

**ASSESSMENT OF METAL POLLUTION IN THE SEDIMENTS OF THE TUCUY,
MARACAS, AND CALENTURITAS RIVERS, CESAR DEPARTMENT, COLOMBIA**

José Mauricio Pérez Royero¹ , Luis Hernando Montoya²,

¹Ingeniera Ambiental y Sanitaria. Magíster en Ciencias Ambientales. Universidad Popular del Cesar. Valledupar, Colombia. Correo electrónico: joseperez@unicesar.edu.co

ORCID: <https://orcid.org/0009-0002-0555-8276>

² Profesor Universidad Popular del Cesar. Valledupar, Colombia.

Correo electrónico: luismontoya@unicesar.edu.co@unicesar.edu.co

ORCID: <https://orcid.org/0000-0002-4463-0077>

Abstract

The purpose of this study was to assess the concentration of the metals Al, As, Cd, Cr, Cu, Fe, Ni, Pb, and Zn in the bottom sediments of the Tucuy, Maracas, and Calenturitas rivers, which belong to the Calenturitas River Basin in the Department of Cesar, Colombia, during the rainy season (November 2017) and the dry season (March 2018). For this purpose, three sampling stations were established in each of the rivers. **Methods:** To evaluate the environmental contamination associated with the presence of the studied metals, five indices were used: enrichment factor (EF), pollution load index (PLI), potential ecological risk index, probability of adverse effects on biota (PELQ), comparisons with the TEC and PEC values, and the ecological risk management quotient (ERMQ). **Resultados y Conclusiones:** The results indicate that the studied water bodies are contaminated with metals, with the Tucuy River showing the least contamination. The Maracas and Calenturitas rivers exhibit moderate contamination, with enrichment levels of metals such as As, Cu, Cr, and Ni ranging from moderate to moderately severe. The Calenturitas River, in particular, requires a comprehensive water management plan for the recovery and protection of its watershed

Keywords: Pollution, metals, rivers, sediments

1. Introduction

Surface water sources are considered the driving force behind a country's social and economic development. However, their use and exploitation generate variability and environmental impacts that alter their condition and quality, mainly due to anthropogenic activities in river basins. The discharge of domestic, agricultural, and mining wastewater significantly affects the chemical and biological quality of water and sediments, negatively influencing the quality of life of nearby populations [1].

Sediment contamination by metals in water bodies is a critical issue, as elements such as Cd, Pb, and Ni possess accumulation and toxicity properties [2]. Likewise, metals such as As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn can cause severe health problems in human populations because

some of these substances tend to bioaccumulate and biomagnify within trophic networks, becoming persistent in ecosystems [3].

Furthermore, the interaction between water column flow and the riverbed determines the behavior of sediments and contaminants, resulting in a constant exchange of materials at different spatial and temporal scales. This process largely defines water quality, as fine sediments have a high capacity to adsorb metals. Parameters such as pH, redox conditions, the presence of Fe and Mn oxides and hydroxides, and variations in organic matter content influence the availability of solutes to be transferred from sediments to the water column [4].

The Tucuy, Maracas, and Calenturitas rivers supply water for domestic, livestock, and agricultural uses to the surrounding communities of the department, including the municipalities of Becerril, La Jagua de Ibirico, and El Paso, among others. Consequently, a methodology was implemented to obtain data on metal concentrations in sediments and establish their relationship with physical and chemical variables such as pH and electrical conductivity in water, organic matter, and total coliforms in the sediments of the analyzed water bodies.

Sediments were selected as the sampling unit because they act as temporal integrators of pollution [5], and their characteristics allow them to function as receptors of metals. Considering the granulometric characteristics and the high clay content of the sediment column—which confer a strong capacity to accumulate metals present in the water mass—sediments were chosen as the analytical matrix to determine metal concentrations.

This study provides a baseline for evaluating metal contamination in the bottom sediments of the Tucuy, Maracas, and Calenturitas rivers. The information obtained is of vital importance to environmental and governmental authorities within the jurisdiction, as it supports the development of environmental policies, control measures, management strategies, and action plans aimed at promoting environmental sustainability and protecting the health of populations in the area of influence.

2. Methodology

Study Area

The study area corresponds to the Calenturitas River basin, which encompasses the sub-basins of the Tucuy and Maracas rivers—hydrographic networks of cultural, economic, and environmental importance for the Cesar Department, Colombia. These rivers are valuable for their hydrobiological, faunal, and floristic richness, as well as for the presence of ancestral communities that enrich the region culturally, and for hosting significant coal and gas deposits.

The Calenturitas River has an approximate length of 32 km and is geographically located in the Cesar Department, on the western flank of the Serranía del Perijá, within the jurisdiction of the municipalities of Becerril, La Jagua de Ibirico, and El Paso, in the Department of Cesar, Colombia. The basin's altitude ranges from approximately 50 to 2200 meters above sea level, exhibiting climatic variation and ecological richness characteristic of the central zone of the Cesar Department.



Figure 1. General location map and sampling stations in the Tucuy, Maracas, and Calenturitas rivers.

Sampling Methods

Bottom sediment samples were collected during two climatic periods: the rainy season (November 2017) and the dry season (March 2018). Three sampling stations were established for each of the studied rivers, as shown in Figure 1. pH was measured using method 4500-H⁺, and electrical conductivity (EC) in the water column was determined according to method 2510 B (APHA et al., 2017a; APHA et al., 2017b). *In situ* measurements of pH and electrical conductivity were carried out using a YSI Pro-DSS multiparameter instrument, with three replicates taken every 30 minutes, following the Standard Methods guidelines (2510 B for conductivity and 4500-H⁺ for pH determination). Approximately 10 kg of sediment were collected along the main river channels using a sediment grab sampler at a depth of 10 cm. Samples were stored and transported in polyethylene bags for subsequent laboratory processing and analysis.

Laboratory Analysis

The granulometric analysis followed the Colombian standard I.N.V.E – 123 – 13 (Instituto Nacional de Vías, 2013). For this purpose, 2 kg of pretreated sample from each sampling point were sieved to obtain particles with a diameter equal to or smaller than 63 μm . The retained material in each sieve was weighed to determine the gravimetric composition of the sediments.

For sediment fractions smaller than 63 μm , the percentage of organic matter was determined using the loss-on-ignition method at 550 °C (*Standard Methods*), due to their high affinity with trace metals (Montoya, 2013). Total coliforms in sediments were determined using the defined substrate Colilert technique through the Most Probable Number (MPN) method [6].

Metal contents were determined by atomic absorption spectrophotometry (AAS) using air–acetylene flame for Fe, Ni, and Cr; acetylene–nitrous oxide flame for Al; and voltammetry for As, Pb, Cd, Cu, Cr, and Zn.

Data Processing

Calculation of Sediment Contamination Indicators

The enrichment factor (EF) evaluates the degree of natural or anthropogenic contamination by a metal (Ho et al., 2011). It is calculated according to Equation 1, as proposed by Simex and Helz (1981).

$$EF = \frac{(C_n/C_{Fe})_{Sample}}{(C_n/C_{Fe})_{Background}} \quad (1)$$

Where C_n is the content ($\mu\text{g g}^{-1}$) of element n , and C_{Fe} is the content of the normalization element. The background value for each metal was determined in an area recognized as non-impacted [7]. Table 1 presents the EF values as a means to assess the degree of contamination.

Aluminum (Al) was used as the reference element for normalization since its geochemistry is similar to that of many trace metals, and its natural content in sediments tends to be relatively uniform [8]–[9]. Background concentrations were taken from the sampling station located at the headwaters of the Maracas River, which recorded the lowest concentrations, indicating the least anthropogenic influence within the study region.

Table 1. Reference Enrichment Factor (EF) Values, Maracas River

Date	Sampling Point	Pb	Cd	As	Cu	Zn	Ni	Cr
Rainy Season (24/11/2017)	M.1. L	0,87	0,75	1,07	1,07	1,02	0,94	0,98
	M.2. L	1,57	0,33	1,61	1,08	1,81	1,02	0,99
	M.3. L	2,09	0,28	1,46	1,26	1,75	1,06	1,02
Dry Season (16/03/2018)	M.1. S	1,13	1,26	0,93	0,93	0,98	1,06	1,02
	M.2. S	2,37	1,72	1,60	1,28	3,19	1,14	1,26
	M. 3. S	4,97	0,88	2,49	1,49	3,29	2,32	2,04

Source: Author, 2019.

The Pollution Load Index (PLI) was used to evaluate the level of contamination by heavy metals [10]. It was calculated using Equations (2) and (3), where n is the number of metals, and CF is the contamination factor, determined as the ratio between the concentration of a metal at a sampling station and its background concentration [11].

$$PLI = (CF_1 * CF_2 \dots CF_n)^{1/n} \quad (2)$$

$$CF = \frac{(C_e)_{Sample}}{(C_e)_{Background}} \quad (3)$$

When $PLI > 1$, it indicates contamination; conversely, when $PLI < 1$, no contamination by metals is present.

The reference values for Threshold Effect Concentration (TEC) identify concentrations below which adverse effects on the environment are not expected. The Probable Effect Concentration (PEC) values indicate concentrations above which adverse biological effects are likely to occur [12].

Table 2. Reference TEC and PEC Values

Heavy Metal	TEC ($\mu\text{g g}^{-1}$)	PEC ($\mu\text{g g}^{-1}$)
Arsenic (As)	9,79	33
Cadmium (Cd)	0,99	4,98
Chromium (Cr)	43,4	111
Copper (Cu)	31,6	149
Lead (Pb)	35,8	128
Mercury (Hg)	0,18	1,06
Nickel (Ni)	22,7	48,6
Zinc (Zn)	121	459

Source: MacDonald, 2000.

The Potential Ecological Risk Index (RI) estimates the environmental damage caused by heavy metals in sediments, considering their toxicity and the environmental response to their presence. This method was proposed by the Swedish scientist Hakanson (1980), and its calculation is expressed by Equation (4):

$$RI = \sum E_i = \sum T_i F_i = \sum T_i \frac{C_i}{C_b} \quad (4)$$

Where E_i corresponds to the potential ecological risk coefficient for each heavy metal analyzed; T_i represents the toxic-response factor of each metal; and F_i is the contamination factor, calculated as the ratio between the concentration of the metal in the sediment sample (C_i) and the background reference value (C_b). The toxic-response factors (T_i) standardized by Hakanson [12] are shown in Table 3.

Table 3. Toxic-response factors T_i for heavy metals.

Heavy Metal	Ti Value
Cd	30
As	10
Pb	5
Cu	5

Ni	5
Cr	2
Zn	1

Source: [12]

According to Song et al. [14], the potential ecological risk coefficient (E_i) quantifies the potential hazard of each individual metal, allowing identification of those contributing most significantly to sediment contamination. The overall potential ecological risk index (R_i) reflects the cumulative effect of multiple heavy metals. Table 4 presents the classification of ecological risk levels according to the magnitude of E_i and R_i , indicating the quantitative degree of potential ecological hazards posed by heavy metals in sediments, based on their characteristics and environmental behavior.

Table 4. Classification of potential ecological risk of heavy metals

E_i	R_i	Contamination Level
<30	<50	Uncontaminated
30-60	50-100	Moderately contaminated
60-120	100-200	Heavily contaminated
120-240	>400	Strongly contaminated
>240	-	Extremely contaminated

Source: [14].

The ERMQ (Effect Range Median Quotient) and PELQ (Probable Effect Level Quotient) indices are used to evaluate sediment toxicity at different sampling points within a watershed, assessing the impact of anthropogenic contributions on the aquatic environment [15]-[10]. These indices provide an integrated measure capable of predicting the potential toxicity of sediments to aquatic life and are calculated using Equation (5):

$$ERMQ \text{ o } PELQ = \frac{\sum(C_i/ERM_i \text{ o } PEL_i)}{n} \quad (5)$$

Where C_i represents the concentration of element i in the sediment ($\mu\text{g g}^{-1}$), ERM_i and PEL_i are reference values ($\mu\text{g g}^{-1}$) for each metal, and n is the total number of metals considered. It should be noted that these indices only include reference values for Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn, as presented in Table 5.

Table 5. Reference values ($\mu\text{g g}^{-1}$) for ERM and PEL indices

Element	ERM (μgg^{-1})	PEL (μgg^{-1})
As	70	41.6
Cr	370	160
Ni	51.6	42.8
Cu	270	108
Zn	410	271
Ag	3.7	1.77
Cd	9.6	4.21
Hg	0.71	0.7
Pb	218	112

Source: [16].

Statistical Analysis

The data obtained were analyzed using SPSS software version 20.0. Pearson's correlation coefficients (R) were applied with a significance criterion of $p \leq 0.05$, and a Principal Component Analysis (PCA) was performed to establish the relationships between the concentrations of the studied metals and the measured environmental variables.

Discussion

The pH values of the water at the sampling points from the three studied rivers were predominantly alkaline (Table 6), ranging from 6.99 to 9.45 during the dry season and from 7.9 to 8.99 during the rainy season. These pH values tend to favor the insoluble forms of heavy metals in sediments [17].

Regarding electrical conductivity (EC), the analysis of the water sources revealed that the Calenturitas River exhibited the highest concentrations, with values ranging between 630 and 1120 $\mu\text{S cm}^{-1}$, being greater during the dry period. This behavior is associated with the lower dilution of contaminants due to decreased flow, which increases the concentration of salts and dissolved solids in the water column [18].

The organic matter content (%OM) ranged between 3.33% and 7.31% across all sampling points, with the highest values recorded in the Maracas River. This river showed a greater presence of decomposing vegetal material as a result of domestic wastewater discharges from the municipality of Becerril, which enhances the bioaccumulation and complexation capacity of sediments for the retention of trace heavy metals [10]. This finding is supported by Okoro et al. (2012), who stated that bioaccumulation and complexation are the main processes by which trace metals associate with organic materials such as living organisms and detrital matter.

In terms of total coliforms (TC), measured in the water bodies, values ranged between 390,000 (MPN g⁻¹) and 2,200,000 (MPN g⁻¹), with the highest concentration observed in the Maracas River. This condition is attributed to the discharge of effluents from the municipal wastewater treatment system of the urban area of Becerril (Cesar). Such discharges indicate a significant alteration and contamination of the water source by total coliforms, representing a potential health risk for local users.

Table 6. Results of pH and Electrical Conductivity (EC) in water, and Organic Matter content (%OM) and Total Coliforms (TC) in bottom sediments at the sampling stations of the river.

RIVER	SAMPLING STATION	PH	ELECTRICAL CONDUCTIVITY (μS CM ⁻¹)	ORGANIC MATTER (% OM)	TOTAL COLIFORMS (MPN G ⁻¹)
Rainy Season (24/11/2017)					
CALENTU RITAS	T.1.L.	8.91	138	6.03	390000
	T.2.L.	8.80	360	4.86	450000
	T.3.L.	8.47	611	3.33	590000
	M.1.L.	7.70	252	3.70	50000
	M.2.L.	7.90	258	4.79	900000
	M.3.L.	8.10	263	6.23	2200000
	C.1.L.	8.37	630	4.43	900000
	C.2.L.	8.44	644	5.22	1000000
	C.3.L.	7.90	604	7.27	1100000
Dry Season (16/03/2018)					
CALENTU RITAS	T.1.S.	9.45	125	6.38	270000
	T.2.S.	8.62	710	5.45	390000
	T.3.S.	8.80	533	4.73	740000
	M.1.S.	7.36	2100	4.93	110000
	M.2.S.	7.27	2400	3.88	200000
	M.3.S.	7.83	2224	7.31	500000
	C.1.S.	6.99	1190	4.81	1800000
	C.2.S.	7.00	154°	4.74	1400000
	C.3.S.	7.76	1120	5.54	1200000

The mean concentration values of the studied metals in the Tucuy, Maracas, and Calenturitas rivers during both climatic periods (bimodal) exhibit the same decreasing order: $Fe > Al > Zn > Cu > Ni > Cr > Pb > As > Cd$ (Table 7). The results for the Tucuy River reveal a decreasing trend in concentrations across the sampling stations ($T1 > T2 > T3$) for most metals during the rainy season, with the exception of Zn, which increases at station T2. In contrast, during the dry season, the concentrations of Cd, Pb, Cr, Cu, Al, and Fe increase, which may be associated with the lithological characteristics of the river's headwaters. These characteristics, through natural processes such as rock weathering and erosion of parent material, may contribute to the metal load in the sediments of the main channel of the Tucuy River [3].

Table 7. Concentrations of metals in sediments during the rainy and dry seasons.

RIVER	DATE	SAMPLING STATION	Cd (mg kg ⁻¹)	As (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Cr (mg kg ⁻¹)	Ni (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Al (g kg ⁻¹)	Fe (g kg ⁻¹)
TUCUY	Rainy Season (24/11/2017)	T.1.L.	0.38	6.05	10.53	20.24	29.78	34.68	160.69	7.48	25.80
		T.2.L.	0.05	4.86	7.76	11.51	27.80	34.09	241.51	5.21	19.07
		T.3.L.	0.04	3.64	4.79	10.55	15.18	20.69	88.72	3.99	16.61
	Dry Season (16/03/2018)	T.1.S.	0.81	3.68	12.27	16.07	22.54	34.93	134.96	8.23	28.11
		T.2.S.	0.04	4.06	7.67	13.37	25.52	33.42	155.80	6.06	21.01
		T.3.S.	0.04	4.97	10.12	12.60	18.70	27.71	137.47	6.02	19.29
	Rainy Season (24/11/2017)	M.1.L.	0.1	3.9	5.4	13.9	14.9	22.5	85.0	7.7	19.5
		M.2.L.	0.0	4.2	6.9	10.0	11.5	16.0	106.6	5.4	14.1
		M.3.L.	0.0	3.9	9.4	10.6	12.2	19.3	106.1	5.6	15.5
CALEMARACAS	Dry Season (16/03/2018)	M.1.S.	0.2	3.4	6.9	14.5	16.7	19.3	80.8	7.6	19.2
		M.2.S.	0.2	3.3	8.2	10.0	10.1	15.0	148.3	4.3	12.8
		M.3.S.	0.1	4.4	14.7	13.9	17.7	15.0	131.4	3.7	19.3
	Rainy Season	C.1.L.	0.09	4.52	10.64	13.94	22.21	45.02	142.70	2.12	20.29

Dry Season (16/03/20 18)	(24/11/20 17)	C.2.L.	0.1 0	6.4 9	7.83	16.6 0	23.0 8	34.8 4	190. 50	2.0 2	24.7 3
		C.3.L.	0.0 5	7.3 5	14.3 4	19.7 2	30.5 5	40.8 2	135. 41	4.9 1	31.7 8
		C.1.S.	0.0 4	5.4 3	7.34	14.6 0	18.7 2	31.1 7	140. 13	1.2 7	21.0 6
		C.2.S.	0.0 5	5.1 9	8.76	15.4 4	27.3 9	34.5 3	152. 93	1.8 2	22.6 9
		C.3.S.	0.0 5	5.6 2	13.8 8	17.0 1	23.2 2	25.6 7	141. 68	1.2 7	25.9 4

The concentrations of Cd showed a decreasing trend in the Tucuy River, from station T.1 to T.3, during both the rainy and dry seasons. However, they exceeded the permissible limit established by NOAA at point T.1.I (0.38 mg/kg), increasing its concentration during the dry season to 0.81 mg/kg. Only Cr, Ni, Cu, and Zn exceeded the permissible limits (PL) according to the NOAA Screening Quick Reference Table for Inorganics in Freshwater Sediment. For the studied water bodies during both climatic periods (Table 7), these limits were surpassed, with an overall increase in metal concentrations, which were higher during the dry season. This pattern agrees with the findings of Montoya [10], who stated that during the rainy season, the concentrations of trace metals in sediments tend to decrease because the increased river flow generated by rainfall promotes optimal conditions for greater resuspension of fine sediments ($< 63 \mu\text{m}$).

In the Calenturitas River, the highest metal concentrations were recorded during the rainy season, particularly for Cr, Pb, and Zn (Table 7). This behavior may be associated with increased precipitation, which enhances the transport of sediments and leachates from open-pit coal mining areas a phenomenon also reported in other studies conducted in mining-influenced basins of the Colombian Caribbean [19].

To determine the enrichment factor level, aluminum (Al) was used as the geochemical normalizing element, following the rationale proposed [8]-[9]. In the Tucuy River, Cd and Zn values showed moderate enrichment (EF between 3 and 5) at stations T.1.I and T.2.I during the rainy season (Table 8). This pattern suggests an anthropogenic contribution, possibly linked to agricultural activities and domestic discharges near the river channel, consistent with findings from previous studies on the dynamics of metals in surface sediments [7]-[19].

In the Maracas River, moderate enrichment of Pb and Zn was observed mainly at stations M.1.S and M.3.S during the dry season (Table 8). This increase may be related to agricultural inputs due to the use of agrochemicals in the area, as well as runoff from local anthropogenic activities. Similar results have been reported in other studies identifying elevated trace metal concentrations in rivers influenced by agricultural and mining activities [19]-[20]-[21].

Table 8. Enrichment factor in Tucuy River sediments during the rainy and dry seasons

RIVER	DATE	SAMPLING STATION	Pb	Cd	As	Cu	Zn	Ni	Cr
TUCUY	Rainy Season (24/11/2017)	T.1. L	1.75 1	2.31 8	1.68 5	1.69 7	1.98 4	1.92 8	1.46 0
		T. 2. L	1.85 4	0.40 8	1.94 6	2.39 9	4.28 8	2.58 7	1.19 4
		T.3. L	1.49 3	0.48 6	1.90 2	1.89 9	2.05 5	1.84 3	1.42 8
	Dry Season (16/03/2018)	T.1. S	1.85 6	4.51 5	0.93 3	1.55 5	1.51 6	1.32 7	1.05 5
		T.2. S	1.57 5	0.31 2	1.39 8	2.02 0	2.37 6	2.04 0	1.19 1
		T. 3. S	2.09 3	0.26 8	1.72 2	1.68 7	2.11 2	1.50 6	1.13 1
	Rainy Season (24/11/2017)	M.1. L	0.87	0.75	1.07	1.07	1.02	0.94	0.98
		M.2. L	1.57	0.33	1.61	1.08	1.81	1.02	0.99
		M.3. L	2.09	0.28	1.46	1.26	1.75	1.06	1.02
	Dry Season (16/03/2018)	M.1. S	1.13	1.26	0.93	0.93	0.98	1.06	1.02
		M.2. S	2.37	1.72	1.60	1.28	3.19	1.14	1.26
		M. 3. S	4.97	0.88	2.49	1.49	3.29	2.32	2.04
MARACAS	Rainy Season (24/11/2017)	C.1. L	6.24	1.89	4.44	7.77	6.22	5.07	3.55
		C.2. L	4.83	2.38	6.70	6.33	8.73	5.54	4.44
		C.3. L	3.64	0.51	3.12	3.05	2.55	3.02	2.17
	Dry Season (18/03/2018)	C.1. S	7.17	1.62	8.89	8.97	10.1 7	7.12	6.19
		C.2. S	6.00	1.20	5.95	6.96	7.78	7.31	4.59
		C.3. S	13.5 7	1.65	9.21	7.39	10.2 9	8.84	7.22
CALENTURITA									

In the Calenturitas River, the highest enrichment factor (EF) values for several metals were observed, particularly during the dry season (Table 8). During this period, 80.95% of the records exceeded a value of 3, indicating a moderately severe enrichment, while in the rainy season, 76.19% of the values corresponded to moderate enrichment. The sampling stations

C.3.S and C.2.S stood out, where Pb and Zn reached EF values above 6 and 7, respectively, classified as severe enrichment.

This pattern suggests that, in addition to local inputs associated with mining and agricultural activities, the sediments of the Calenturitas River may also be receiving additional loads from the Tucuy and Maracas rivers, which converge upstream. Similar results were reported by Doria et al. (2017) in the Ranchería River, where an increase in Cd and Zn was observed due to mining influence.

Table 9. Pollution Load Index (PLI).

RIVER	DATE	SAMPLING POINT	PLI
TUCUY	Rainy Season (24/11/2017)	T.1. L	1.773
		T.2. L	1.177
		T.3. L	0.761
	Dry Season (16/03/2018)	T.1. S	1.709
		T.2. S	1.065
		T.3. S	1.011
	Rainy Season (24/11/2017)	M.1. L	0.955
		M.2. L	0.761
		M.3. L	0.811
MARACAS	Dry Season (16/03/2018)	M.1. S	1.034
		M.2. S	0.943
		M.3. S	1.062
CALENTURITAS	Rainy Season (24/11/2017)	C. 1. L	1.282
		C. 2. L	1.373
		C. 3. L	1.445
	Dry Season (18/03/2018)	C. 1. S	1.055
		C. 2. S	1.186
		C. 3. S	1.196

The Tucuy and Calenturitas rivers (Table 9) show the highest values of the Pollution Load Index (PLI) in the headwater zones during both climatic periods, indicating heavy metal contamination in the sediments. This situation explains why the input of metals during the rainy season is significantly higher than initially expected, since, despite the lack of improved

granulometric conditions compared to the dry period, the retention of trace elements in sediments is greater, which may be associated with heavy metals bound to organic matter [10]. For the Maracas River, the PLI exceeds the threshold value of 1 during the dry season at stations M.1 and M.3, indicating that contamination levels may pose potential environmental risks.

Table 10. Comparison of TEC and PEC values with metal concentrations.

RIVE R	META L	TE C	PE C	Rainy 1	Rainy 2	Rainy 3	Dry 1	Dry 2	Dry 3
mg kg ⁻¹									
TUCUY	As	9.79	33	6.048*	4.858*	3.64*	3.682*	4.063*	4.968*
	Cd	0.99	4.9 8	0.376*	0.046*	0.042*	0.805*	0.041*	0.035*
	Cr	43.4	111	20.24*	11.51*	10.55*	16.07*	13.37*	12.6*
	Cu	31.6	149	34.68* *	34.09* *	20.69* *	34.93* *	33.42* *	27.71*
	Pb	35.8	128	10.534 *	7.756*	4.787*	12.267 *	7.672*	10.12*
	Ni	22.7	48. 6	29.78* *	27.80* *	15.18*	22.54*	25.52* *	18.70*
	Zn	121	459	160.69 **	241.51 **	88.72*	134.96 **	155.80 **	137.47 **
	As	9.79	33	3.94*	4.20*	3.92*	3.40*	3.30*	4.41*
	Cd	0.99	4.9 8	0.12*	0.04*	0.03*	0.21*	0.16*	0.07*
	Cr	43.4	111	13.92*	10.00*	10.60*	14.45*	10.00*	13.91*
	Cu	31.6	149	22.50*	16.00*	19.30*	19.32*	15.00*	15.00*
	Pb	35.8	128	5.39*	6.87*	9.44*	6.92*	8.17*	14.74*
CALENTURIT MARACAS AS	Ni	22.7	48. 6	14.94*	11.45*	12.23*	16.68*	10.09*	17.70*
	Zn	121	459	84.98*	106.59 *	106.13 *	80.77*	148.33 **	131.37 **
	As	9.79	33	4.52*	6.49*	7.35*	5.43*	5.19*	5.62*
	Cd	0.99	4.9 8	0.09*	0.10*	0.05*	0.04*	0.05*	0.05*
	Cr	43.4	111	13.94*	16.60*	19.72*	14.60*	15.44*	17.01*

Cu	31.6	149	45.02*	34.84*	40.82*	31.17*	34.52*	25.67*
			*	*	*		*	
Pb	35.8	128	10.64*	7.83*	14.34*	7.34*	8.76*	13.88*
Ni	22.7	48.6	22.21*	23.08*	30.55*	18.72*	27.39*	23.22*
				*	*		*	*
Zn	121	459	142.70	190.50	135.41	140.13	152.93	141.68
			**	**	**	**	**	**

* No adverse effects on the aquatic environment are expected.

** Some adverse effects on the aquatic environment may occur.

For the Tucuy River, the Cu concentrations at sampling stations T.1 and T.2 during both climatic periods, Zn at all sampling stations except T.3 during the rainy season, and Ni at stations T.1 and T.2 in the rainy season and T.2 in the dry season, exceeded the TEC values (Table 10). A similar condition was observed in the Maracas River, where Zn concentrations during the dry period at stations M.2 and M.3 surpassed the TEC threshold. In the Calenturitas River, Zn concentrations at all sampling stations during both rainy and dry seasons also exceeded the TEC values (Table 10). However, all water bodies remained below the PEC limits. These results suggest that some adverse effects on the aquatic environment may occur, although such effects are likely to be infrequent or limited.

Table 11. Potential Ecological Risk Index of the Recorded Metal Concentrations.

RIVER	SAMPLING POINT	Pb	Cd	As	Cu	Zn	Ni	Cr	RI
TUCUY	T.1. L – Rainy	8.6	68.0	16.5	8.3	1.9	9.4	2.9	115.5
	T. 2. L – Rainy	6.3	8.3	13.2	8.2	2.9	8.8	1.6	49.3
	T. 3. L – Rainy	3.9	7.6	9.9	4.9	1.1	4.8	1.5	33.7
	T.1. S – Dry	10.0	145.5	10.0	8.4	1.6	7.1	2.3	184.8
	T. 2. S – Dry	6.2	7.4	11.1	8.0	1.9	8.1	1.9	44.5
	T. 3. S – Dry	8.2	6.3	13.5	6.6	1.7	5.9	1.8	44.0

MARACAS	M.1. L - Rainy	-	4.4	22.6	10.7	5.4	1.0	4.7	2.0	50.8
	M.2. L - Rainy	-	5.6	6.9	11.4	3.8	1.3	3.6	1.4	34.1
	M.3. L - Rainy	-	7.7	6.2	10.7	4.6	1.3	3.9	1.5	35.8
	M.1. S - Dry		5.6	37.7	9.3	4.6	1.0	5.3	2.0	65.5
	M.2. S - Dry		6.6	29.0	9.0	3.6	1.8	3.2	1.4	54.5
	M.3. S - Dry		12.0	12.7	12.0	3.6	1.6	5.6	2.0	49.5
	C.1. L - Rainy		8.6	15.7	12.3	10.8	1.7	7.0	2.0	58.1
	C. 2. L - Rainy	-	6.4	18.8	17.7	8.3	2.3	7.3	2.3	63.1
	C. 3. L - Rainy	-	11.6	9.9	20.0	9.8	1.6	9.7	2.8	65.4
	C.1. S - Dry		6.0	8.1	14.8	7.5	1.7	5.9	2.1	45.9
	C. 2. S - Dry		7.1	8.6	14.1	8.3	1.8	8.7	2.2	50.7
	C. 3. S - Dry		11.3	8.2	15.3	6.1	1.7	7.3	2.4	52.4
			Uncontaminated	Moderately Contaminated		Heavily Contaminated		Very Heavily Contaminated		

Table 11 shows that Cd is the only metal exhibiting a contamination level according to the Potential Ecological Risk Index. The Tucuy River, at sampling point T1 during both climatic periods, and the Maracas River, at sampling point M1 during the dry period, exceeded the threshold value of 30 (Table 11).

Table 12. ERMQ and PELQ Toxicity Indices of the Recorded Metal Concentrations.

RIVER	DATE	SAMPLING POINT	PELQ	ERMQ
TUCUY		T. 1. L	0.295	0.189

CE	-	-	1										
	.671*	0.031											
	*												
CT	-	0.212	-	1									
	0.307		0.13										
			0										
As	0.020	0.429	-	0.37	1								
			0.23	1									
			0										
Cu	0.358	0.182	-	0.13	.591*	1							
			0.42	4	*								
			4										
Ni	0.319	0.418	-	0.00	.699*	.821*	1						
			0.26	4	*	*							
			0										
Cr	0.107	.532*	-	0.00	.737*	.598*	.756*	1					
			0.12	7	*	*	*						
			8										
Cd	0.457	0.257	-	-	0.11	0.21	0.33	.526*	1				
			0.27	0.33	0	8	4						
			6	1									
Pb	0.153	.808*	0.11	0.15	0.43	0.24	0.40	.537*	0.18	1			
		*	1	2	5	8	9		2				
Zn	0.308	0.151	-	0.02	0.45	.517*	.606*	0.18	0.09	0.17	1		
			0.10	4	1		*	2	2	6			
			2										
Fe	0.262	.569*	-	0.04	.714*	.700*	.807*	.920*	0.37	.583*	0.25	1	
			0.26	7	*	*	*	*	4		4		
			2										
Al	0.454	0.114	-	-	-	-	-	-	.488	-	-	-	1
			0.32	.576*	0.37	0.17	0.09	0.01	*	0.13	0.28	0.02	
			3		8	5	0	9		9	4	4	

CE = Electrical Conductivity; **MO** = Organic Matter Content (%); **CT** = Total Coliforms; **Pb** = Lead Concentration; **Cd** = Cadmium Concentration; **As** = Arsenic Concentration; **Cu** = Copper Concentration; **Zn** = Zinc Concentration; **Ni** = Nickel Concentration; **Cr** = Chromium Concentration; **Fe** = Iron Concentration; **Al** = Aluminum Concentration.

To understand the relationships among the different physicochemical parameters and the analyzed metals in the Tucuy, Maracas, and Calenturitas Rivers, a Pearson correlation analysis was applied (Table 13). This analysis allows the identification of associations that suggest possible common origins of contaminants and similar transport processes within the watershed. A strong positive correlation ($R > 0.70$; $p < 0.01$) was identified between Fe and other metals,

with Fe showing the highest number of associations—particularly with Cr (0.920), Ni (0.807), Cu (0.700), and As (0.714). Likewise, a strong positive correlation was observed between Ni and Cu (0.821), as well as with As (0.699). Cr exhibited significant correlations with Ni (0.737), As (0.737), and Cu (0.598). Finally, a strong positive relationship was observed between Pb and organic matter (0.808), indicating that this metal may be influenced by the presence of organic compounds in the sediment. These associations suggest a common origin of the metals, possibly related to lithological inputs and anthropogenic activities that affect the dynamics of the basin [10]-[22].

On the other hand, the low correlation between Fe and Cd ($R = 0.374$) and Fe and Zn ($R = 0.254$) indicates an external input source, distinct from the lithological background, for these two metals. If Fe is considered a geochemical normalizing metal, it should exhibit a consistent behavior in riverbed sediments; thus, the lack of association with Cd and Zn suggests a discrepancy in the behavior and distribution of these metals. According to ATSDR [20]-[21], high concentrations of these metals in sediments are typically associated with the use of fertilizers and pesticides.

Cr exhibited positive associations ($R > 0.5$; $p < 0.05$) with Cd (0.526) and Pb (0.537), indicating a potential shared source, although their total contributions may not originate from a single source. A moderate linear correlation ($R > 0.5$; $p < 0.05$) was also found between %OM and Cr (0.532), as well as with Fe (0.569), and a strong positive correlation ($R > 0.8$; $p < 0.01$) with Pb. Finally, no metals were correlated with total coliforms, pH, or electrical conductivity, suggesting that these variables do not influence the increase or decrease of metal concentrations, nor do they reflect environmental exposure linked to total coliform levels.

Principal Component Analysis

A Principal Component Analysis (PCA) was applied to the correlation matrix to reduce the dimensionality of the variable set, identify covariation structures among metals and physicochemical parameters, and distinguish possible sources (lithogenic vs. anthropogenic) and transport/retention processes in sediments. This approach is standard in environmental geochemistry to reveal patterns not evident in univariate analyses (Jolliffe, 2002; Shrestha & Kazama, 2007) and is consistent with previous applications in mining-influenced basins of the Colombian Caribbean [19].

Three principal components were extracted, explaining 72.65% of the total variance in the sampling points. The factorial plane I–II (Figure 2) contained the most relevant information, accounting for 59.89% of the total variance. On the positive axis of Factor I, which represents 40.16% of the total variance, metals such as Ni, Cu, Zn, and As exhibited a common trend, suggesting a shared anthropogenic origin likely associated with mining activities in the area. Additionally, although Al and EC appear close on the negative side of Factor I, their behavior indicates antagonism. Nevertheless, this proximity may reflect an equilibrium between dissolved ions in the water (increased ionic saturation) and a lower concentration of Al in sediments.

In Factor II, which explains 19.73% of the total variance, a clear association between %OM and Pb concentration in sediments was observed. This finding was corroborated by Montoya (2013), who, after performing speciation analyses in river sediments, found that some metals such as Cu, Ni, and especially Pb, show a strong affinity for the organic fraction of sediments. Similarly, Cr was associated with Fe, suggesting a potential common origin. According to Montoya [10], both metals presented more than 60% association with the lithogenic fraction in sediments from the Oka River in Spain. However, although these metals may exhibit a similar preliminary behavior, their origins (lithogenic or anthropogenic) could differ [10].

Factor III, representing 12.75% of the total variance, showed a strong negative association with electrical conductivity and a moderate one with Cd and Al (Figure 3).

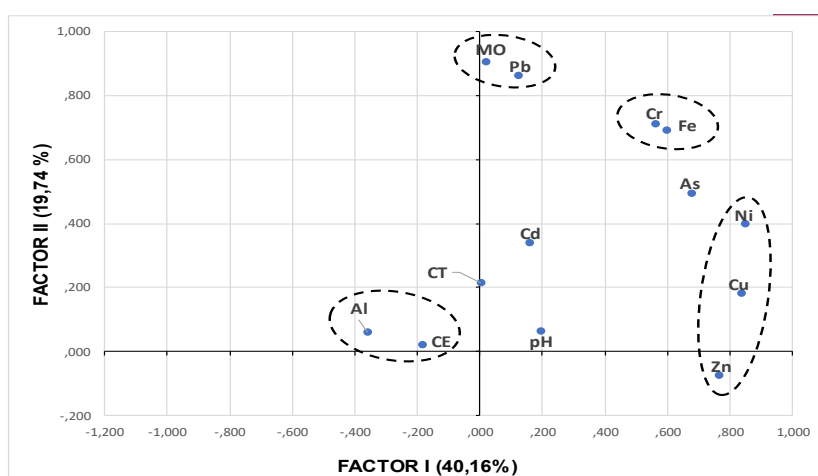


Figure 2. Principal Component Analysis based on the correlations between Factor I and Factor II.

Likewise, total coliforms (TC) and Zn are associated, which suggests that they may share a common origin. According to Moreno (2003), this is because both parameters naturally occur in the environment and may reach significant levels in aquatic systems due to discharges from animals and humans. Additionally, an antagonistic behavior between Zn and Al can be observed, which is related to the differentiated contribution of these metals from their parent rocks. This results from sediment formation processes derived from rocks of the Serranía del Perijá, where weathering, erosion, transport, and deposition processes associated with hydrodynamics lead to the redistribution of these metals [23].

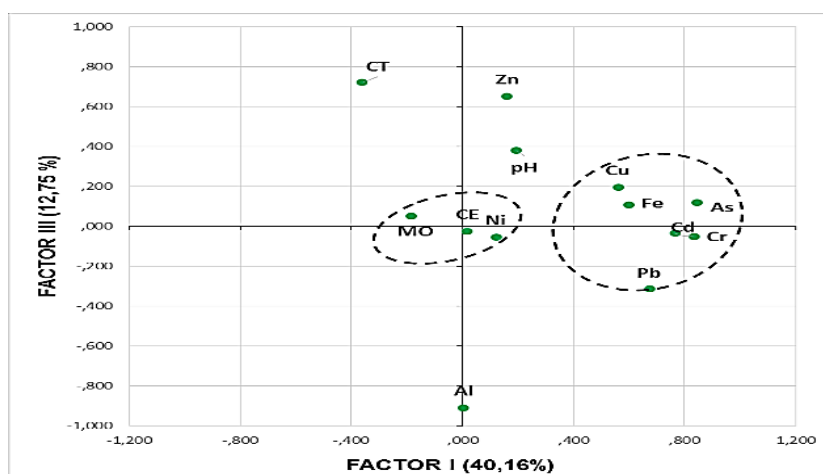


Figure 3. Principal Component Analysis based on the correlations between Factor I and Factor III.

The factorial planes I–III, which account for 52.91% of the variance in the dataset, corroborate the association between TC and Zn, confirming the findings of Moreno (2003), who indicated that the presence of these two substances is due to domestic and industrial wastewater discharges into water bodies, explaining their correlation.

Conclusions

This study assessed metal contamination in bottom sediments of the Tucuy, Maracas, and Calenturitas rivers under two hydrological regimes. All trace metals analyzed were detected, showing spatial and temporal heterogeneity, with higher concentrations in headwaters and during low-flow periods. The integrated assessment of the applied indicators confirms an overall scenario of low to moderate contamination, with localized hotspots requiring priority attention.

According to the TEC/PEC criteria applied, frequent exceedances of TEC values (mainly for Zn, Cu, and Ni) were observed without surpassing PEC thresholds, suggesting that the probability of adverse biological effects at the regional scale is low, and when present, it is punctual and associated with specific sampling stations and seasonal conditions. The enrichment factor (EF) revealed clear evidence of anthropogenic contributions superimposed on the geogenic background. Calenturitas showed the highest enrichment levels, with severe episodes for Pb and Zn during the dry period; Tucuy exhibited moderate enrichment of Cd and Zn in the headwaters; and Maracas displayed moderate enrichment of Pb and Zn at specific dry-season points. Consistently, the pollution load index (PLI) exceeded the reference threshold in the Tucuy headwaters and several Calenturitas sites, confirming a contaminated status on a composite scale.

The potential ecological risk (RI) was mainly influenced by Cd, which reached moderate to high categories in headwaters; therefore, this metal should be prioritized in monitoring and management actions. The composite toxicity indices (mPELQ and mERMQ) were within

ranges corresponding to low probabilities of adverse effects on biota, consistent with the absence of PEC exceedances and the localized nature of the sites with $PLI > 1$ and $EF > 3$.

The correlation and principal component analyses revealed two dominant controlling factors: (i) a lithogenic gradient explaining the co-variation of Fe with Cr, Ni, and Cu (and the proximity of As), and (ii) an organic retention mechanism linking the percentage of organic matter (%OM) with Pb. The weak association of Fe with Cd and Zn suggests non-lithogenic sources (land use, runoff, and wastewater discharges), whereas the higher %OM in certain stretches favors complexation/adsorption and retention of metals in sediments. Variations in pH and redox conditions could remobilize retained fractions, increasing their bioavailability.

References

- [1] Madera, A Y. (2014). Evaluación de la calidad del agua en algunos puntos afluentes del río Cesar (Colombia) utilizando macroinvertebrados acuáticos como bioindicadores de contaminación.
- [2] De La Cruz, N., Alderete, Á., & Laffón, S. (2013). Acumulación de metales pesados en sedimentos del ecosistema manglar en Laguna de Términos, Campeche, México. *Foresta Veracruzana*, 15(1), 25-30.
- [3] Herrera, J., Rodríguez, J., Coto, J., Salgado, V., y Borbón, H. (2013). Evaluación de metales pesados en los sedimentos superficiales del río Pirro. *Tecnología en Marcha*, 26 (1), 28-36.
- [4] Bidegain, JC y Jurado, S. (2011) Adsorción de contaminantes en sedimentos del Holoceno de la Región de la Plata. *Revista Ciencia y Tecnología de los materiales*. N° 1, pág. 75-84.
- [5] Lima Cazorla, Lázaro; Olivares-Rieumont, Susana; Columbie, Isaida; de la Rosa Mederos, Daniel; Gil Castillo, Reinaldo. (2005). Niveles de plomo, zinc, cadmio y cobre en el Río Almendares, Ciudad Habana, Cuba. *Revista Internacional de Contaminación Ambiental*. 21 (3). 115-124.
- [6] Almendros, G., Gonzales, F., González, J., Knicker, H., & de la Rosa, J. (2010). Protocolos y técnicas analíticas e instrumentales para evaluar el impacto del fuego sobre la materia orgánica del suelo. Valencia: Universitat de València, Càtedra Divulgación de la Ciencia.
- [7] Sakan, S., Dordević, D., Manojlović, D., & Predrag, P. (2009). Assessment of heavy metal pollutants accumulation in the Tisza river sediments. *Journal of Environmental Management*, 3382-3390.
- [8] Bhuiyan, M. A. H., Parvez, L., Islam, M. A., Dampare, S. B., & Suzuki, S. (2010). Heavy metal pollution of coal mine-affected agricultural soils in northern Bangladesh. *Journal of Hazardous Materials*, 173(1-3), 384-392. <https://doi.org/10.1016/j.jhazmat.2009.08.085>
- [9] Varol, M. (2011). Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. *Journal of Hazardous Materials*, 195, 355-364.

- [10] Montoya, L. (2013). Efectos de las crecidas en el transporte de material particulado y contaminantes asociados: aplicación al caso del río Oka (Urdaibai), País Vasco. Bilbao, España: Universidad del País Vasco-Euskal Herriko Unibertsitatea.
- [11] Yang, Z., Wang, Y., Shen, Z., Niu, J., & Tang, Z. (2009). Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China. *Journal of Hazardous Materials* 166, 1186-1194.
- [12] Mac Donald, Ingersoll, C., & Berger, T. (2000). Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *The Journal of Archives of Environment Contamination Toxicology*, 39, 20-31.
- [13] Hakanson, L. (1980). Ecological risk index for aquatic pollution control. A sedimentological approach. *The Journal of Water Research.*, 14, 975-1001
- [14] Song, J., Yang, X., Zhang, J., Long, Y., Zhang, Y., & T., Z. (2015). Assessing the Variability of Heavy Metal Concentrations in Liquid-Solid Two-Phase and Related Environmental Risks in the Weihe River of Shaanxi Province. *The International Journal Environmental Research Public Health*, 12, 8243-8262.
- [15] Leorri, E., Cearreta, A., Irabien, M., & Yusta, I. (2008). Geochemical and microfaunal proxies to assess environmental quality conditions during the recovery process of a heavily polluted estuary: The Bilbao estuary case (N. Spain). *Science of the Total Environment*, 12-27.
- [16] Violintzis, C., Arditoglou, A., & Voutsas, D. (2009). Elemental composition of suspended particulate matter and sediments in the coastal environment of Thermaikos Bay, Greece: Delineating the impact of inland waters and wastewaters. *Journal of Hazardous Materials*, 166, 1250-1260.
- [17] Reddy, KR y DeLaune, RD (2008) Biogeoquímica de los humedales: ciencia y aplicaciones. CRC Press, Boca Raton. <http://dx.doi.org/10.1201/9780203491454>
- [18] Ospina, O., Garcia, G., Gordillo, J., y Tovar, K. (2015). Evaluación de la turbiedad y la conductividad ocurrida en temporada seca y de lluvia en el río Combeima (Ibagué, Colombia). *Ingeniería Solidaria*, 12 (19), 19-36.
- [19] Doria, C., Gómez, J., & Marrugo, J. (2017). Metales en sedimento del río Ranchería, La Guajira. *Bistua: Revista de la Facultad de Ciencias Básicas*, 15(2), 64–68.
- [20] ATSDR. (2005). Toxicological profile for Nickel. Springfield: U.S Department of Health and Human Services, Agency for Toxic Substances and Disease Registry.
- [21] Larios, M. (2014). Niveles de Cd, Co, Cr, Cu, Ni, Pb, y Zn en los suelos de ribera de la cuenca del río Turia. Barcelona: Universidad de Lleida.
- [22] WAKIDA-KUSUNOKI, Armando T. y AMADOR-DEL ANGEL, Luis Enrique. Aspectos biológicos del pleco invasor *Pterygoplichthys pardalis* (Teleostei: Loricariidae) en el río Palizada, Campeche, México. *Rev. Mex. Biodiv.* [online]. 2011, vol.82, n.3 [citado 2025-11-03], pp.870-878. Disponible en: <http://www.scielo.org.mx/scielo.php?script=sci_arttext&pid=S1870-34532011000300013&lng=es&nrm=iso>. ISSN 2007-8706.
- [23] RESOLUCIÓN 520 DE 2007, [UPME]