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Article

Spatio-Temporal Characterization of Physicochemical Variables in an Estuary in the Brazilian Semi-Arid Region

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RESUMO
Objetivou-se avaliar a dinâmica espaço-temporal das variáveis físico-químicas de um ambiente estuarino no semiárido brasileiro. A pesquisa foi conduzida ao longo do ano de 2023, no estuário do rio Apodi-Mossoró, a partir da geração de mapas geoespaciais para representar as variações nas concentrações da salinidade, do cálcio (Ca^{2+}) e do magnésio (Mg^{2+}), abrangendo os compartimentos do alto, médio e baixo estuário. Os resultados revelaram uma sazonalidade determinante na estruturação da salinidade estuarina, com maiores diluições nos períodos chuvosos e salinização acentuada na estação seca, bem como um crescente gradiente iônico do baixo para o alto estuário com valores máximos registrados nos períodos secos, refletindo a intensificação da intrusão marinha e a retração da influência fluvial. Esses padrões evidenciam que a dinâmica da salinidade no estuário é altamente sensível às variações sazonais, reforçando a importância de um monitoramento contínuo para subsidiar estratégias de manejo e conservação em ecossistemas costeiros sob influência da hipersalinidade.
Palavras-chave: parâmetros físico-químico; hipersalinidade; avaliação geoespacial; variação sazonal; ecossistema costeiro.

ABSTRACT
This study aimed to evaluate the spatiotemporal dynamics of physical and chemical variables in an estuarine environment in the Brazilian semiarid region. The study was conducted throughout 2023 in the Apodi-Mossoró River estuary. Geospatial maps were generated to represent variations in salinity, calcium (Ca^{2+}), and magnesium (Mg^{2+}) concentrations, covering the upper, middle, and lower estuary compartments. The results revealed a seasonality that determines estuarine salinity, with greater dilutions during the rainy season and accentuated salinization during the dry season. The study also demonstrated a growing ionic gradient from the lower to the upper estuary, with maximum values recorded during the dry season, reflecting the intensification of marine intrusion and the decline of river influence. These patterns demonstrate that salinity dynamics in the estuary are highly sensitive to seasonal variations,

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reinforcing the importance of continuous monitoring to inform management and conservation strategies in coastal ecosystems under the influence of hypersalinity.
Keywords: physicochemical parameters; hypersalinity; geospatial assessment; seasonal variation; coastal ecosystem.

Introduction

Estuaries are complex coastal ecosystems that play a key role in connecting freshwater and marine environments (Silva 2000; Ribeiro 2010; Reinke and Sangiogo 2023). These environments are characterized by physicochemical parameters, whose variations are influenced by hydrological, climatic, and geomorphological factors, especially salinity (Domingos et al. 2015). Within this context, in semi-arid regions, such as northeastern Brazil, the scarcity of rainfall, associated with high evaporation rates, makes estuaries particularly susceptible to hypersalinity, affecting ecological dynamics and multiple uses of water (Carvalho 2022; Galvão and Fioreze 2012).

From this perspective, the Apodi-Mossoró River estuary, located in the western region of the state of Rio Grande do Norte, is a typical example of a hypersaline estuarine environment (Rocha et al. 2011). Located in a hydrographic basin of high socio-environmental relevance, the estuary shows remarkable spatial and temporal variability, reflected in its physical and chemical parameters, especially during periods of prolonged drought. For example, salinity can exceed 70 ppt in certain sections of the estuary in response to low river discharge, intense evaporation, and marine intrusion (Medeiros et al. 2018).

Another factor contributing to increased salinity is salt farming, which has a strong influence on local environmental dynamics. This economic activity, which involves the production of sea salt through the evaporation of seawater in shallow ponds in the Apodi-Mossoró river estuary, generates concentrated effluents, commonly called brine, which, when discharged into the estuarine environment, significantly alter the physical and chemical composition of the water (Cavalcanti et al. 2005; Baraúna et al. 2015).

Although these effluents are characterized by high concentrations of salts, mainly calcium ions (Ca^{2+}) and magnesium (Mg^{2+}) ions, in addition to salinity itself, the inclusion of these ions in the spatiotemporal analysis is justified by their relevance as indicators of anthropogenic saline intrusion, allowing the degree of impact of salt farming on the different compartments of the estuary to be assessed. Salinity, in turn, is directly related to the presence of dissolved ions and varies according to the tides, the season, and the inflow of fresh water, playing an important role in the structuring of estuarine ecosystems (Lopes 2017). Thus, the integrated analysis of these parameters is very important for understanding the processes that regulate the water balance and local geochemical dynamics, contributing to environmental planning, biodiversity conservation, and water resource management (Vieira et al. 2005).

Given this perspective, this study aimed to analyze and interpret the physical-chemical patterns of the Apodi-Mossoró River estuary during the dry and rainy seasons, with an emphasis on salinity, calcium (Ca^{2+}), and magnesium (Mg^{2+}). In addition, we sought to identify spatial and temporal patterns, as well as to ensure understanding of the dynamics of salinity in this hypersaline environment, which represents an essential step in supporting monitoring, impact mitigation, and sustainable planning actions in the region.

Materials and Methods

Study area

The study was conducted in the Apodi-Mossoró river estuary, which is a transition zone between river and marine environments, where fresh water from this river interacts with the saline waters of the Atlantic Ocean. According to Carvalho et al. (2018), this estuarine environment is located on the coast of the state of Rio Grande do Norte, covering the municipalities of Mossoró, Grossos, and Areia Branca (Figure 1). For a more detailed analysis, the area was divided into eight points (P1 to P8), distributed along the estuary as follows: P1 and P2 to indicate the collection points in the upper estuary; P3 to P6 in the middle estuary; P7 and P8 in the lower estuary (Table 1).

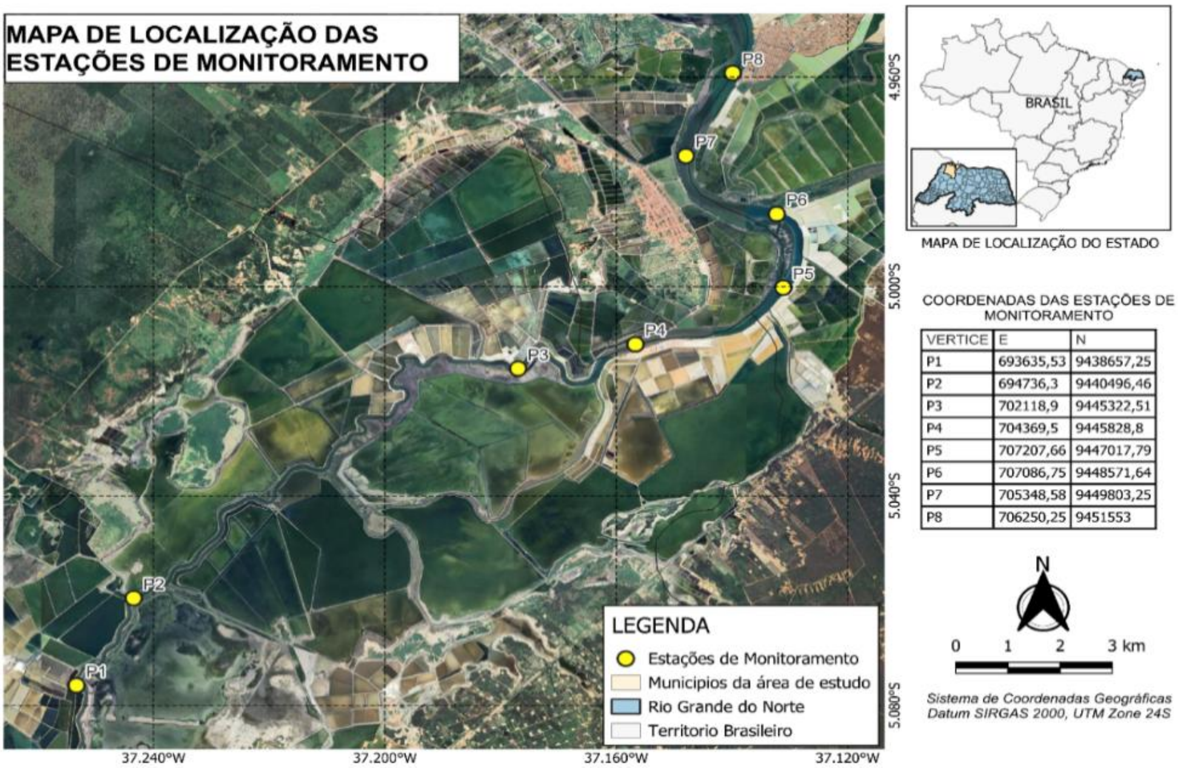

Figure 1. Floodplain of the Apodi-Mossoró River estuary. Source: prepared by the authors (2025).

Table 1. Location of sampling points on the Apodi-Mossoró River.

Monitoring stations	Latitude	Longitude
P1	693,635.53	9,438,657.25
P2	694,736.3	9,440,496.46
P3	702,118.9	9,445,322.51
P4	704,369.5	9445828.8
P5	707,207.66	9,447,017.79
P6	707,086.75	9,448,571.64
P7	705,348.58	9,449,803.25
P8	706,250.25	9451553

Source: prepared by the authors (2025).

Parameters analyzed

The decision to analyze calcium and magnesium ions specifically, in addition to salinity, is due to their presence in the effluents produced by salt farming, a predominant activity in the region. These parameters therefore serve as potential indicators of saline effluent discharge, acting as markers that allow the anthropogenic contribution to the natural saline intrusion of the estuary to be assessed.

The study was conducted throughout 2023, covering a complete hydrological cycle in the region. The data were grouped into four quarters (January to December), allowing for the evaluation of physical-chemical variations as a function of local climate seasonality. According to Alvares et al. (2013), the Apodi-Mossoró river estuary region has a semi-arid BSw'h' climate, characterized by two well-defined periods: a rainy season, which generally occurs between February and June, and a dry season, between July and January.

The average annual rainfall is below 750 mm, with uneven distribution of rainfall both temporally and spatially. In contrast, potential evapotranspiration is significantly high, ranging between 1,500 and 1,600 mm per year, which accentuates the water deficit in the region and limits the availability of surface and groundwater.

According to data from the Agricultural Research Company of Rio Grande do Norte (EMPARN), the municipality of Mossoró recorded 704.6 mm of accumulated precipitation from January to December 2023. These values fall within the expected annual range for the Apodi–Mossoró river basin (63.2–750 mm). March and April stand out as the rainiest months (150.2–240.4 mm), confirming the characterization of the second quarter as the period of maximum rainfall, in line with historical data for the region.

Each quarter of the study reflects a distinct phase of seasonality, according to data provided by the National Institute of Meteorology (INMET 2023). Thus: in the first quarter (Jan.-Mar.), there is a transition from the dry period to the beginning of the rainy season; sparse rainfall (average monthly precipitation ~30–80 mm), with river flow still reduced. In the second quarter (April-June), there is a period of more intense rainfall, with average monthly precipitation varying between 100 and 180 mm, which favors an increase in river flow and dilution of salts. The third quarter (July-September), in turn, is characterized by the transition from the rainy season to the dry season; a gradual reduction in rainfall (~50 mm/month), favoring the advance of saline intrusion. Finally, in the fourth quarter (Oct.-Dec.), the season is completely dry, with monthly rainfall below 20 mm, high evaporation rates, and maximum marine influence on the estuary.

Salinity was determined *in situ* with the aid of a portable refractometer, duly calibrated before each collection campaign. The concentrations of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions were analyzed in the laboratory by complexometric titration with EDTA (ethylenediaminetetraacetic acid), using the black indicator erythromellitic acid T. The procedure followed the guidelines of *Standard Methods for the Examination of Water and Wastewater* (Baird et al. 2017).

Data analysis

The results obtained for each parameter at the collection stations were organized and analyzed based on the quarterly average, in order to smooth out monthly variations and facilitate seasonal interpretation. Subsequently, the data were georeferenced according to the coordinates of the respective collection stations. From these points, an interpolated spatial model was generated using the IDW (Inverse Distance Weighting) interpolation method in QGIS software version 3.22.

This procedure allowed the creation of thematic maps representing the spatial variations in salinity, calcium, and magnesium for each quarter, facilitating the analysis and interpretation of the spatial distribution of the parameters in the estuary.

Results

Analysis of salinity levels

The spatial dynamics of salinity in the estuary showed a strong relationship with the rainfall regime, highlighting the influence of seasonal conditions on its longitudinal structure.

In the first quarter, corresponding to the beginning of the rainy season, the estuary exhibited characteristics typical of an inverted system, with increasing salinity from the mouth to the upper course. The values ranged from 40 $g \cdot L^{-1}$at the mouth to 55 $g \cdot L^{-1}$in the upper portion, a pattern characteristic of environments where evaporation exceeds river inflow, favoring the accumulation of salts in the innermost regions (Figure 2-A).

During the second quarter, with increased precipitation and consequent increase in continental runoff, there was a reversal in the saline profile, causing the system to assume a positive or classic behavior. During this period, the highest concentrations were recorded at the mouth (35 $g \cdot L^{-1}$), while in the upper estuary, the values became undetectable due to intense dilution caused by fresh water (Figure 2-B).

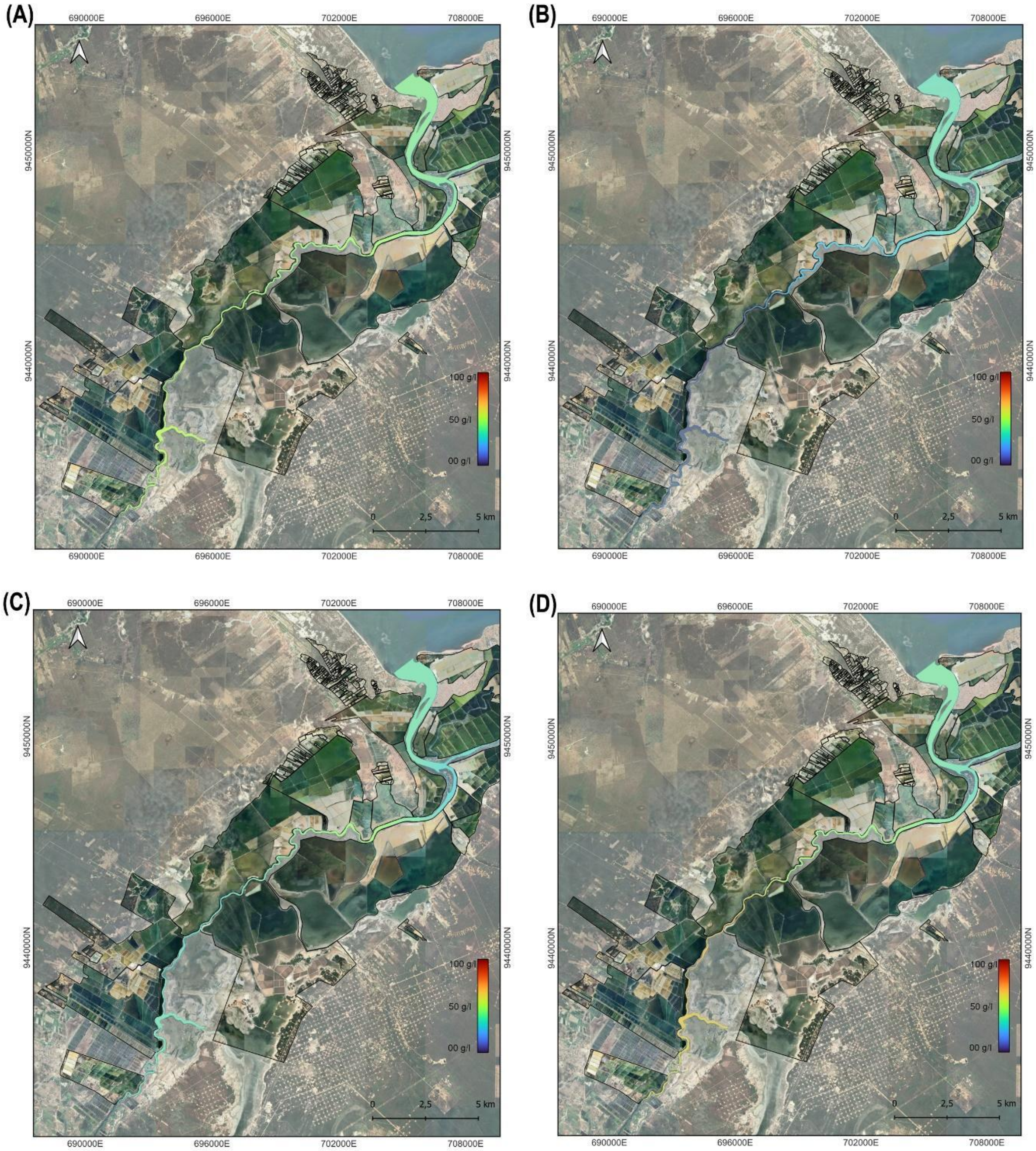

Figure 2. Geospatial representation of salinity levels in the Apodi-Mossoró River estuary. (A) First quarter; (B) second quarter; (C) third quarter; (D) fourth quarter. Source: prepared by the authors (2025).

The third quarter marked the transition to the dry season, when evaporation began to predominate over precipitation. Despite this, there was still significant water retention, especially in the middle to upper estuary. An increase in concentrations was then observed in the middle course (50 $g \cdot L^{-1}$), resulting from progressive salinization as it moves away from the mouth, an effect partially mitigated by the residual water present in the upper zones (Figure 2-C).

In the fourth quarter, the intensification of the evaporative process, typical of semi-arid regions, enhanced the accumulation of salts, resulting in a marked inverse gradient. Concentrations reached 90 $g \cdot L^{-1}$in the upper estuari , contrasting with the 40 $g \cdot L^{-1}$observed at the mouth, reinforcing the role of evaporation as a driving force for hypersalination in the interior portions during the dry season (Figure 2-D).

Analysis of calcium (Ca^{2+}) levels

The spatial variability of Ca^{2+} levels in the estuary showed a strong influence of seasonal rainfall conditions, highlighting the sensitivity of this ion to hydrological dynamics along the longitudinal gradient. According to the results represented in the thematic maps, it can be observed that the calcium concentration (g L^{-1}) changes throughout the quarters, especially from January to March (Figure 3). During the first quarter (Figure 3-A), corresponding to the beginning of the rainy season, higher concentrations of Ca^{2+} were found near the mouth, varying between 0.6 and 0.8 g L^{-1} , while in the innermost portions the values were lower (~0.4 g L^{-1}). This pattern characterizes a classic or positive behavior, typical of estuarine environments under the influence of marine intrusion, where the concentration of marine ions decreases from the mouth to the upper estuary (P1 and P2).

In the second quarter (April to June), there was a general decrease in calcium concentrations along the estuarine channel, reflecting the intensification of precipitation, which favored the dilution of dissolved ions. The levels varied between 0.0 and 0.4 g L^{-1}, with lower values predominating mainly in the upper and middle estuary (Figure 3-B), which reinforces the importance of river inflow in modulating salinity and ionic load.

With the end of the rainy season and the beginning of the dry period (third quarter), Ca^{2+}levels rose again in the lower estuary, reaching values close to 0.8 g L^{-1}(Figure 3-C), due to the advance of the salt wedge and greater marine influence. In the middle estuary, values ranged from 0.4 to 0.6 g $^{L^{-1}}$, while in the upper estuary they remained low (0.0 to 0.4 g $^{L^{-1}}$), evidencing the persistence of the positive gradient. This behavior highlights the conservative nature of calcium in estuarine environments, whose distribution significantly follows salinity variation and is controlled by factors such as saline intrusion, tides, and rainfall.

In the fourth quarter (Figure 3-D), Ca^{2+}levels remained relatively moderate to high in the lower estuary (0.6–0.8 g L^{-1}) and lower inland (0.4–0.6 g L^{-1}). This trend indicates the gradual recovery of marine influence with the intensification of evaporation and the reduction of river discharge at the end of the dry season.

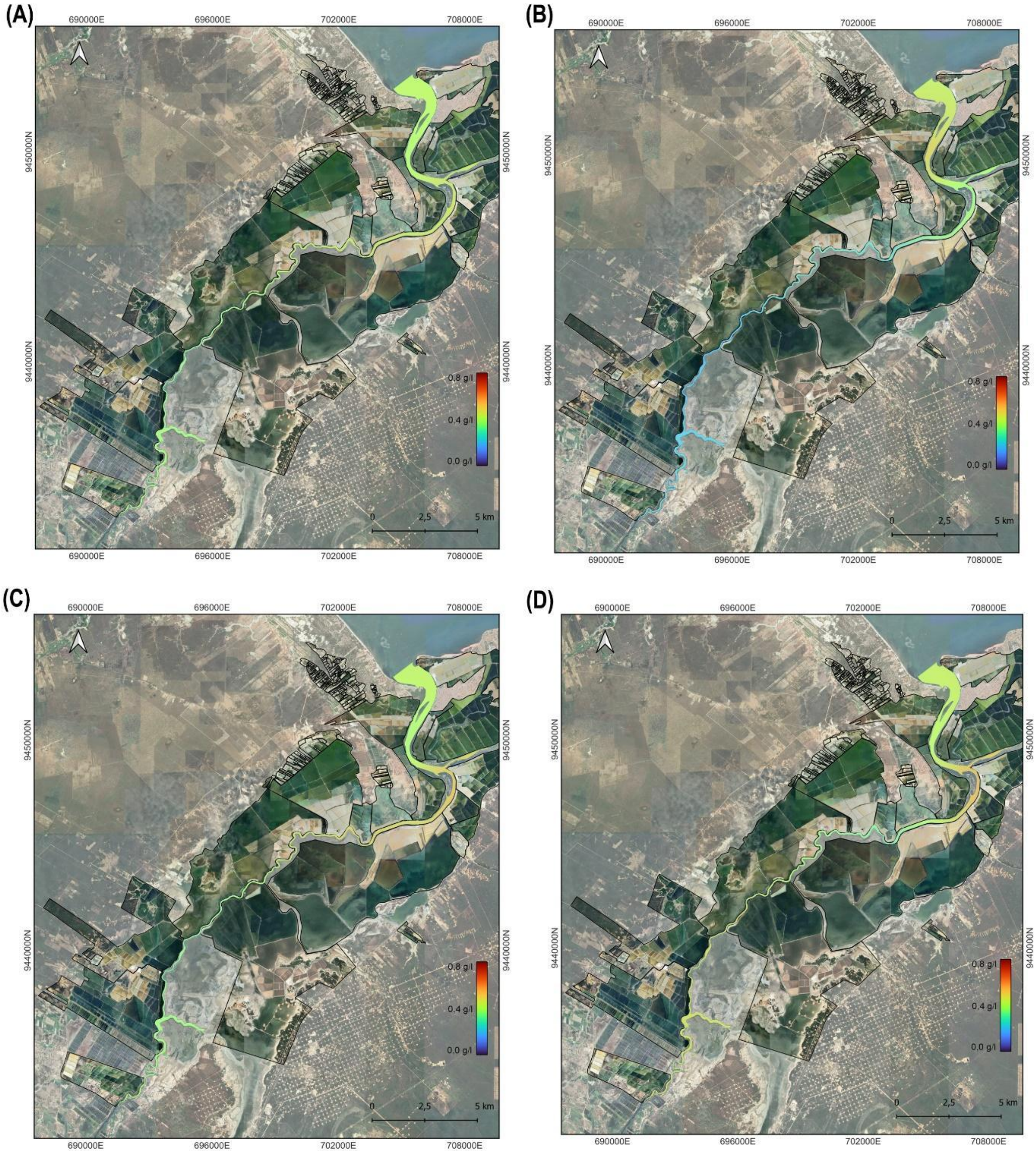

Figure 3. Geospatial representation of calcium (Ca^{2+}) levels in the Apodi-Mossoró River estuary. (A) First quarter; (B) second quarter; (C) third quarter; (D) fourth quarter. Source: prepared by the authors (2025).

Analysis of magnesium (Mg^{2+}) levels

The spatial distribution of magnesium (Mg^{2+}) levels revealed a pattern with predominantly higher values in the upper Apodi-Mossoró River estuary throughout 2023. This distribution suggests the presence of an inverse gradient, where concentrations increase from the lower to the upper estuary, indicating the accumulation of ions in inland regions, possibly associated with low water renewal and evaporation. In the first quarter, Mg^{2+}levels were highest in the upper estuary, reaching up to 5.9 g L^{-1}, while the portions closest to the mouth recorded lower concentrations, around 2.1 g L^{-1}(Figure 4-A). This pattern shows a system with a strong influence of evaporation in inland areas, in addition to the possible retention of ions from concentrated effluents (mother liquors) from salt pans. Low river flow and the incipient onset of rains were not sufficient to reverse this accumulation.

During the second quarter, there was a general reduction in magnesium concentrations, especially in the middle and upper estuary, with values between 2.6 and 3.4 g $^{L-1}$, while the lower estuary remained at levels around

1.8 to 2.5 g $^{L^{-1}}$ (Figure 4-B). This distribution suggests that the increase in river discharge characteristic of the rainy season contributed to diluting the ions in the more internal regions, temporarily reestablishing a more typical gradient, with decreasing concentration from the mouth to the interior.

In the third quarter, corresponding to the beginning of the dry season, the distribution of magnesium (Mg^{2+}) levels in the Apodi-Mossoró River estuary again showed an inverse gradient, with the highest concentrations located in the upper estuary, indicating the return of hypersaline conditions in the interior regions (Figure 4-C). The average Mg^{2+}values in the upper estuary (P1 and P2) exceeded 4.5 g $^{L^{-1}}$, revealing a significant accumulation of salts, probably caused by the drastic reduction in river discharge, intense evaporation, and water stagnation, which hinder renewal and promote the concentration of dissolved ions.

In the middle estuary (P3 to P6), the levels varied between 2.8 and 3.3 g $^{L^{-1}}$, suggesting a transitional condition, influenced both by the saline wedge coming from the mouth and by the accumulation of salts transported from the upper estuary. This intermediate range was relatively homogeneous, possibly due to the lower hydrodynamic movement characteristic of the period, which promotes longer water residence time and favors magnesium retention.

Finally, in the lower estuary (P7 and P8), the values recorded were the lowest of the quarter, ranging between 1.5 and 2.0 g L^{-1}. This condition suggests less pronounced marine intrusion during this period, possibly due to less intense tides or the permanence of waters with lower ionic content from continental drainage during the previous quarter. Thus, contrary to the classic pattern, in which higher salinity is expected at the mouth, the quarter revealed a reversal of the ionic gradient, reaffirming the internal hypersaline behavior of the system and highlighting the role of evaporation and salt retention as structuring forces of the estuary's geochemistry during the dry season.

In the fourth quarter, high Mg^{2+}levels were maintained and intensified in the upper estuary, with values close to 6.0 g L^{-1}, the highest recorded throughout the year (Figure 4-D). This significant accumulation is directly related to the intensification of the water deficit characteristic of the end of the dry season, marked by scarce rainfall, marked evaporation, and zero river flow. The combination of these factors contributes to water stagnation and the trapping of salts in the innermost portions of the estuary, preventing ion renewal and favoring local hypersalinity.

In the middle estuary (P3 to P6), Mg^{2+}levels varied between 4.0 and 5.0 g L^{-1}, revealing a transition zone under the combined effect of attenuated marine intrusion and the redistribution of salts from the innermost regions. This intermediate range presents itself as a point of partial salt accumulation, influenced by both the tide and the ionic load from the upper estuary, and is also affected by the morphology of the channel and the residence time of the waters.

In the lower estuary (P7 and P8), magnesium values were slightly lower, ranging from 2.8 to 37.5 g L^{-1}, which contrasts with the classic pattern of estuaries dominated by marine intrusion. This reduction may be associated with the higher dilution rate caused by seawater, which compensates for the effects of evaporation.

The persistence of this inverse gradient, with increasing values from the mouth towards the interior, reinforces the importance of continental hypersalinity in the system, driven by climatic factors such as evaporation , and rainfall scarcity, in addition to the possible contribution of anthropogenic action, especially the discharge of effluents from salt farming (mother waters), rich in $Mg^{(2+)}$). This behavior highlights the need for a critical assessment of the origin of ions and the hydrochemical compartmentalization of the estuary for the planning of conservation and impact mitigation strategies.

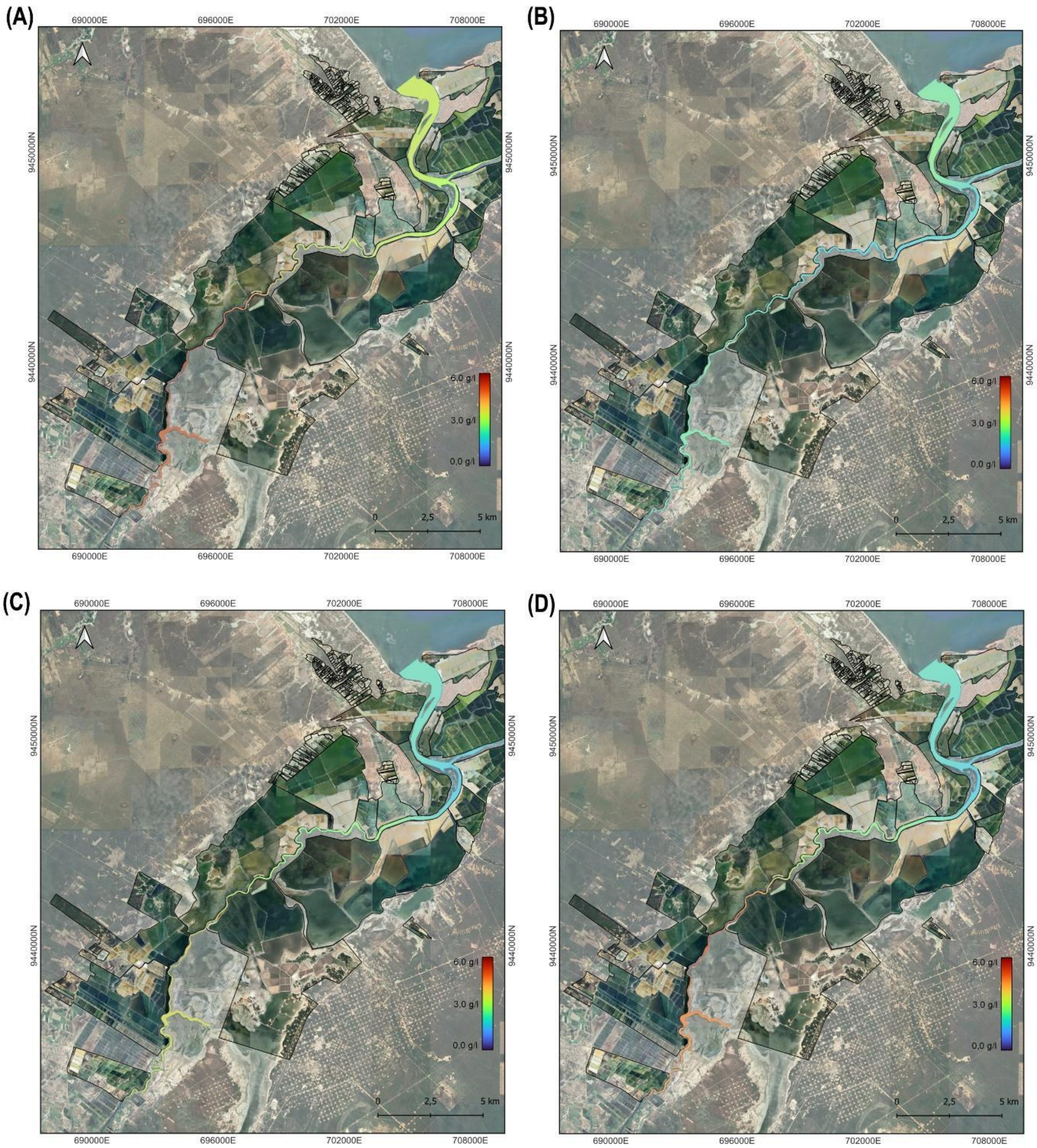

Figure 4. Geospatial representation of magnesium (Mg^{2+}) levels in the Apodi-Mossoró River estuary. (A) First quarter; (B) second quarter; (C) third quarter; (D) fourth quarter. Source: prepared by the authors (2025).

The results indicate that, unlike the classic pattern observed in many estuaries, Mg^{2+}tends to accumulate preferentially in the upper portions of the Apodi-Mossoró estuary, especially during the dry season. This highlights the importance of considering the local influence of factors such as intense evaporation and reduced river discharge, combined with salt farming, which act synergistically in the modulation of water quality. Thus, magnesium is consolidated as an effective geochemical marker of continental hypersalinity in estuarine ecosystems in the Brazilian semiarid region.

Discussion

Based on the precipitation data obtained, the annual accumulation was 829.7 mm, a value that falls within the historical range of the Apodi-Mossoró river basin. Rainfall distribution was highly uneven between quarters, reflecting the strong seasonality of the local semi-arid climate. The first quarter (January to March) totaled 356 mm, marking the transition from the dry season to the beginning of the rainy season, with intermittent rainfall.

The second quarter (April to June) had the highest rainfall of the year, with 375.3 mm, characterizing the peak period of the rainy season, responsible for the increase in river flow and dilution of dissolved salts. The third quarter (July to September) recorded only 54.8 mm, while the fourth quarter (October to December) had 43.6 mm, evidencing the prolonged drought in the second half of the year, with strong effects on the salinization of the estuary.

These climate data help explain the variation in salinity and dissolved ion levels throughout the year. During the second quarter, the significant increase in river flow induced by rainfall resulted in a significant dilution of salinity and Ca^{2+} and Mg^{2+} levels, especially in the upper and middle estuary, as shown in the thematic maps. In contrast, in the third and fourth quarters, low rainfall and intense evaporation favored the accumulation of salts in inland regions, reversing the ionic gradient expected for classic estuaries and consolidating a pattern of continental hypersalinity.

According to studies by Silva (2000) and Ribeiro (2010), this gradient is characteristic of estuarine environments, where continental and marine waters mix. Furthermore, the marked presence of these ions in the sections furthest from the mouth confirms the strong saline intrusion, a phenomenon amplified by the semi-arid conditions of Rio Grande do Norte, where low rainfall and high evaporation rates favor hypersalinity, according to research conducted by Rocha et al. (2011) and Carvalho et al. (2018).

In this study, salinity increases due to the intrusion of ocean waters into the estuary, especially during dry periods. Similarly, Silva (2010), when studying trace metal concentrations in Recife estuaries, demonstrated salinity variation, recording the influence of seasonality and saltwater dilution in the estuary.

Cunha (2018), when conducting studies on the dilution capacity of the Apodi-Mossoró River, reported an average of 282.24 g L^{-1} (SD = 4.34; CV = 1.54%), more than 8 times higher than the salinity of seawater, and varied between a maximum of 290 g L^{-1} and a minimum of 275 g L^{-1} , being the parameter with the highest polluting potential among those analyzed for salt industry effluents. This was considered the basis for determining the dilution capacity of the estuary and, consequently, the maximum effluent discharge rate.

D'Aquino et al. (2011), in turn, consider the spatial distribution of salinity as an indicator of the dynamic interaction between the forces produced by river discharge, outside the estuary, and by the tide, both outward and inward, producing the horizontal density gradient known as baroclinic.

However, during the dry season, there is an advance of the marine domain into the interior of the estuary, intensifying salinity values and raising the concentrations of $Ca^{2+}$and Mg^{2+}ions. From this perspective, in the Apodi-Mossoró River estuary, the the potential contribution of salt farming to the elevated levels of Ca^{2+} and Mg^{2+}, especially in areas close to salt pans, as effluents rich in these ions can interfere with the interpretation of natural gradients, making it necessary to differentiate between marine intrusion and anthropogenic sources, especially during periods of low water renewal. Thus, this type of response indicates that there are no relevant processes of local removal or addition of these elements, such as salt precipitation or direct anthropogenic influence (Schaeffer-Novelli et al. 1990).

The study conducted by Monteiro et al. (2015) points out that in the Curuçá River estuary, in northeastern Pará, during high tide, coastal waters are displaced to the estuary, increasing salinity (Silva et al. 2008). This increase in salinity is associated with the intrusion of seawater, which is rich in ions such as calcium (Ca^{2+}) and magnesium (Mg^{2+}). On the other hand, during the ebb tide, there is a greater influence of fresh water, reducing salinity and, consequently, the concentrations of these ions.

During the rainy season (January to June), a trend of dilution of ionic levels was observed, especially in the second quarter. This behavior can be attributed to increased river discharge, which reduces the influence of seawater and promotes greater water renewal in the estuary (Domingos et al. 2015). However, even during this season, the Lower Estuary continues to show high levels of $Ca^{2+}$and Mg^{2+}, demonstrating the persistent oceanic influence in this portion of the system.

In addition, the observed spatial heterogeneity reinforces the need for environmental zoning for the estuary, considering that each compartment (Upper, Middle, and Lower) has distinct hydrochemical characteristics. This differentiation is important for monitoring and management strategies, especially in the face of climate change, which can intensify the effects of prolonged drought and saline intrusion (Santos et al. 2023).

The results obtained are in line with the specialized literature on estuaries in semi-arid regions, such as the work carried out by Batista et al. (2020), which highlights the importance of climatic and hydrological control on the ionic composition of water. The integrated analysis of salinity, calcium, and magnesium also proves to be an effective tool for assessing marine influence and mixing processes in the estuary, contributing to the understanding of its geochemical dynamics.

Final Considerations

The analysis of salinity, calcium (Ca^{2+}), and magnesium (Mg^{2+}) levels in the Apodi-Mossoró River estuary revealed spatial and temporal patterns strongly associated with seasonal hydrological dynamics, rainfall patterns, and marine influence. The distribution of ions generally followed variations in rainfall volume, the advance of saline intrusion, and the effects of evaporation, possibly intensified by anthropogenic pressures such as the discharge of effluents from salt farming.

For future studies, the use of hydrodynamic and geochemical modeling is recommended to better understand water and solute flows, in addition to the inclusion of other physical-chemical and biological parameters that contribute to a more integrated assessment of the environmental quality of the estuary.

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