THE ORIGIN OF WATER IN THE MARIMBUS WETLAND, CHAPADA DIAMANTINA, BRAZIL: STABLE ISOTOPIC CONSTRAINTS

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ABSTRACT

The Marimbus wetland is in a lowered valley covered by alluvial sediment, resembling flooded sinkholes backswamp in drylands that remains permanently-to-seasonally flooded in the Chapada Diamantina. To determine the origin of the Marimbus wetland waters, isotopic analyses were performed at several points. The samples presented values of $\delta^{18}O(V_{SMOW})$ and $\delta^{2}H(V_{SMOW})$ ranging from -21.1‰ to 9.0‰ and from -3.13‰ to 3.31‰, respectively. Most of the samples data match with the global meteorological curve. The sinkhole's morphological features suggest that the waters of the Marimbus wetland area are not of carbonate karstic origin since the isotopic signature is within the global meteoric curve, indicating that its source was rainfall and that it is undergoing intense evaporation. They are rounded-shaped ponds typically found in silica karts environments covered alluvial fans and floodplains.

Keywords: Marimbus wetland; isotopic analysis; Chapada Diamantina

INTRODUCTION

The Marimbus wetland is located in a lowered valley and made up of alluvial sediment, resembling flooded sinkholes where we find a backswamp in drylands that remains permanently-to-seasonally flooded in the Chapada Diamantina. This area consists of an interface between Una-Utinga sedimentary basin (Figure 1), from the Neoproterozoic age (Salitre Formation), corresponding to the transition from glacial to marine environments (SAMPAIO et al., 1994; MARTINS et al., 2008), where carbonates form notably karsts, abundant in caves, and Mesoproterozoic metarenites from Chapada Diamantina Supergroup. Dozens of lowlands terrains (resembling dolines) can be seen in their surroundings. The Encantada pond with sinkhole morphological features, with an area of 800 m², is filled with water all year round (Figure 1). This landscape is interpreted as a carbonate basin, it is unclear the origin of the water, if from metasandstone or the carbonate basin (Figure 1).

This article comes to fill in the gaps related to the topic herein. The main objective of this work is to use stable isotopic data $\delta^{18}O(V_{SMOW})$ and $\delta^2H(V_{SMOW})$ to assess the origin of water, whether silica karst or carbonate karts groundwater.

Physiographic Settings

The Chapada Diamantina (State of Bahia) represents the most prominent geomorphic unit in northeastern Brazil, which elevations exceeding 2000 m. It is characterized as an extensive residual plateau, oriented N-S, considered the extension of the northern Espinhaço mountain range. Due to its prominent elevation, it is subjected to an intense weathering and erosion. The Sincorá mountain range is the central mountain range in the region, with peaks reaching 1600 m (Figure 2). An opento-soft folding system with N-S plunging controls the morphology of the Sincorá mountain range. Its results in the Pai-Inácio anticline and Una-Utinga syncline (MAGALHÃES et al., 2015), which forces the groundwater flow to the east, in that area (Figure 2). This structural feature is related to the Neoproterozoic collisions (from 950-520 Ma) that led to the assembly of Gondwanaland and the formation of the orogenic belts (MAGALHÃES et al., 2015).



Figure 1 | Geomorphological features at Chapada Diamantina, Paraguaçu catchment limits and Marimbus wetland location. The topographic profile (A - A') show Pai-Inácio anticline to Una-Utinga syncline (MAGALHÃES et al., 2015), with water flow to the east.

The climate of Chapada Diamantina is humid, being an enclave a semiarid domain. This region is a point of convergence of air masses, which generates a very complex climate mosaic. Four air masses act in this region: Continental Equatorial; Continental Tropical; Atlantic and Polar Tropical. Their joint action provides a rainy tropical forest climate with 1 to 3 dry months (KÖPPEN, 1936). The eastern edge of the mountain is wetter and may be the natural cause of Una-Utinga sedimentary basin carbonates dissolving faster and developing a lowered valley.



Figure 2 | Geological domains around Marimbus wetland (SAMPAIO et al., 1994).

MATERIALS AND METHODS

Stable isotope analysis (δ^{18} O and δ^{2} H) of water surface

Surface water samples were collected from the Marimbus wetland, São José, Santo Antônio, and Paraguaçu rivers to determine their origin through ¹⁸O and ²H isotopic analysis. The samples were packaged and stored in amber glass bottles with caps and lids, with volumes equal to 50 mL. During collection, the vials were filled to avoid isotopic fractionation. Each vial was identified, covered with clear plastic wrap, and kept refrigerated until analysis. The ¹⁸O and ²H measurements were made by Mass Spectrometer (Finningan MAT Delta Plus) and H-Device Thermo Quest Finningan automatic reactor at the Applied Nuclear Physics Laboratory of the Federal University of Bahia. The measurement error is ± 1 ‰ for hydrogen and ± 0.1 ‰ for oxygen.

The method presented by BRAND et al. (2000) was used to determine the deuterium-hydrogen ratio (D / H). The authors propose the transformation of water into hydrogen by reducing water at 850°C with metallic chrome. In this case, approximately 1.0 μ l aliquots of each water sample are injected into an automatic reactor, where the oxidation reaction of chromium occurs at 850°C, with the consequent release of H₂. The released H₂ enters the mass spectrometer, where it is analysed. The technique used to determine the δ^{18} O values in water is the isotopic equilibrium between carbon dioxide and water at a controlled temperature of 25°C for at least 18 hours (BRAND et al., 2000).

RESULTS

The origin of water's source

To determine the origin of the Marimbus wetland waters, isotopic analyses were performed at several points (Figure 2). The samples presented values of $\delta^{18}O$ (V_{SMOW}) and $\delta^{2}H$ (V_{SMOW}) ranging from -21.1 ‰ to 9.0 ‰ and from -3.13 ‰ to 3.31 ‰, respectively. Most of the samples presented data coinciding with the global meteorological curve (CRAIG, 1961), due to the marked influence of precipitation in the runoff.

Figure 3 shows the excess deuterium parameter of the waters collected in the Marimbus wetland. The values of this parameter ranged from -21 ‰ to +17 ‰. The figure shows a group of samples with negative values and another with positive values of this parameter. Samples MB1 through MB6 were collected in the permanently flooded area. MB1 to MB3 in the Encantada pond, MB4 and MB5 in a large lake, and MB6 in a shallow lake that undergoes more evaporation due to the little water and water depth volume, presenting the most negative value of excess deuterium (-21 %). Samples MB1, MB2, MB3, MB4, MB5, and MB6 show different behaviors than the other samples. They have a negative excess deuterium parameter, consisting of a higher water enrichment in δ^{18} O concerning δ^2 H. Therefore, the points located in the floodplain (annually flooded) of the north and central portions of the Marimbus contain water that presents an underground recharge component that undergoes considerable evaporation. To confirm the different isotopic compositions, a local evaporation line was developed only for samples MB1 to MB6. The following linear regression defined this curve: $\delta^2 H =$ $5.097\delta^{18}$ O - 8.76 ‰. Note that the slope coefficient of line 5.097 is less than that of the Global Meteoric Line (GML), 8, which in turn, characterizes water presenting more evaporation (ROZANSKI et al., 1993).



Figure 3 | Excess deuterium parameter (‰) in the surface waters in the Marimbus wetland.

The negative excess deuterium in these samples indicates waters undergoing considerable evaporation or underground recharge with waters more evaporated than precipitated. When evaporation occurs in water bodies, deuterium-containing water molecules evaporate more quickly than ¹⁸O-containing molecules. This effect causes an

¹⁸O enrichment concerning deuterium in the remaining water, and consequently, the calculated values of deuterium excess will become more negative as its evaporative loss increases. Samples collected between sites MB7 and MB20 show a significant influence of rainwater. The sample points in the chart below are very close to the GML.

Another evidence of rainfall in the isotopic composition is recorded in the values of excess deuterium that varied between +6.1 and +16.5‰, with an average value of +10.9±3.0‰, very close to the linear coefficient of the GML $\delta^2 H = 8$. $\delta^{18}O+10.8$ ‰. It does not corroborate the values obtained by Sales (2017), when the Santo Antônio river crossed carbonate rocks (Figure 4). There, the excess deuterium, calculated with their isotopic data, ranged from +9.3 to +16.2‰, with an average value of +12.9±2.2‰ (Figure 4). MB19 and MB20, collected in the Garapa and Paraguaçu rivers before reaching the Pantanal, presented the highest values of excess deuterium: + 14.8 ‰; + 15.3 ‰ and + 16.5 ‰, respectively.



Figure 4 | Excess deuterium parameter, and stable isotopic data δ^{18} O in the surface waters in the Marimbus wetland (in green) and from the carbonate karstic aquifer (in blue), and red line represents the Global Meteoric Line.

DISCUSSIONS

Hydrological behavior analysis indicates that Marimbus is a freshwater wetland, flooding periodically, currently located in a lithological depression. However, the isotopic

enrichment of its waters can result from the recharging of cloud rains that are not generated in the region, with several consecutive episodes. This causes a rapid depletion of the ¹⁸O in the cloud rendering positive excess deuterium. The data collected in the southern portion points MB8 to MB18 exhibit slightly positive deuterium values, closer to the value of the GML coefficient, indicating that the meteoric waters were their primary source of recharge. The MB16 and MB17 points, collected in the southern Marimbus wetland, show the lowest values of deuterium for this data group: +7.9 and +7.6 ‰, respectively. The MB7 point, gathered at the confluence of the São José and Santo Antônio rivers, presents the lowest value of positive deuterium due to its proximity to the sedimentation rings of the central portion of the wetland. It suggests the interaction between groundwater and river, which maintains the minimum levels in the dry period and amplifies the quotas in the rainy periods. The similarity in isotopic information at these points is due to the marked influence of precipitation on runoff. These waters are typical of the floodplain, which remains saturated for extended lengths of time (back swamps) and is often isolated from the river channel due to aggradation occurring elsewhere on the floodplain (Lisenby et al., 2019).

The waters in the carbonate karstic aquifer that feed into the springs of the Santo Antônio river in the Irecê carbonate basin range from calcic sodium chlorinated composition to calcium bicarbonate (Salles, 2017). The isotopic composition of aquifer waters refers to the natural waters of an isolated karstic system, its isotopic signature distinct from the waters of the Marimbus wetland (see Figure 2). Still, these body waters are alkaline saline and present pH values of up to 10, with the presence of bicarbonate, chlorinated and sodic waters (Barbiéro et al., 2002). Some of these ponds are isolated from pluvial surface flow and are characterized by white-sand beaches and brackish to saline water during Holocene-Pleistocene.

CONCLUSIONS

In the Marimbus wetland, the nature of the aquatic-terrestrial interface is spatially and seasonally shifting, which can be used to classify water accumulation as a wetland. Remote sensing was used for the consistent decadal mapping and delineation of the Marimbus wetland, identifying the permanent, seasonal and temporary hydrological changes. The sinkhole's morphological features at the Marimbus wetland area are not of carbonate karstic origin since the isotopic signature is within the global meteoric curve, indicating that its source was rainfall and that it is undergoing intense evaporation.

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