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Research article

Assessment of water quality and emerging pollutants in two fish species from the mallorquin swamp in the Colombian Caribbean

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ABSTRACT

The Mallorquín Swamp, an important ecosystem in Atlántico, Colombian Caribbean, underwent environmental monitoring at eight points during rainy, transition, and dry seasons. This was to assess water quality, seasonal variation, and the bioaccumulation of metals, emerging pollutants, and organic compounds in the fish *Ariopsis canteri* and *Mugil incilis*. Water parameters were analyzed using descriptive statistics and multifactorial ANOVA with the Tukey HSD test for seasonal differences. Normality and variance of the fish results were verified, and differences between groups were evaluated using ANOVA or Kruskal-Walli's method when data transformation failed. Spearman correlation was used to relate the results. Water sampling revealed variations in temperature, dissolved oxygen, salinity, and nutrient levels. Significant differences in alkalinity and hardness were observed across seasons and sample points. The most probable number (MPN) levels of Total coliform and *E. coli* peaked near areas with domestic wastewater inputs, reaching $5.4x10^6$ and $4.0x10^6$ MPN, respectively, indicating potential microbiological contamination of water. Fish samples revealed high concentrations of persistent substances such as methylmercury, polycyclic aromatic hydrocarbons (PAHs), and emerging pollutants. Heavy metal analysis showed elevated iron levels (5.28 ± 0.657 mg/L), while emerging pollutants, including ibuprofen (218 μg/L) and naproxen (343.89 μg/L), exhibited high concentrations near human settlements. *Ariopsis canteri* showed higher bioconcentration tendencies for methylmercury (238.5 ± 100 μg/kg), and acenaphthene (7782 ± 4123.8 μg/kg), possibly influenced by its feeding habits and habitat preferences. In contrast, *Mugil incilis* exhibited higher bioaccumulation trends of PAH (2376.23 ± 599.63 μg/kg acenaphthene) and emerging pollutants like galaxolide (139.49 ± 34.98 μg/kg), possibly due to its mobility and exposure to various contaminants in their environment. These findings emphasize the need to monitor and manage aquatic ecosystems' health to mitigate anthropogenic influences on water quality and biodiversity. This research serves as a reference for global conservation efforts, emphasizing the need for comprehensive monitoring and regulatory frameworks to protect aquatic environments and ensure their sustainability for future generations.

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1. Introduction

Estuary ecosystems are of great ecological importance, providing habitats and breeding grounds for numerous species adapted to freshwater and saltwater conditions [1]. These ecosystems also provide vital human services, such as water filtration, flood protection, fisheries, and recreation [2,3]. However, increasing pollution from wastewater and human settlements has led to biodiversity loss and the degradation of these critical environments [2,4].

Among the pollutants of growing concern are emerging pollutants (EPs) such as Naproxen (NAP), Ibuprofen (IBU), Caffeine (CAF), Galaxolide (GAL), Tonalide (TON), Methyl dihydrojasmonate (MDHJ), and Bisphenol A (BPA). These substances persist in the environment and have the potential to bioaccumulate in fish and other aquatic organisms, posing risks to both ecosystems and human health [5,6]. The extensive and often indiscriminate use of pharmaceuticals and personal care products has led to increased concentrations of these contaminants in surface waters, groundwater, and wastewater, where they have been shown to cause adverse effects on aquatic life [7–10].

Monitoring water quality and its relationship with geographic variables and seasonal changes is essential for conserving estuaries [11]. However, the presence of EPs in water bodies represents a significant challenge, mainly due to the limited understanding of their long-term behavior and the lack of effective strategies to mitigate their environmental impact [12]. For instance, over-the-counter drugs, such as IBU, NAP, and CAF, have been detected in water bodies worldwide. Concentrations as high as 1.42 μg/L of IBU have been reported in the Pearl River Delta, China [13], NAP levels up to 21,285 μg/L in corrégo da Onça, Brazil [14], and 52.22 μg/L of CAF in Chumbao River, Perú [15]. Similarly, MDHJ, GAL, TON, and BPA, have been identified in rivers, lakes, and oceanic ecosystems across continents, with concentrations ranging from 5.89 μg/L to 488 ng/L [16–19]. EPs have been detected in fish tissues, with Ojemaye and Petrik [20], and Pico et al. [21] reporting levels of up to 28.55 ng/g of CAF and 224 ng/g of BPA, respectively.

These contaminants pose significant risks. For example, TON and GAL are toxic to aquatic organisms and have been linked to human neurological damage. BPA disrupts endocrine function, causing feminization in male species, congenital disabilities, and developmental delays. IBU and NAP increase the risk of gastrointestinal ulcers, kidney damage, and gill alterations in fish species [22]. Moreover, the lack of comprehensive regulations for managing these pollutants exacerbates sustainable water resource management challenges.

While several studies have been conducted on EPs in Colombian water bodies, research on bioaccumulation in fish is scarce, especially in regions like the Caribbean. Despite significant pollution concerns on the Caribbean coast waters, most studies have

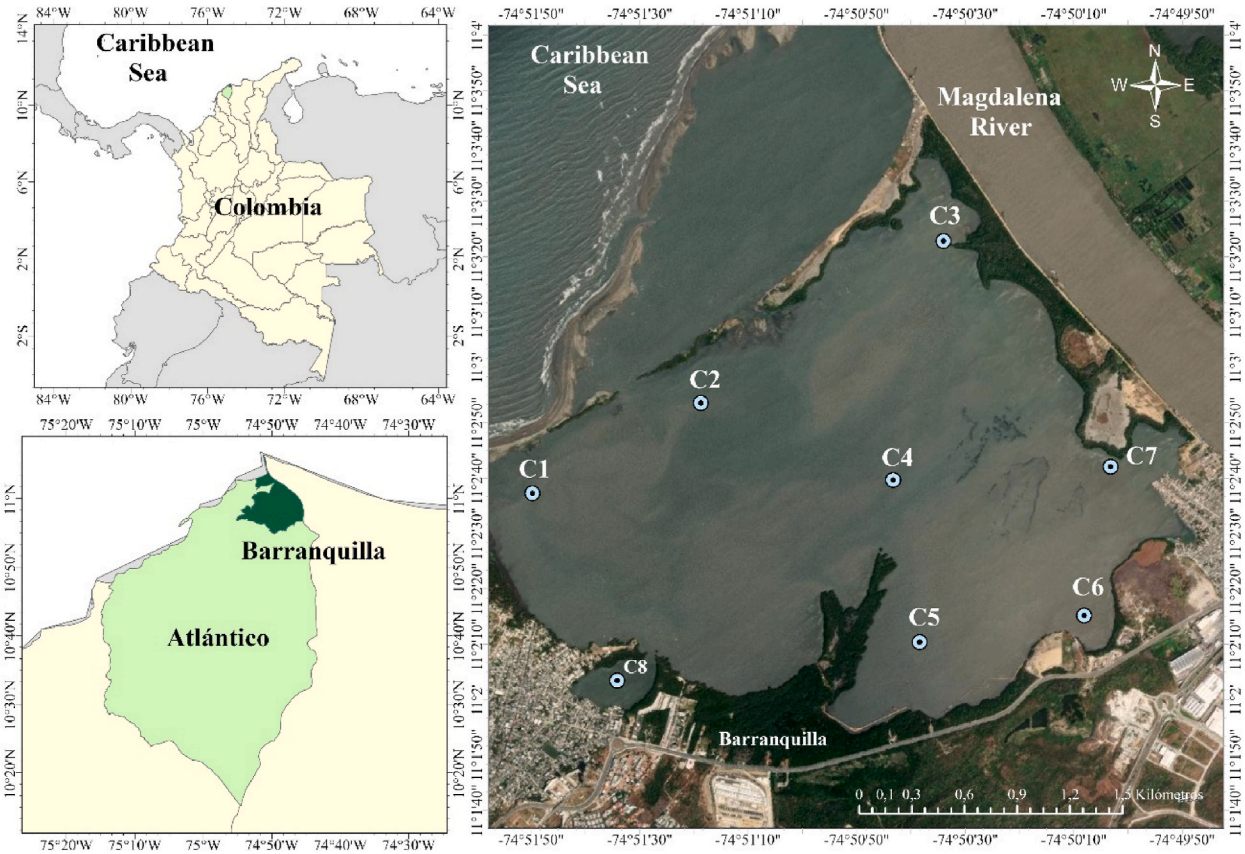

Fig. 1. Monitored points at the Mallorquin Swamp in Colombia.

focused on the Andean region. For example, IBU has been detected in the La Fe (LF) and Río Grande (RG) reservoirs in Antioquia [23], and in the estuarine and coastal areas of the Gulf of Morrosquillo, Córdoba, with concentrations ranging from 0.067 to 1.092 μg/L [24,25]. During the rainy season in the Gulf of Urabá, IBU concentrations ranged from 0.12 to 0.46 μg/L, while CAF levels were reported between 0.080 and 0.944 μg/L [25]. Additionally, NAP and IBU have been recorded at levels between 0.047 and 10.21 μg/L in the surface waters of Córdoba [26]. Despite these findings, bioaccumulation of EPs in fish muscle has not been consistently detected, as evidenced by Aristizabal-Ciro et al. [23] in a study of reservoirs in the Department of Antioquia.

The Mallorquin Swamp, located in Atlántico, Colombia, is a vital ecological area providing habitat for a wide variety of flora and fauna [27]. Unfortunately, this swamp has suffered from increasing pollution due to human settlements and industrial activities. This problem becomes even more complex because the inhabitants of the nearby areas use the swamp to supply fish for consumption and, therefore have not only been exposed to the different contaminants in the body of water but also to the loss of fish species in the area [27,28].

Potentially toxic elements (PTEs) pollution of estuarine ecosystems is a pressing environmental and public health issue, especially in areas where local communities rely on fish consumption. While there is evidence of EPs contamination in different regions, there is a significant lack of knowledge about how these pollutants accumulate in fish species, particularly in the Caribbean region of Colombia. The absence of data on the presence and impact of EPs in the living organisms of the Mallorquín Swamp is impeding the development of effective conservation and mitigation strategies.

This research aims to address this gap by evaluating water quality, and the bioaccumulation of metals, EPs, and organic contaminants in the muscle tissue of two species: *Ariopsis canteri* and *Mugil incilis*. This study will provide the first comprehensive assessment of these contaminants in the fish of the Mallorquín Swamp, offering critical insights into their persistence, environmental impact, and potential risks to ecosystems, biodiversity, and human health. Additionally, this research will contribute to developing targeted mitigation strategies, providing valuable data for the environmental sciences and pollution control efforts.

2. Materials and methods

2.1. Study area

The Mallorquín Swamp, located in the northernmost part of the Atlántico department, Colombia (Fig. 1), is situated at coordinates 11°02′47.8″ N, 74°50′52.9″ W. Its boundaries include the Caribbean Sea to the north, the Circunvalar highway to the south, the Magdalena River to the east (connected through two artificial tubes), and the mouth of the Arroyo León stream to the west. In addition, it is in the northern part of the city of Barranquilla, in an area consisting mainly of mangrove forests and tropical dry forests, which provide protection to the town from strong winds and are a source of different native fish species such as *Mugil incilis*, *Cetengraulis edentulus*, *Diapterus rhombeus*, *Eugerres plumieri* and *Ariopsis canteri* [27,28].

The approximate extension of the Mallorquín Swamp is 650 ha; its depth fluctuates between 0.3 m and 1.5 m [29]. Its salinity and surface water temperature vary from 20 to 32 and 24 °C to 30 C, respectively [27,28]. Due to its location, this body of water is exposed to different sources of contamination, such as the mouth of the León stream, the border area with the Caribbean Sea and the Magdalena River, the interaction with the surrounding populations such as the Flora, the beach, inhabitants of stilt houses settled on the banks of the body of water, companies and the influence of the mangrove area and plant species on the quality of the resource [29,30]. According to the above, eight (8) sampling stations were established in this research (Fig. 1, Table 1). This selection was made by taking reference studies previously carried out in the area and including strategic points that receive contributions from the different sources of contamination mentioned.

2.2. Water sampling

Water samples were collected at the eight monitoring points indicated in Fig. 1 and Table 1. Integrated samples were taken at three depths: approximately 20 cm from the bottom, the middle of the water column, and 10 cm from the surface of the Mallorquín swamp. Each water sample was tested for temperature (T), pH, dissolved oxygen (DO), total dissolved solids (TDS), conductivity, and salinity using a Hach HQ40D portable multimeter.

Sampling campaigns were performed in three different seasons: rainy (September–October 2022), transition (November–December 2022), and dry (January–February 2023) to observe the impact of environmental conditions on water quality. The water samples were

Table 1
Summary of the anthropogenic influences in each monitored site.

Site	Anthropogenic influence	coordinates
C1	León stream entrance	11°02′38.0"N 74°51′50.9"W
C2	Caribbean Sea entrance	11°02′54.6"N 74°51′19.7"W
C3	Magdalena River and Caribbean Sea entrance	11°03′23.5"N 74°50′34.1"W
C4	mixing zone	11°02′40.6"N 74°50′44.8"W
C5	Near Industries	11°02′10.1"N 74°50′38.0"W
C6	Near Former landfill, near a concrete plant	11°02′15.8"N 74°50′08.3"W
C7	Near stilt houses	11°02′42.9"N 74°50′03.6"W
C8	Surrounded by houses without sewage system	11° 2′3.50"N 74°51′34.10"W

preserved and analyzed following the methodologies outlined in the Standard Methods (SM) for the Examination of Water and Wastewater, 23rd Edition [31].

SM: 2130B determined Turbidity, acidity, and alkalinity. TDS by gravimetry SM: 2540D; hardness was estimated by volumetric titration SM: 2340C; biological oxygen demand (BOD_5) was measured using a membrane electrode system SM: 5210B and Chemical Oxygen Demand (COD) was calculated by titration SM: 5220C. SM: 4500B determined Nitrates (NO_3^-) and nitrites (NO_2^-) using ultraviolet spectrophotometric screening and colorimetric methods. Total nitrogen (N_T) was analyzed by the Macro-Kjeldahl method and ammonium (NH_4^+) was determined using the titrimetric Method, both using SM: 4500B. SM: 4500-P D averaged total phosphorus (P_T) by the stannous chloride method. Chlorides (Cl^-) were measured using the argentometric method SM: 4500B. Total Coliform and *Escherichia coli* were estimated using the fermentation technique using the most probable number table (MPN) by Colombian Technical Standard, NTC 4939.

Total phenols were extracted with chloroform as solvent by SM: 5530C and determined by spectrophotometry. Heavy metals were measured with Atomic Absorption Spectrometry SM: 3111B, in the case of Fe, Air Acetylene was used; for Cr and Cd, the electrothermal method was used. To determine EPs such as IBU, NAP, MDHJ, GAL, TON, and BPA, water samples were initially filtered through a 7-μm pore. Extraction was performed in Supel-Select HLB cartridges (60 mg/3 mL) or C18 cartridges at a 2 mL/min rate. The cartridges were allowed to dry, and then the retained analytes were eluted with 3 fractions of 2 mL of ethyl acetate: acetone (50:50) each, then carried to a stream of nitrogen until dry. Derivatization was then performed by adding 15 μL of BSTFA +1 % TMCS and 15 μL of pyridine to the vial containing 100 μL of the reconstituted residue. The vials were closed and shaken. The derivatization reaction was performed at 65 °C for 20 min, then the vials were filled to 1 mL. The samples were allowed to cool to room temperature for subsequent analysis by gas chromatography coupled to mass, GC-MS. This methodology was adapted from the study by Arrubla et al. [32].

To quantify PAHs, including naphthalene, acenaphthylene (ACTHYL), acenaphthene (ACTHE), fluorene, phenanthrene, anthracene, fluoranthene (FLUO), pyrene (PYR), benzo(a)anthracene, chrysene and indene (1,2,3-cd)Pyrene), water samples were stored at 4 °C and sent to the laboratory. Solid-phase extraction (SPE) was performed using an RP-18 column, preconditioned with 2.5 mL of methanol and 5 mL of 5 % NaCl. The extraction process was conducted under vacuum at a constant pressure of −0.8 atm. The column was then dried at 70 °C for 1 h, and the retained compounds were eluted with 1.5 mL of hexane. The eluent was then concentrated to 1 mL using a cold nitrogen evaporation technique. Quantification of analytes was carried out via gas chromatography-mass spectrometry (GC-MS) equipped with a flame ionization detector (FID), following EPA methods 3510 C and 8100 [33–35].

All analyses on water and fish samples were carried out in the Water and Food Analysis Laboratory of the Universidad Tecnológica de Pereira, which has methodologies accredited by the Institute of Hydrology, Meteorology and Environmental Studies (IDEAM) of Colombia.

2.3. Fish sampling

In January 2023, *Mugil incilis* and *Ariopsis canteris* were collected from the Mallorquin swamp. These were carried out during the dry season when the highest presence of fish, particularly the endemic species *M. incilis*, has been reported in the swamp [36]. The fish were caught using a net along the length of the swamp at the water monitoring points. In total, 15 individuals from each species were analyzed. After capture, taxonomic identification of the species was carried out, and the size and weight of the specimens were taken. The viscera were then removed, and the rest of the bodies were stored individually in plastic bags with ice. Dissection was carried out in the laboratory to take muscle samples [37], which were used for analytical measurements to detect EPs, PAHs, methyl mercury (MMER), and heavy metals.

To quantify EPs and PAHs, 0.5 g of homogenized fish tissue was placed in a glass mortar and mixed with 2.5 g of florisil and 1.5 g of anhydrous sodium sulfate for 3 min. The mixture was transferred to a 6 mL SPE column packed with polypropylene fiber and an absorbent layer consisting of 0.8 g of anhydrous sodium sulfate and 0.5 g of C18. A second polypropylene fiber was added to the top of the column to complete the setup. The analytes were eluted with acetonitrile in a 24-place SPE vacuum manifold, maintaining a flow rate of approximately 0.5 mL/min until 5 mL of eluent was collected. The eluent was then concentrated under a nitrogen stream at 28 °C. The resulting residue was dissolved in 0.5 mL of acetonitrile and passed through a 0.22 μm filer. Derivatization was performed following the procedure previously described for water samples.

Finally, after the solid-phase extraction the EPs as IBU, NAP, MDHJ, GAL, TON, and BPA, as well as PAHs such as naphthalene, ACTHYL, acenaphthene ACTHE, fluorene, phenanthrene, anthracene, FLUO, PYR, benzo(a)anthracene, chrysene and indene (1,2,3-cd)Pyrene), were quantified by GC-MS as outlined by Xiao et al., [38].

Groundfish tissue was subjected to an acid solution with a Berghof microwave digestion system to quantify heavy metals. Analysis was then carried out by atomic absorption spectrometry. Ni, Pb, Cr, and Cd were analyzed by the electrothermal method; a continuous hydride generator was used. For Zn, Ag, and Cu the direct flame method with air-acetylene was used. For total Hg cold steam was used. MMER was quantified with a DMA-80 mercury analyzer according to method 7473, EPA.

2.4. Statistical analysis

Water parameters were analyzed using descriptive statistics for the three seasons (rainy, transition, and dry). The mean, standard deviation, minimum, and maximum were determined for each case. In addition, a multifactorial ANOVA was performed to relate the variables and establish significant differences between seasons and sampling points, followed by the Tukey HSD post hoc test. All these

analyses were made using Statgraphics XVI-II software.

Fish analysis was conducted using SigmaPlot v. 12.5 software. Results were reported as mean ± standard deviation (SD). Normality and homogeneity of variance were verified using the Shapiro-Wilk and Brown-Forsythe tests, respectively [39,40]. Statistical differences between means for the different groups were assessed using analysis of variance ANOVA, followed by Dunnett's test. When transformation failed, the Kruskal-Wallis's test was applied to the untransformed data as appropriate. Spearman correlations were performed for the parameters within each fish species. In all cases, p values < 0.05 indicate correlations significantly different from zero, with a confidence level of 95.0 %.

3. Results and discussion

3.1. Mallorquin water

Table 2 shows the physicochemical parameters measured across the three seasons. During the rainy season, the temperature of swamp Mallorquín was higher than the other seasons (mean: 30.8 °C) (Table 2), probably due to the increase in the contribution of rainwater and wastewater. In the transitional and dry seasons, water temperature decreased (mean: 27.9 °C) due to the intensification of wave action caused by intense winds (>8 m/s) in December and January [41], Temperature behavior agrees with the results found by Fernandez-Maestre et al. [42], which are expected in coastal waters. When comparing monitoring points, no significant changes in temperature were found (Table S1).

pH levels ranged between 7.91 and 8.05 across the three seasons, indicating slightly basic water. However, no significant differences were observed in pH across the three seasons. However, when comparing between sampling points, a significant increase was evident at point C8. (Table 2 y Table S1). DO (Table 2) remained at favorable levels for aquatic biota (>5 mg/L) [43] and showed significant differences at various swamp points, being higher at C7 and C8 with oxygen saturations above 100 % (Table 2 y S1). These points are located near stilt houses and urban settlements without sewage systems, suggesting eutrophication and elevated oxygen levels due to algal presence [44,45].

Salinity, on the other hand, exhibited very high values during transition (mean: 53.8 %) and dry seasons (mean: 51.9 %) (Table 2). This could be attributed to increased seawater influx from the Caribbean Sea, potentially leading to a shift in the estuarine ecosystem balance. Conductivity followed a similar trend to salinity, with averages ranging between 20.9 and 33.5 mS/cm (Table 2). No significant statistical changes are evident when comparing these parameters between monitoring points (Table S1). This trend in low conductivity is like those found in Cartagena Bay (24.2–38.4 mS/cm) [42] due to the freshwater input, in this case, León stream.

Alkalinity showed significant differences between stations (Table 2) but not between sampled points (Table S1), and a trend was observed in hardness across different seasons. Overall, it can be stated that the measured alkalinity values in the Mallorquín swamp were elevated during the dry and transitional seasons compared to the rainy season. This trend might be linked to the pH dynamics within the ecosystem. In the context of the Mallorquín swamp, the hardness parameter is related to the calcium and magnesium salt content. It is highly expected that its concentration will rise during the dry and transitional seasons due to reduced water availability resulting from evapotranspiration phenomena in the hydrological system, as documented by Colina & Luna, [46].

During the transitional period, higher concentrations of chlorides were recorded at points C2, C3, and C4 (Table 2 y S1). In the rainy season, chloride concentrations were lower than those in the dry and transitional periods (Table 2). In the current study, chloride ranges were quantified from 1004.5 mg Cl^-/L to 51193 mg Cl^-/L, it is important to highlight that the measured concentrations of this ion are high due to the exchange of water between the Mallorquín swamp and the Caribbean Sea, which can be correlated with the salinity values presented in this study. The quantified concentrations of sulfates followed a similar trend to that of hardness and chlorides, exhibiting higher values during the dry and transitional seasons.

The TDS concentration between stations (Table 2) in the swamp remained relatively stable between the rainy and transitional seasons. Still, it increased during the dry season, reaching maximum values at point C6 (321 mg/L), which showed a significant increase compared to the other sampling points (Table S1). The total range measured for TDS during all three seasons at all points fell between 14 and 321 mg/L. When comparing the results with the regulations issued by the local environmental authority (Establishment Public Environmental Barranquilla Verde), specifically Resolution 851 of 2020 [47], it was found that the results are above the quality reference value < 20 mg/L.

According to Conagua [48], SST levels are classified as follows: excellent (<25 mg/L), good quality (25–75 mg/L), acceptable (75–150 mg/L), contaminated (150–400 mg/L), and highly contaminated (>400 mg/L). The average values fall within the acceptable range during the rainy and transition seasons, while they reach the contaminated category during the dry season, where the highest levels are observed. This trend can be explained by the lower water levels during the dry season, resulting from reduced rainfall and diminished contributions from streams and runoff. The decreased water volume concentrates suspended solids, leading to higher particle density. Additionally, anthropogenic activities such as agriculture, construction, and deforestation intensify during the dry season, further increasing sediment and particle input into the swamp.

On the other hand, when comparing the TDS levels at the different sampling points (Table S1), point C6 presented a higher average (162.33 mg/L). This can be related to an industrial concrete plant near the sampling site, which can be a potential source of particles.

Regarding nutrients, nitrates and nitrites did not exhibit significant differences across the sampled seasons or points. Nitrite levels remained consistently low, below 0.41 mg/L. However, an atypically high value of 53.1 mg/L for nitrates was observed at point C8 (Table 2), which also presented the highest average value compared to the other monitored locations (Table S1). This point is enclosed, showing elevated eutrophication levels and algae presence. As previously acknowledged, these algae could elevate DO levels and oxygen saturation to the point of causing an increase in nitrification reactions with the ammonia from domestic wastewater [44,45].

Table 2
Summary of statistical parameters of water variables measured in Mallorquín Swamp during the rainy, transition, and dry seasons.

Season	*Rainy*				*Transition*				*Dry*			
Variable	***Mean***	***SD***	***Minimum***	***Maximum***	***Mean***	***SD***	***Minimum***	***Maximum***	***Mean***	***SD***	***Minimum***	***Maximum***
T, °C	30.8	1.54	27.8	32.3	27.9	1.32	26.3	30.6	27.9	1.71	25.9	30.6
DO, mg/L	7.37	2.29	5.29	12.6	8.09	0.616	7.25	8.79	8.82	2.15	7.37	13.5
OS, %	104	33.5	74.4	179	104	8.44	91	113	114	31.8	94.9	182
pH	7.95	0.337	7.56	8.6	7.91	0.107	7.75	8.02	8.05	0.132	7.87	8.26
Salinity, %	33.2	1.98	30.6	35.6	53.8	2.3	50.6	56.4	51.9	2.51	47.2	55
Conductivity, mS/cm	20.9	6.88	16.8	37.8	33.5	1.32	31.5	35.1	24.2	4.51	21.8	35.3
Turbidity, NTU	37.7	25.6	11.3	91.4	21.2	17.5	1.31	50.6	124	209	18.9	638
Total Acidity mg/L	7.5	2.41	4	10.8	33.5	18.4	13.7	59.5	6.89	2.78	2.1	10.8
Alkalinity, mg/L	98.1	10.9	90	122	130	8.03	121	142	125	5.34	117	132
Total Hardness, mg/L	3900	403	3220	4530	8480	1870	7400	13000	6930	352	6380	7270
BOD_5 mg/L	22	3.16	18	25	6.5	3.3	2	13	6.33	3.79	2	9
COD mg/L	61	100	7	307	69.1	15	50	102	43.6	14.9	18	71
TDS, mg/L	104	28.9	54	148	87.9	13.4	74	115	176	73.4	105	321
Nitrates, mg/L	1.73	0.568	1.01	2.71	8.96	17.9	1.82	53.1	2.23	0.566	1.08	3.02
Nitrites, mg/L	0.0443	0.0288	0.01	0.09	0.174	0.084	0.04	0.3	0.194	0.119	0.05	0.41
Total Nitrogen, mg/L	5.72	2.21	2.9	9.35	4.8	0.543	3.98	5.72	3.16	0.701	2.1	4.21
Total Phosphorus mg/L	0.12	0.10	0.05	0.30	0.07	0.01	0.06	0.08	0.07	0.01	0.07	<0.05
Chloride, mg/L	1150	146	1000	1490	32700	11500	21700	51200	21100	746	19800	21800
Sulphates, mg/L	1510	104	1300	1660	2740	32.9	2690	2780	3090	647	2710	4680
Total Coliform, MPN	2.36E+06	2.83E+06	3.70E+04	7.00E+06	7.52E+07	1.89E+08	2.00E+04	5.40E+08	1.68E+06	4.17E+06	6.80E+04	1.20E+07
E-coli, MPN	1.81E+05	3.29E+05	0.00E+00	9.20E+05	6.64E+06	1.42E+07	0.00E+00	4.00E+07	1.03E+04	8.38E+03	0.00E+00	1.80E+04
Total Iron, mg Fe/L	1.84	0.657	1.08	2.88	0.809	0.45	0.32	1.57	1.79	1.51	0.49	5.28

This effect may have been exacerbated by temperature and solar radiation at sampling (approximately 12 noon) [49]. Total nitrogen levels exhibited significant seasonal variations, as depicted in Table 2. The total nitrogen measured was higher in the rainy and transition seasons than in the dry ones (Table 2), with average concentrations being higher for points C7 and C8 (Table S1).

Total phosphorus presented values between 0.05 and 0.30 mg/L, with higher values during the rainy season. BOD_5 in the Mallorquin swamp was influenced by the season as shown in Table 2 Rainy season showed higher values of organic matter content, this might be due to the increased entrance of residual waters from the Magdalena River and the León stream [50–52].

During the monitoring conducted across different climatic seasons at Mallorquin Swamp, it was observed that most sampling points did not exceed a concentration of 7.0 $x10^4$ MPN for total coliforms and 9.0 $x10^3$ MPN for *E. coli*, except during the transition period. During this phase, concentrations of 5.4 $x10^5$ MPN for total coliforms and 1.3 $x10^5$ MPN for *E. coli* were observed at point C7. Total coliforms of 5.4 $x10^6$ MPN and *E. coli* of 4.0 $x10^6$ MPN were recorded at point C8 (Table 2). These points experience higher input of domestic wastewater due to stilt settlements and houses without sewage systems along the swamp's edges. A similar pattern was observed in Santa Marta Bay and the Ranchería River estuary, where areas closest to human settlements exhibited the highest coliform counts [53,54].

PAHs (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo(a) Anthracene, Chrysene, Indene(1,2,3-cd)Pyrene) were analyzed in the water sampled at the different sampling sites and stations. However, no values higher than the quantification limit of the methodology were found for the periods evaluated, which is why this information was not reported.

The results for heavy metals showed that only Fe, Cd, and Cr^{+6} were found in some points of the Swamp, and others were below the detection levels. Therefore, Table 3 presents only the values found above the limit of the analytical quantification performed. Iron concentrations (2 and 3) varied from 1.08 to 2.88 mg/L during the rainy season, reaching maximum levels at the C1 and C5 points. In the transition season, iron levels ranged from 0.32 to 1.57 mg/L, while during the dry season, concentrations were measured between 0.49 mg/L and 5.28 mg/L, surpassing the limit established by regulations in Colombia (5 mg/L) (Resolution 851, 2020) [45]. This elevated iron concentration was recorded at point C8, likely due to the continuous discharge of wastewater into this location. Other heavy metals in the Mallorquin swamp were cadmium and hexavalent chromium, with low concentrations, as shown in Table 3, nonetheless, point C4 appears to be the most contaminated point.

Related to EPs (Table 4), the results of the samples showed values above the detection limit of the analytical method used. The high content of IBU was identified at point C4, along with elevated levels of NAP at points C4, C5, C7, and C8; meanwhile, in points C1, C2, C3, and C8 the values were below the detection point of the method. These points are in proximity to human settlements lacking sewage systems (Table 1), so discharges from these areas might be responsible for the presence of these contaminants in the water body.

Ibuprofen has been previously detected in Colombia, specifically in the estuarine and coastal zone of the Gulf of Morrosquillo in Córdoba, with concentrations ranging from ~0.067 to 1.092 μg/L [55,24]. In the Gulf of Urabá region, during the rainy season, reported concentrations of IBU ranged between 0.12 and 0.46 μg/L, CAF from 0.080 to 0.944 μg/L [25], and NAP in surface waters in Córdoba from 0.056 to 0.417 μg/L in populated areas [26]. Thus, the concentrations found in the swamp are considerably high, potentially attributed to the prevalent self-medication culture in Colombia [56]. NAP has been previously identified as a potential threat to certain fish species, exhibiting toxicity and acting as an endocrine disruptor [57,58]. Therefore, high concentrations of NAP could pose health risks for the biota of the Mallorquín Swamp, highlighting the need for constant monitoring of this type of contaminant to promote the preservation of this ecosystem.

The remaining studied contaminants were found to be below the detection limits of the utilized method (Dihydrojasmonate <11.0 μg/L, GAL <8 μg/L, TON <8 μg/L, BPA <6.0 μg/L, CAF <8 μg/L). This observation may be associated with their partition coefficients and solubility, making them more likely to be present in sediments or fish populations [37].

3.2. Fish results

Thirty fish were collected, comprising 15 individuals from each species. *A. canteri* exhibited a mean standard length of 29.4 ± 4.7 cm and a body mass of 583.8 ± 212.2 g. In contrast, *M. incilis* displayed a mean standard length of 17.1 ± 2.3 cm and a body mass of 149.8 ± 65.4 g. The specimens' body mass variation occurred due to the limited availability of this species during the capture season,

Table 3
Heavy metals measured during different seasons in the Mallorquin swamp.

Season	Point	Cr^{+6} (mg Cr^{+6}/L)	Cd (mg Cd/L)
Rainy	C1	<0.01	0.004
	C2	<0.01	<0.001
	C3	<0.01	<0.001
	C4	<0.01	0.004
	C8	<0.01	0.005
Dry	C4	<0.01	<0.001
	C6	0.016	<0.001
Transition	C1	0.011	<0.001
	C4	0.015	<0.001

Table 4
Emerging pollutants found in the Mallorquin swamp.

Season	Point	Ibuprofen, (μg/L)	Naproxen, (μg/L)
Rainy	C4	218.1	18.72
	C5	<10.0	226.75
	C7	<10.0	343.89
	C8	<10.0	50.23

so fish of different sizes and species were taken. In addition, the captures were made at various points within the swamp to obtain representative samples of the study area.

Fig. 2 depicts the percentage of contaminant detection in the present study. In *A. canteri* samples, substances with detection rates exceeding 50 % included MMER, ACTHE, BPA, PYR, TON, and GAL. For *M. incilis*, the substances surpassing the 50 % detection threshold were GAL, TON, MDHJ, BPA, and MMER (Table S2 y Table S3). These findings indicate a persistent presence of substances, particularly MMER, in the studied species. Other research has identified fish samples, and the presence of the substances found in the present study [24,59–61].

In Fig. 3 (A/B), it is evident that PAHs were found in higher concentrations in samples from both species, with a stronger presence in *A. canteri*. The order of PAHs concentrations from highest to lowest was ACTHE > PYR > ACTHYL > FLUO. Interestingly, FLUO was not detected in the *M. incilis* samples. On the other hand, MMER concentrations in *A. canteri* were higher than those in *M. incilis*. This contrasts with the accumulation pattern observed for EPs, where *M. incilis* showed a higher bioconcentration trend, especially for the compounds GAL and MDHJ.

Regarding concentration results, as previously mentioned, the highest values were observed in the PAHs group, specifically for ACTHE, with 7782 ± 4123.8 μg/kg and 2376.23 ± 599.63 μg/kg for *A. canteri* and *M. Incilis,* respectively. Following closely was MMER with 238.5 μg/kg ± 100 in *A. canteri*, and GAL with 139.49 μg/kg ± 34.98 in *Mugil incilis*. The species investigated exhibit distinct patterns of contaminant bioaccumulation influenced by the chemical properties of the quantified substances and the feeding and migration behaviors of the investigated species.

A. canteri, an endemic species of Colombia's Caribbean coast found in the Atrato, Sinú, and Magdalena rivers, inhabits coastal and brackish marine waters. It appears to be particularly reliant on mangroves [62]. This carnivorous, demersal fish [63] displays specific feeding and movement characteristics that might explain the higher bioconcentration tendency for substances such as PAHs and MMER in *A. canteri* samples. This pattern likely mirrors the water quality features of the ecosystem where this fish undergoes its life cycle [64]. In contrast, *M. incilis* is a species associated with mangroves and spawns in coastal areas of the continental Caribbean [65, 66], including estuarine ecosystems such as the Mallorquín swamp. Subsequently, it migrates to the adjacent sea between December and March [28]. This species is categorized as a detritivorous fish - Pelagic Benthos [63].

Considering the information above, it could be inferred that *M. incilis* is likely exposed to more substances, including the EPs quantified in the study samples, due to its mobility However, given its dietary habits, food sources may also explain the persistent presence of contaminants such as PAHs and MMER. Concerning the chemical characteristics of the substances identified in this investigation, they possess high partition coefficients, indicating a strong affinity for lipid accumulation [37,60].

In this research, Spearman correlation analysis was conducted to examine the relationships between the variables under investigation (Table 5). The correlation coefficients highlighted in bold correspond to the cases where p values < 0.05 were presented. For *A. canteri*, the results revealed negative correlations between BPA-ACTHYL (−0.886), BPA-ACTHE (−0.745), GAL-ACTHYL (−0.886), and GAL-ACTHE (−0.817). Simultaneously, positive correlations were determined in this species, specifically between GAL and BPA (0.783) and MDHJ-BPA (0.714). Otherwise, positive associations were evident in the species *M. incilis*, particularly between the PAHs,

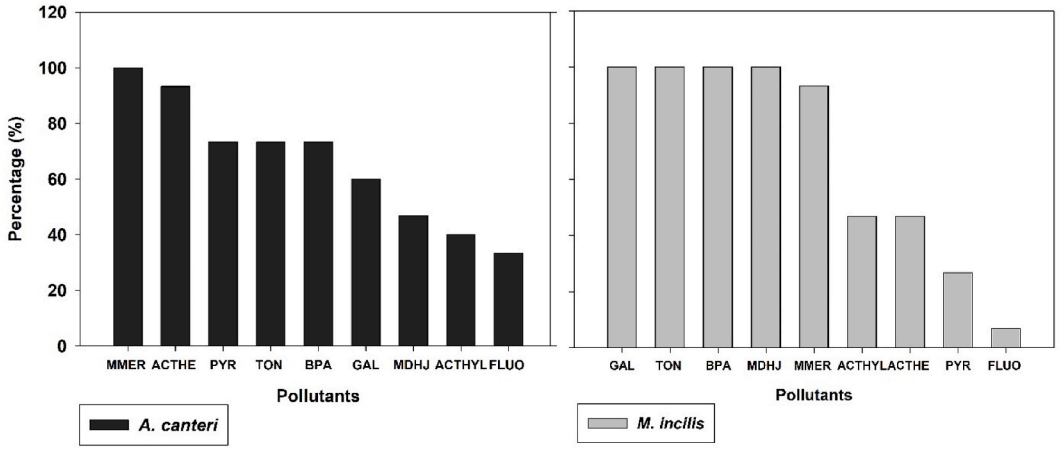

Fig. 2. Percentage of detection in *Mugil incilis* and *Ariopsis canteri*.

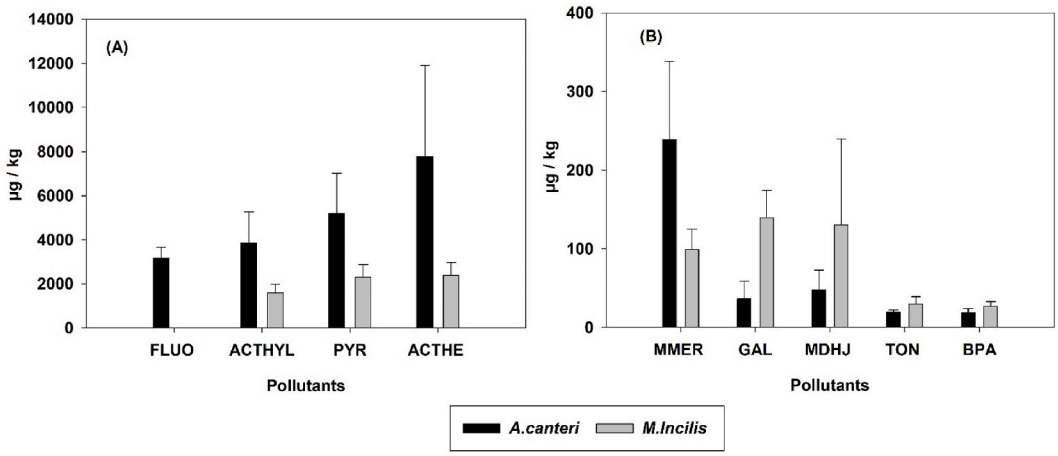

Fig. 3. Concentrations of PAH (A), MMER, and EPs (MDHJ, GAL, BPA) (B). Results are expressed as means ± SD.

ACTHE-ACTHYL (0.929), and the EPs MDHJ-GAL (0.729). The results could be due to the lifestyle of species which has mobility between the sea and Mallorquín swamp [28], having a greater possibility of exposure to several types of contaminants. This behavior could be attributed to the carnivorous diet of this species and the fact that its life cycle remains in the Mallorquín swamp [62]; this phenomenon may reflect the quality characteristics of the water body.

In addition to previous findings, this study compared MMER concentrations in *M. incilis* samples to the FAO/WHO permissible value (500 µg/kg) (Table 6) for non-predatory fish consumption, given the species is of commercial importance in the region. The results indicated that only one sample out of the total exceeded this regulatory limit, registering a 618.17 µg/kg value. Notably, other similar studies conducted in the Mallorquín swamp with the species *Mugil curema* reported that the concentrations of mercury found in the analyzed samples did not surpass the permissible limit established by Resolution 122 of 2012 issued by the Ministry of Social Protection of Colombia By delving into these intricate aspects, our study aims to expand the understanding of potential environmental hazards posed by pollutants on *M. incilis* and *A. canteri*, thereby providing valuable contributions to the fields of environmental sciences and pollution control [67].

Regarding PAHs and EPs present in fish muscles from aquatic bodies in Colombia, there are few studies, especially in the species *A. canteri* and *M. incilis*, as well as for the Mallorquín swamp, for which there are no previous reports of these contaminants. For this reason, a comparison was made with studies carried out in other bodies of water at national and international levels (Table 6).

In a study in the Colombian Caribbean region, total PAH values of 3720 µg/kg were reported in Cartagena Bay (Table 6). When comparing these results with those obtained in our research, it is observed that the reported values are higher. This difference could be because the reference study was conducted in 2008 and the contamination levels could have increased over time. Similarly, at an international level Adelawe et al. [71], also found lower PAH values in tissues of the fish *Sarotherodon melanotheron* and *Clarias gariepinus* from the Ogun and Eleyele rivers of Nigeria, reporting maximum concentrations of 730, 1340, 690, and 1650 µg/kg for ACTHYL, ACTHE, FLUO, and PYR.

Table 5
Spearman correlation coefficients between studied variables.

Fish specie	Parameter (µg/kg)	MMER	ACTHY	ACTHE	FLU	PYR	BPA	GAL	TON	MDHJ
A. canteri	MMER	1.000								
	ACTHY	0.143	1.000							
	ACTHE	−0.077	0.314	1.000						
	FLU	0.000	0.600	0.200	1.000					
	PYR	0.064	0.143	−0.064	0.600	1.000				
	BPA	−0.318	**−0.886**	**−0.745**	−0.700	−0.364	1.000			
	GAL	−0.150	**−0.886**	**−0.817**	−0.700	−0.050	**0.783**	1.000		
	TON	0.182	−0.200	−0.073	−0.900	−0.236	0.182	0.450	1.000	
	MDHJ	−0.250	−0.486	−0.464	0.300	−0.071	**0.714**	0.571	−0.107	1.000
M. incilis	MMER	1.000								
	ACTHY	0.286	1.000							
	ACTHE	0.250	**0.929**	1.000						
	FLU	0.000	0.000	0.000	1.000					
	PYR	1.000	0.800	0.400	0.000	1.000				
	BPA	0.024	0.286	0.071	0.000	0.800	1.000			
	GAL	0.046	0.286	0.000	0.000	0.400	0.261	1.000		
	TON	0.279	0.143	0.071	0.000	1.000	0.000	0.296	1.000	
	MDHJ	0.081	0.107	−0.071	0.000	−0.800	0.241	**0.729**	0.368	1.000

Table 6
Comparison of EP concentrations found with national and international regulations and other studies. N. A: Information not available.

Parameter	Maximum reported value (μg/kg)		Minimum value reported (μg/kg)		Maximum allowed value (μg/kg)	
	A. canteri	*M. incilis*	*A. canteri*	*M. incilis*	National reference	International reference
MMER	582.37	618.17	147.51	75.24	500 [68,69]	500 [68,69]
ACTHYL	5470	2217.2	<400	<400	3720 [70]	730 [71]
ACTHE	15070	3541.2	<400	<400		1340 [71]
FLUO	3760	1580.4	<400	<400		690 [71]
PYR	8440	13167.6	<400	<400		1650 [71]
GAL	68.15	184.53	<16	71.75	N. A.	538.4 [37]
TON	25.77	58.26	<13	16.98	N. A	57.8 [37]
BPA	28.71	42.95	<12	18.74	N. A	23.1 [37]
MDHJ	87.15	493.65	<LOD	42.42	N. A	N. A

In contrast to the above, the study conducted by Bandowe et al. [72], who evaluated total PAHs in fish tissues (*Drapane Africana*, *Cynoglossus senegalensis,* and *Pomadasys perotet*) from different water bodies located in Ghana, reported concentrations of up to 28006, 12056, 16257 μg/kg, respectively. These results are of a similar order of magnitude to those reported for the species *A. canteri* and *M. incilus* taken in the Ciénaga de Mallorquín, demonstrating that the bioaccumulation of PAHs is related to the sources of contamination and the characteristics of the water body.

These findings are concerning because PAHs are contaminants that significantly impact on aquatic life, especially fish. Although fish can metabolize these compounds, the biotransformation reactions can produce reactive metabolites that form covalent bonds with cellular macromolecules such as RNA and DNA. This process can lead to the development of mutagenesis and carcinogenesis, overwhelming g the DNA repair capacity in fish. Furthermore, fish can accumulate PAHs, which can have health consequences for consumers, especially in coastal areas like the one being studied, where fish is a traditional protein in inhabitants' diet [73]. Specifically, the species *A. canteri* and *M. incilis* are common in the region.

For BPA, GAL, TON, and MDHJ, no national or international regulations related to the species studied were found. Therefore, a study carried out in the Northeast Atlantic Ocean (Douro River estuary, Portugal) [37] was taken as a reference, where the presence of endocrine disrupting compounds (EDCs) in the muscles of different fish (BPA, GAL, and TON) was evaluated. Higher concentrations were found in the *M. cephalus* species with maximum values (Table 6) of up to 538.4, 57.8, and 23.1 μg/kg for GAL, TON, and BPA, respectively. The values presented in the *M. incilus* species in this study were higher for TON and BPA. As mentioned above, this is related to the presence of different sources of anthropogenic contamination in the study area and the characteristics of this species.

Finally, it is important to mention that the results shown regarding the concentration of MMER, PAHs, GAL, TON, BPA, and MDHJ, although in some cases like those reported in other investigations, highlight the critical importance of monitoring and managing pollution in aquatic ecosystems. The detection of high levels of contaminants, such as methylmercury and PAHs, in commercially important fish species highlights the urgent need for regulatory measures to protect both the environment and public health. This study not only provides a valuable basis for future research but also emphasizes the need for sustainable practices to mitigate pollution and safeguard biodiversity in the Mallorquín Swamp. Collaboration between scientific, regulatory, and community stakeholders will be vital to achieve these goals and ensure the long-term health of this crucial ecosystem.

4. Conclusions

The comprehensive environmental assessment of the Mallorquín Swamp revealed complex dynamics influenced by seasonal variations and anthropogenic activities. The water quality analysis identified fluctuations in physical and chemical parameters, with notable variations in alkalinity, hardness, and nutrient levels. The presence of elevated concentrations of total coliforms and *E. coli* (5.4 $X10^6$ MPN and 4.0 $X10^6$ MPN, respectively) at sampling points C7 and C8 indicate potential water contamination, particularly because there are areas close to human settlements that lack adequate sewage systems.

Heavy metal analyses demonstrated elevated levels of iron at points C1 and C7 located at the entrance to the León stream and industrial area, which are related to a greater potential for contamination. The presence of emerging pollutantss such as IBU and NAP at concentrations of 218 μg/L and 343.89 μg/L respectively in the swamp suggest significant exposure levels for the biota. Point C4, identified as a mixing point, exhibited the highest contamination levels, attributed to the cumulative impact of settlements and water inflows in the swamp.

Fish analysis unveiled persistent contaminants, such as methylmercury and PAHs, with species-specific bioaccumulation patterns. *Ariopsis canteri* showed a higher tendency to accumulate PAHs and methylmercury, potentially influenced by its feeding habits and habitat preferences. In contrast, *Mugil incilis* exhibited higher bioaccumulation trends for emerging pollutans, possibly due to its mobility and exposure to diverse contaminants.

The findings emphasize the vulnerability of the Mallorquín Swamp to anthropogenic influences, urging the implementation of proactive measures to safeguard this critical ecosystem. Therefore, future studies should monitor temporal changes in contaminant levels and identify their sources. Evaluating bioremediation techniques and developing community engagement strategies are crucial to improving conservation in the Mallorquín Swamp. Continuous monitoring, regulatory interventions, and community awareness are essential to mitigate environmental impacts and ensure the sustainability of the Mallorquín Swamp for future generations.

Ethics declarations

The study was conducted strictly by the ethical principles established in Colombia for using animals in research. Ethical approval was granted by the Universidad del Atlántico Ethics Committee, an allied institution in the project that funded this research (BPIN: 2020000100382 - SGR). The research adhered to all relevant international standards governing the ethical treatment of animal subjects in scientific experimentation.

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Data availability

Data will be made available on request.

CRediT authorship contribution statement

Cindy Elles-Pérez: Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Maria Guzman-Tordecilla:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Yuliceth Ramos:** Writing – review & editing, Writing – original draft, Visualization, Validation, Formal analysis, Data curation, Conceptualization. **Margarita Castillo-Ramírez:** Writing – review & editing, Visualization, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Andrea Moreno-Ríos:** Writing – review & editing, Writing – original draft, Investigation. **Carolina Garzón-Rodríguez:** Writing – original draft, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Jacqueline Rojas-Solano:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e39005.

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