics of detected heavy metalconcentrations in the Sinú River by season.

	Zn		Fe		Mn	
	Dry period	Rainy period	Dry period	Rainy period	Rainy period	Dry period
Average	$(5.8 \pm 1.0) \times 10^{-5}$	$(8.5 \pm 2.0) \times 10^{-5}$	$(18.13 \pm 3.00) \times 10^{-4}$	$(44.24 \pm 5.00) \times 10^{-4}$	$(8.5 \pm 0.9) \times 10^{-5}$	< LQ∗
Vr. Maximum	$(1.0 \pm 0.1) \times 10^{-4}$	$(11.3 \pm 0.5) \times 10^{-5}$	$(289.3 \pm 0.5) \times 10^{-5}$	$(560.2 \pm 0.3) \times 10^{-5}$	$(10.2 \pm 0.3) \times 10^{-5}$	< LQ∗
Vr. Minimum	$(3.4 \pm 0.6) \times 10^{-5}$	$(5.3 \pm 0.5) \times 10^{-5}$	$(75.8 \pm 1.0) \times 10^{-5}$	$(23.52 \pm 0.03) \times 10^{-4}$	$(6.9 \pm 1.0) \times 10^{-5}$	< LQ∗
SD	2×10^{-5}	2.6×10^{-5}	0.000518	0.000884	1.6×10^{-5}	< LQ∗

3.2. Heavy metals in the Sinú River

The results shown in 0.005 602 kg m^{-3}tab:2 indicate that, to date, the Sinú River does not contain quantifiable levels of the assessed metals, except for zinc, iron, and manganese, which are shown in 0.005 602 kg m^{-3}tab:3. This result reveals an almost zero risk of contamination by most of these metals at the time of this study.

The limits of quantification of the method used to measure heavy metals in the Sinú River were as follows: for iron, 1×10^4 kg m^{-3}; for manganese, 5×10^{-5} kg m^{-3}; for zinc, 3×10^{-5} kg m^{-3}; for cadmium, 3×10^{-5} kg m^{-3}; for cobalt, 1×10^{-4} kg m^{-3}; for chromium, 8×10^{-5} kg m^{-3}; for lead, 0.0002 kg m^{-3}; for mercury, 2×10^{-7} kg m^{-3}; for nickel, 1×10^{-4} kg m^{-3}; and for copper, 8×10^{-5} kg m^{-3}.

Table 2. Non-quantifiable monitored metals by sampling station in the Sinú River.

Station	Hg	Co	Ni	Pb	Cu	Cd
E1	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
E2	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
E3	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
E4	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
E5	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
E6	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
E7	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
E8	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
E9	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
E10	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
E11	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
E12	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
E13	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
E14	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
E15	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ
E16	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ

In the dry season, two modes of distribution of zinc and iron in the Sinú River were distinguished. The first observed mode occurred from sampling sites Santa Ana (E1) to Gallo Crudo (E9); and the second from Monteria (E10) to the river mouth at Tinajones (E16). Whereas in the rainy season, zinc concentrations were evenly distributed along the Sinú River, with the exception of the Tierralta (E3) and New River (E4) stations.

These results are associated with water dynamics, characterized by the absence of polluting water discharges in the upper part of the river. This behavior can be extended to the Urrá complex, where the river begins to receive direct and indirect household, workshop, and health facility discharges. At this point, the river also receives residues from livestock farming and agriculture. From the municipality of Tierralta downstream, the river receives household waste, chiefly from the urban areas of the municipalities of Monteria, Lorica and other smaller populations. The sewage of Cereté exerts its greatest influence on the big swamp of the lower Sinú through the Bugre channel (Corporación Autónoma de los Valles del Sinú y San Jorge, 2000).

Table 3. Concentration ($\mathrm{kg\,m^{-3}}$) of detected heavy metals in the Sinú Riverby season.

SEASONS	Dry season			Rainy season		
	Zn	Fe	Mn	Zn	Fe	Mn
E-1	$(3 \pm 1) \times 10^{-5}$	$(108 \pm 4) \times 10^{-5}$	< LQ*	$(6 \pm 3) \times 10^{-5}$	$(37 \pm 2) \times 10^{-4}$	< LQ*
E-2	$(4 \pm 2) \times 10^{-5}$	$(76 \pm 3) \times 10^{-5}$	< LQ*	$(6 \pm 3) \times 10^{-5}$	$(418 \pm 4) \times 10^{-5}$	$(7 \pm 4) \times 10^{-5}$
E-3	$(8 \pm 4) \times 10^{-5}$	$(89 \pm 5) \times 10^{-5}$	< LQ*	$(8 \pm 4) \times 10^{-5}$	$(418 \pm 4) \times 10^{-5}$	$(9 \pm 5) \times 10^{-5}$
E-4	$(10 \pm 5) \times 10^{-5}$	$(88 \pm 4) \times 10^{-5}$	< LQ*	$(8 \pm 4) \times 10^{-5}$	$(418 \pm 4) \times 10^{-5}$	$(10 \pm 5) \times 10^{-5}$
E-5	$(4 \pm 2) \times 10^{-5}$	$(151.0 \pm 0.5) \times 10^{-5}$	< LQ*	$(6 \pm 3) \times 10^{-5}$	$(446 \pm 3) \times 10^{-5}$	$(10 \pm 5) \times 10^{-5}$
E-6	$(4 \pm 2) \times 10^{-5}$	$(148 \pm 4) \times 10^{-5}$	< LQ*	$(7 \pm 4) \times 10^{-5}$	$(516 \pm 3) \times 10^{-5}$	$(9 \pm 5) \times 10^{-5}$
E-7	$(6 \pm 3) \times 10^{-5}$	$(194 \pm 6) \times 10^{-5}$	< LQ*	$(7 \pm 4) \times 10^{-5}$	$(235 \pm 3) \times 10^{-5}$	< LQ
E-8	$(6 \pm 3) \times 10^{-5}$	$(183 \pm 7) \times 10^{-5}$	< LQ*	$(9 \pm 5) \times 10^{-5}$	$(533 \pm 2) \times 10^{-5}$	$(8 \pm 4) \times 10^{-5}$
E-9	$(7 \pm 4) \times 10^{-5}$	$(215 \pm 7) \times 10^{-5}$	< LQ*	$(8 \pm 4) \times 10^{-5}$	$(528 \pm 4) \times 10^{-5}$	$(8 \pm 4) \times 10^{-5}$
E-10	$(5 \pm 3) \times 10^{-5}$	$(268 \pm 4) \times 10^{-5}$	< LQ*	$(5 \pm 3) \times 10^{-5}$	$(488 \pm 4) \times 10^{-5}$	$(8 \pm 4) \times 10^{-5}$
E-11	$(6 \pm 3) \times 10^{-5}$	$(279 \pm 5) \times 10^{-5}$	< LQ*	$(9 \pm 5) \times 10^{-5}$	$(472 \pm 4) \times 10^{-5}$	$(8 \pm 4) \times 10^{-5}$
E-12	$(5 \pm 3) \times 10^{-5}$	$(289 \pm 5) \times 10^{-5}$	< LQ*	$(6 \pm 3) \times 10^{-5}$	$(506 \pm 3) \times 10^{-5}$	$(8 \pm 4) \times 10^{-5}$
E-13	$(4 \pm 2) \times 10^{-5}$	$(236 \pm 3) \times 10^{-5}$	< LQ*	$(6 \pm 3) \times 10^{-5}$	$(489 \pm 5) \times 10^{-5}$	$(7 \pm 4) \times 10^{-5}$
E-14	$(6 \pm 3) \times 10^{-5}$	$(193 \pm 5) \times 10^{-5}$	< LQ*	$(8 \pm 4) \times 10^{-5}$	$(456 \pm 3) \times 10^{-5}$	$(7 \pm 4) \times 10^{-5}$
E-15	$(4 \pm 2) \times 10^{-5}$	$(211 \pm 6) \times 10^{-5}$	< LQ*	$(8 \pm 4) \times 10^{-5}$	$(560 \pm 5) \times 10^{-5}$	$(10 \pm 5) \times 10^{-5}$
E-16	$(8 \pm 4) \times 10^{-5}$	$(176 \pm 3) \times 10^{-5}$	< LQ*	$(11 \pm 2) \times 10^{-5}$	$(515 \pm 3) \times 10^{-5}$	$(8 \pm 4) \times 10^{-5}$
*Limits of Quantification	3×10^{-5}	1×10^{-4}	5×10^{-5}	3×10^{-5}	1×10^{-4}	5×10^{-5}

3.2.1. Zinc levels

In the rainy season, the mean concentration of zinc was higher than in the dry season ($8 \times 10^{-5}\,\mathrm{kg\,m^{-3}}$tab:1), and this difference was statistically significant ($p < 0.05$). This effect is associated with the increase in suspended material generated by rainfall runoff from pipes and streams that discharge their waters to the river. However, none of assessed sites revealed average zinc levels exceeding the maximum permissible limit, as established by current national regulations for drinking water ($0.003\,\mathrm{kg\,m^{-3}}$), agricultural use ($0.002\,\mathrm{kg\,m^{-3}}$), drinking and domestic water ($0.015\,\mathrm{kg\,m^{-3}}$), livestock farming $0.025\,\mathrm{kg\,m^{-3}}$ (Resolution 2115 of the year 2007 and National Decree 1594 of 1984).

In comparison with other rivers in Latin America, the Matanaro river in Peru presented zinc concentrations with a mean value of $5.8 \times 10^{-5}\,\mathrm{kg\,m^{-3}}$ (Custodio *et al.*, 2020), similar to those reported in the present study for the dry season. In Mexico, reported river zinc values ranged between $3 \times 10^{-5}\,\mathrm{kg\,m^{-3}}$ and $8 \times 10^{-5}\,\mathrm{kg\,m^{-3}}$, in the water of the Conchos River (Holguín *et al.*, 2006; Rubio-Arias *et al.*, 2010; Gudiño-Guzmán *et al.*, 2020). These values are also comparable to the zinc levels found by the present study in the Sinú River. In Spain, studies carried out in the Monfragüe natural park, in the Tagus and Tiétar rivers, showed a concurring total zinc value of $2 \times 10^{-5}\,\mathrm{kg\,m^{-3}}$ for both streams, which is higher than those found in filtered water (García Cambe, 2002) but is safe for human consumption. In the present study zinc mean values were $5.8 \times 10^{-5}\,\mathrm{kg\,m^{-3}}$ and $8.5 \times 10^{-5}\,\mathrm{kg\,m^{-3}}$, for dry and rainy season, respectively.

3.2.2. Iron levels

With a frequency of occurrence of 100 % along the Sinú River, iron levels were considerably high in both seasonal periods, and there was a statistically significant difference ($p < 0.05$) between the iron concentrations found in the two seasons. Higher iron levels in the rainy season are likely due to stream runoff and irrigation districts, dragging organic and inorganic constituents and suspended materials into the river bed. Garbarino (1995) reported that the transport of certain pollutants (heavy metals in suspended sediment) increases in periods when the water flow of a river is high.

Taking into account Colombian regulations and the EPA for drinking water, the observed iron concentrations in the Sinú River, for both seasons, exceeded the permitted threshold of 0.0003 kg m^{-3}. However, if we take into account national regulations on the use of water for agricultural purposes (National decree 1594 of 1984), the maximum allowed concentration of iron is 0.005 kg m^{-3}. In this regard, the iron concentrations observed in the rainy season at sampling sites E6, E8, E9, E12, E15, and E16 (with values of 0.005 16 kg m^{-3}, 0.005 33 kg m^{-3}, 0.005 27 kg m^{-3}, 0.005 06 kg m^{-3}, 0.0056 kg m^{-3} and 0.005 16 kg m^{-3}; respectively) exceeded the permitted limit. During the dry season none of the stations revealed iron levels surpassing the limit for agricultural use. Adequate treatment should be applied in both seasons, and especially during rainfall, to bring Sinú River iron concentrations down to acceptable water levels for human consumption.

In the San Pedro River (Mexico), observed high levels of iron were associated with close-by mining activity. The highest concentrations of this metal were obtained during the rainy season, with values ranging from 0.000 23 kg m^{-3} to 0.985 kg m^{-3} in 1997 (stage I) and from 0.000 26 kg m^{-3} to 0.015 23 kg m^{-3} in 1999 (stage II). In the dry season, values ranged from 0.000 21 kg m^{-3} to 0.018 kg m^{-3} in stage I and up to 0.011 kg m^{-3} in stage II (Gómez-Álvarez *et al.*, 2004). Likewise, in the natural waters of the Conchos River, in Sonora (Mexico), a considerable increase in iron was detected, reaching a concentration of 0.003 07 kg m^{-3}, although it did not remain constant and decreased to a value of 0.001 36 kg m^{-3}. The predominance of the HMs studied occurred in the following order, Fe > Zn > Mn in both seasons. This finding is similar to what has been observed in the Kalingarayan Canal in India (Mohanakavitha *et al.*, 2019).

3.2.3. Manganese levels

In the dry season, no quantifiable values of manganese were evidenced, in any of its forms, in the Sinú River, and in the rainy season, this metal appeared in 43.7 % of the all samples analyzed. When detected, manganese concentrations fluctuated from 7×10^{-5} kg m^{-3} to 1×10^{-4} kg m^{-3}, exceeding the limit established by EPA (5×10^{-5} kg m^{-3}) for drinking water in all seasons except for samples from sites E1 and E7, which had values below the limit of quantification. Also, sampling sites E4, E5, and E15 revealed manganese concentrations of 1×10^{-4} kg m^{-3}, being at the threshold established by the current national regulation in Colombia (Resolution 2115 of 2007).

Manganese levels in the San Pedro River (in Mexico) ranged between 7×10^{-5} kg m^{-3} to 0.0065 kg m^{-3} in the dry season of 1997 and between 9×10^{-5} kg m^{-3} to 0.085 kg m^{-3} during the rainy season of the same year. In 1999, during the dry period, manganese concentrations ranged between 5×10^{-5} kg m^{-3} to 0.0041 kg m^{-3} and in the rainy season, between 2×10^{-5} kg m^{-3} to 0.006 23 kg m^{-3} (Gómez-Álvarez *et al.*, 2004). These findings parallel ours, in that higher manganese levels were observed during the rainy season. Moreover, Holguín et al. (2006) reported in the Cochos River (Mexico), within the first four months of monitoring, manganese concentrations ranging between 0.000 34 kg m^{-3} to 0.000 42 kg m^{-3}, which decreased in their last two samplings due to seasonal variation.

The observed mean concentration of manganese in the Sinú River was 8.5×10^{-5} kg m^{-3}, not exceeding the maximum allowed for agricultural use (0.0002 kg m^{-3}) according to the Colombian national decree 1594 of 1984. Since the department of Córdoba has a strong agricultural activity, the observed manganese levels in the Sinú River are likely due to these activities and to the discharge of wastewater into its stream (Zhou *et al.*, 2020).

3.3. Water quality indices

Heavy metals are well known for their impact on aquatic life and human health. That is why it is necessary to know their concentrations in water bodies and inform local government environmental policies. To this end, different water quality indices, including the HEI, HPI, Cd, and HMTLwere calculated in this study. These indices are indicative of HM contamination in the Sinú River.

3.3.1. Water Quality in the Sinú River

The obtained average quality indices (WQI) for the dry and rainy seasons in each of the stations monitored in the Sinú River are shown in 0.0002 kg m^{-3}tab:4. In the dry season water quality in all the study sites was classified as regular according to the standards established by Rojas (1991), except for sites E6 and E16, which were classified as acceptable.

Table 4. Water quality index values, according to Rojas (1991), for sites along the Sinú River by season.

Stations	Dry	Rainy	Classification
E1	67.7 ± 0.4	57.8 ± 0.4	R*
E2	70.1 ± 0.1	59.7 ± 0.4	R
E3	66.7 ± 0.4	59.0 ± 0.1	R
E4	68.3 ± 0.2	55.7 ± 0.4	R
E5	69.1 ± 0.1	58.4 ± 0.2	R
E6	70.0 ± 0.1	58.0 ± 0.1	R
E7	73.2 ± 0.1	53.3 ± 0.2	Ad**, Rr***
E8	68.7 ± 0.4	57.6 ± 0.4	R
E9	67.4 ± 0.2	56.5 ± 0.3	R
E10	69.6 ± 0.3	56.5 ± 0.3	R
E11	69.6 ± 0.3	58.1 ± 0.1	R
E12	67.4 ± 0.2	56.5 ± 0.3	R
E13	69.6 ± 0.3	56.4 ± 0.2	R
E14	67.3 ± 0.2	56.1 ± 0.1	R
E15	67.5 ± 0.3	59.8 ± 0.4	R
E16	71.5 ± 0.3	60.2 ± 0.1	Ad**, Rr***
Average	69.0 ± 0.1	57.5 ± 0.3	R

In the rainy season, the Sinú River, from site Santa Ana (E1) to its mouth in the Caribbean Sea, at site Tinajones (E16), showed a slight deterioration in the quality of its water with respect to the dry season; although in its classification, in general terms, the water quality category was the same for both periods. This water quality decrease was associated with an increase in turbidity, which was the parameter contributing the most to water quality according to the correlation test. Also, lower values were determined in the share of oxygen saturation of the rainy season compared to the dry season, which is consistent with the increase in CDO levels in most stations.

All determined water quality parameters revealed increased values during the rainy season, except for OD and pH, confirming water deterioration in this season. Even though parameter values in the rainy season were higher, this did not significantly contribute to shifting the water quality category.In general terms, the quality of the water of the Sinú River is regular; with indices obtained in the dry season being slightly better than in the rainy season.

In the Sinú River, water of the best quality was detected during the dry period at stations E2, E7, and E16 with WQI values of 70.1, 73.2, and 71.5, respectively, which were classified as acceptable in these stations. It is noteworthy that none of the indices obtained during the rainy season managed to change its classification as regular. This classification could be due to different factors such as livestock, agriculture, and mining, which exert a considerable influence on the department of Cordoba; however, studies are necessary to quantify this influence.

3.3.2. Heavy metal pollution in the Sinú River

The obtained values of the index of heavy metals (HEI) in the Sinú River allowed the assessment of water quality in terms of HMs (0.0002 $\mathrm{kg\,m^{-3}}$tab:5). These index values revealed high pollution in the Sinú River. Particularly during the rainy season, the HEI values surpassed 20. This finding agreed with obtained values for the degree of contamination (Cd), which are greater than 3, indicating high deterioration due to heavy metals in both seasons. Since the soils around the river contain abundant heavy metals and these can reach the river by run-off, this is a plausible explanation for the marked water pollution observed in the rainy season.

Table 5. Heavy metal index (HEI) and degree of pollution (Cd) values of the Sinú River

	Dry	**Rain**		**Dry**	**Rain**		**Dry**	**Rain**
Metal	M_i (kg/m3)	M_i (kg/m3)	MAC_i	M_i/MAC_i	M_i/MAC_i	S_i	$\mathcal{C}$	$\mathcal{C}$
Zn	$(5.8 \pm 0.4) \times 10^{-5}$	$(8.5 \pm 0.3) \times 10^{-5}$	0.005	0.0116 ± 0.0003	0.017 ± 0.003	0.005	-0.9884	-0.983
Fe	$(181.3 \pm 0.2) \times 10^{-5}$	$(442.4 \pm 0.2) \times 10^{-5}$	0.0002	9.0650 ± 0.0003	22.12 ± 0.01	0.0002	8.065	21.12
Mn	-	$(8.5 \pm 0.3) \times 10^{-5}$	5×10^{-5}	9.0766 ± 0.0003	1.7 ± 0.2	5×10^{-5}		0.70
HEI				18.0±0.1	24.0±0.1			
Cd							7.08	20.84

***MACi values taken from Siegel 2002**

As for the heavy metal pollution index (HPI; 0.0002 $\mathrm{kg\,m^{-3}}$tab:6), the average value of the metals investigated during the rainy season was considered because, during this season the highest concentrations of heavy metals were reported (0.0002 $\mathrm{kg\,m^{-3}}$tab:1), and this river is the year-round source of drinking water to the city of Montería, capital of the department of Córdoba, and surrounding municipalities.

The obtained HPI values (0.0002 $\mathrm{kg\,m^{-3}}$tab:6), and in light of the guidelines established by WHO (2017) for drinking water, revealed stark pollution by heavy metals in the Sinú River, indicating that its water is not suitable for human consumption without an adequate treatment to reduce its HMs content. According to national (Colombian) water quality standards, the obtained HPI for the Sinú River of 144.5, substantially exceeds the established threshold of 100. This fact indicates that there is a high risk of damage to human health caused by the current high concentrations of

Table 6. HPI (Rain) for MP in Sinú River. Taken from WHO (2017) for drinking water.

Metal	M_i **(kg/m3)**	S_i	I_i	Q_i	W_i **(k/Si)**	$W_i \cdot Q_i$
Zn	$(8.5 \pm 0.3) \times 10^{-6}$	0.005	0.003	145.8	0.0002	0.029
Fe	$(4424 \pm 2) \times 10^{-6}$	0.001	1x10-4	480.4	0.001	0.480
Mn	$(8.5 \pm 0.3) \times 10^{-5}$	0.001	0.002	−191.5	0.001	−0.192
Sum					**0.0022**	**0.318**
HPI	144.5					

heavy metals in this river (0.0002 kg m^{-3}tab:6). With this high HPI value, plans to reduce and control contamination by heavy metals must be considered, in addition to maintaining continuous monitoring of the surface waters of this important river in the Colombian department of Córdoba.

3.3.3. Toxicity load for heavymetals in the Sinú River

The HMTL index quantifies the pollutant load of a water body and emphasizes the need to remove heavy metals from the body of water to be safe for human use. HMTL also evaluates and warns on the content of heavy metal content in water that can be harmful to human health, informing better water resource management decisions. The obtained heavy metal toxicity loads in the Sinú River were 0.053 and 0.1329 during the dry and rainy seasons, respectively (0.0002 kg m^{-3}tab:7). The dry period revealed the lowest toxicity load due to heavy metals, while the highest levels occurred in the rainy period, with zinc boosting the highest pollutant load. However, none of the individually studied metals exceeded the permissible levels for human consumption except for iron.

Table 7. Toxicity load for heavy metals (HMTL) according to ATSDR (2019) in the Sinú River by season.

			M_i **(kg/m3)**			
Metal	dry	rain	HISi	HMTL(dry)	HMTL(rain)	HMTL permissible kg/m3
Zn	0.058 ± 0.004	0.074 ± 0.002	913	0.052 954	0.067 562	4.575
Fe	1.813 ± 0.001	4.611 ± 0.001	–	–	–	–
Mn		0.082 ± 0.001	797	–	0.065 354	0.798
sum				0.053	0.1329	5.373

Even though the Sinú River revealed pollution by heavy metals, in light of the obtained HMTL indices, the river is not an overly hazardous drinking water source, chiefly because zinc, manganese, and iron were the only quantifiable metals among all of the monitored metals, and iron, which accounts for the greatest pollutant load, is not classified in the NPL. This could explain why there is a high load of heavy metals in the Sinú River and yet it does not pose a risk to human health (0.0002 kg m^{-3}tab:7).

4. Conclusions

According to the WQI, the water of the Sinú River is rated as of regular quality on average; although, in some sampling sites during the dry season water quality improves, changing its quality degree to acceptable, with an WQI above 70.

In terms of water pollution due to heavy metals, the HMTL, Cd, HEI, and HPI indices show that there is contamination by heavy metals, due to detected high levels of iron, zinc, and manganese. Of these metals the one with the highest concentration levels was iron. Iron is not found in the NPL and zinc and manganese, individually, do not exceed the limits established in the Colombian Standard about sources of water for consumption. However, when studied as a whole the river presents pollution.

The obtained WQI values revealed a similar trend throughout the 16 monitoring stations and a regular quality level in the two seasonal periods. The lowest quality levels occurred during the rainy season. At the time of the study, no quantifiable levels of copper, chromium, cadmium, lead, nickel, and mercury were found. In contrast, quantifiable levels of iron, zinc, and manganese were found. However, in the case of manganese, its presence was only quantifiable in the rainy period. The authors recommend a permanent monitoring of the quality of their water to know the health of the water body.

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6. Conflict of interest

The authors declare that they have no conflict of interest in carrying out this study.

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Calidad del agua y niveles de metales pesados en el río Sinú, una fuente de agua potable en el Caribe colombiano

Resumen: El objetivo del presente trabajo fue evaluar la calidad del agua del río Sinú, en el nor-occidente de Colombia, en las épocas seca y lluviosa. El índice de calidad del agua (WQI), el índice de polución por metales pesados (HPI), el índice de evaluación de metales pesados (HEI), el grado de toxicidad por metales pesados (HMTL) y el grado de contaminación (Cd) fueron calculados a partir de análisis hechos a muestras de agua tomadas a largo de todo el río en 16 puntos de muestreo. Se llevaron a cabo muestreos integrales y en algunos casos puntuales, dependiendo de la morfología de la corriente. Se realizaron cinco muestreos en los períodos seco y de lluvias desde marzo del 2008 a abril del 2009. Todas las muestras fueron tomadas por triplicado en cada sitio de muestreo. Para la determinación de los metales en las muestras se empleó un espectrómetro de absorción atómica Thermo electron, modelo S4AA System. De los metales monitoreados sólo se encontraron niveles cuantificables de zinc, hierro y manganeso con concentraciones promedio de 8.5×10^{-5}, 0.004424 y 8.5×10^{-5} kg/m^3, respectivamente, en época de lluvias. En conjunto, los valores obtenidos de los índices (WQI = 63.5, HPI = 145, HEI = 24, HMTL = 0.1329 y Cd = 20.8), revelaron que existe contaminación por metales pesados en el río Sinú, aunque no se nota un nivel de toxicidad que afecte a la salud humana.

Palabras Clave: contaminación, espectroscopía, agua, hierro, zinc, manganeso, río Sinú.

Qualidade da água eníveis de metais pesados no rio Sinú, uma fonte de água potável no Caribe colombiano

Resumo: O objetivo deste trabalho foi avaliar a qualidade da água do rio Sinú em períodos-estacionais secos e chuvosos, levando em consideração o índice de qualidade da água (WQI), índice de poluição por metais pesados (HPI), índice de avaliação de metaispesados(HEI), carga tóxica por metais pesados (HMTL) e grau de contaminação (Cd).Uma amostragem abrangente e, em alguns casos, pontual foi utilizada de acordo com a morfologia da corrente. Foram realizadas cinco amostragens nos períodos seco e chuvoso, entre março de 2008 e abril de 2009. A área de estudo compreendeu dezesseis estações amostrais ao longo do rio.Todas as amostras foram coletadas em triplicata em cada um dos pontos de amostragem. Para a determinação dos metais, foi utilizado um espectrômetro de absorção atômica Thermo-electron, modelo S4AA System. Dos metais monitorados, apenas foram encontrados níveis quantificáveis de Zn, Fe e Mn com valores médios de 8,5x10-5, 0,004424 e 8,5x10-5kg/m3, respectivamente, na estação chuvosa. Os resultados mostram índices de HPI (145), HEI(24), Cd (20,8), WQI(63,5) e HMTL (0,1329). De acordo com os resultados, há contaminação por metais pesados no rio, porém, o nívelde toxicidade não afetaa saúde humana.

Palavras-chave: contaminação, espectrometria, água, ferro, zinco, manganês, rio Sinú.

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