



Hydrogeochemical and Isotopic ($\delta^2\text{H}$ - $\delta^{18}\text{O}$) Investigations of Hydrologic Dynamics of the Southern Urucuia Aquifer System, Brazil
Investigação Hidrogeoquímica e Isotópica ($\delta^2\text{H}$ - $\delta^{18}\text{O}$) da Dinâmica Hidrológica do Sistema Aquífero Urucuia Meridional, Brasil

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Resumo

A integração de dados hidrogeoquímicos e isotópicos ($\delta^2\text{H}$ - $\delta^{18}\text{O}$) possibilitou a reconstrução da dinâmica hidrológica do Sistema Aquífero Urucuia meridional. Este sistema é uma combinação de aquíferos que são responsáveis pela perenidade dos rios durante a recessão das chuvas. Neste estudo, foram coletadas amostras de água de precipitação, superficiais e subterrâneas. A interpretação dos dados hidrogeoquímicos permitem a subdivisão dos aquíferos em três tipos principais: livre regional, confinado e livre com nível freático profundo. Esse último têm origem a partir de uma deflexão do fluxo subterrâneo no extremo ocidental da área de estudo. A ocorrência de níveis silicificados e fraturados segmentam os tipos aquíferos e representa uma zona de mistura e interface, permitindo uma drenança vertical entre os aquíferos e uma grande variabilidade de fácies hidrogeoquímicas. A evolução hidrogeoquímica ocorre através de sistemas de fluxo local, intermediário e regional. O acúmulo de sólidos dissolvidos é o principal mecanismo de controle da composição da água subterrânea representada pelas mudanças sistemáticas de espécies aniônicas de HCO_3 para SO_4 a Cl , e troca catiônica entre Ca e Na . A descarga ocorre através do escoamento de base, que têm composição híbrida de fácies Na-Ca-Cl a Na-Cl entre aqueles dos aquíferos livre regional e confinado. A análise dos isótopos estáveis evidencia que as águas superficiais e subterrâneas estão localizadas na mesma faixa de valores, o que indica uma conexão entre os reservatórios. Durante a estação chuvosa, a composição isotópica das do aquífero livre regional se assemelha à da precipitação, sendo a recarga realizada principalmente pela infiltração direta das águas das chuvas. No entanto, ocorre uma modificação desta composição na estação seca devido ao forte enriquecimento isotópico causado pelo processo de evaporação. Dessa forma, a variação sazonal na composição isotópica representa um ciclo contínuo. Em outras palavras, à medida que a estação chuvosa se aproxima, a coluna de ar atmosférico fica cada vez mais saturada com vapor de água, o que resulta em uma diminuição considerável dos efeitos da evaporação na recarga das águas subterrâneas.

Palavras-chave: Sistema Aquífero Urucuia Meridional; evolução hidrogeoquímica; isótopos estáveis

Abstract

The integration of hydrogeochemical and isotopic data ($\delta^2\text{H}$ - $\delta^{18}\text{O}$) allowed the reconstruction of the hydrological dynamics of Southern Urucuia Aquifer System. This system is a combination of aquifers that are responsible for the perennity of the rivers during the rainy recession. In this study, water samples were collected from three sources: rainfall, rivers and pumping wells. The hydrogeochemical data lead to subdivide the aquifers in three main types: regional unconfined, confined, and unconfined with deep

water level. The unconfined aquifer with deep water level originates from an groundwater flow deflection in the westernmost portion of the study area. The occurrence of silicified and fractured levels divide the aquifer types and represents a mixing and interfaced zone, allowing a leakage between aquifers and a great variability of hydrogeochemical facies. The hydrogeochemical evolution occurs by local, intermediate and regional flow systems. The buildup of dissolved solids is the major controlling mechanism of the groundwater composition represented by the systematic changes of anion species from HCO_3 to SO_4 to Cl , and cationic exchange between Ca and Na . The discharge occurs through the baseflow of rivers, which have hybrid composition between regional unconfined and confined aquifer from Na-Ca-Cl to Na-Cl . The analysis of stable isotopes shows that the surface water and groundwater are located in the same range of values, which indicates a connection between the reservoirs. During the rainy season, the regional unconfined isotopic composition becomes similar to the precipitation isotopic composition, with the main recharge occurring mostly by direct infiltration of rainwater. However, there is a modification of this composition in the dry season due to strong isotopic enrichment caused by the evaporation process. The seasonal variation in the isotopic composition represents a continuous cycle. In other words, as the rainy season approaches, the atmospheric air column becomes increasingly saturated with water vapor, what results in a considerably diminishment of evaporation.

Keywords: Southern Urucuia Aquifer System, hydrogeochemical evolution, stable isotopes

1 Introduction

The Urucuia Aquifer System (UAS) (Gaspar & Campos, 2007) is the most important hydrogeologic unit in the Sanfransiscana basin. This region has shown, over the years, an increasing water demand for socio-economic development, which is a factor that affects the volume of water flowing on the surface and results in significant geoenvironmental change. The most relevant impact is the depletion of grantable capability of surface water sources (Aquino *et al.*, 2003). Thus, some production segments are turning to the drilling of deep wells, requiring the generation of new technological and scientific knowledge for the rational use of each source in order to maintain a balance between surface and groundwater systems.

In recent decades, the hydrochemical aspect and the quality of the water in the UAS have received the attention of some researchers (e.g., Aquino *et al.*, 2003; Barbosa, 2016). However, there are few studies related to the application of stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) (e.g., Nascimento *et al.*, 2003). The objective is to characterize the hydrological dynamics of the UAS in its southern portion – Formoso and Arrojado river basins – through the identification and quantification of the major chemical constituents, properties of rainwater, surface water and groundwater, and analysis of stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$). This allows the reconstruction of the local hydrological cycle from its origin as precipitation, to aquifer recharge, groundwater flow and river discharge.

2 Sampling and Analytical Methods

Hydrochemical and isotopic analyses ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) were obtained in 39 shallow groundwater wells and at 7 different localities of the rivers, over four campaigns: two of them were performed in groundwater during dry season in the months of September/October 2005, and May 2006. The other two analyses were performed in December 2005 and November 2006, when the groundwater presented a wet season. Additionally, two samples of rainfall were

collected. The sampling procedure consisted of purging the water wells in compatible flows with its ability to recovery, allowing the removal of stagnant water and the collection of a representative sample.

Water samples for chemical analyses were stored in polyethylene plastic bottles of 1000 mL acidified with nitric acid (for cations), and amber glass bottles of 1000 mL acidified with sulfuric acid to the analyses of the compounds of the nitrogenized series and phosphate. All samples were refrigerated. Measurement of temperature, pH, conductivity, and dissolved oxygen took place in the field. Geochemical analyses were performed using the atomic absorption spectrometry (ASTM) at the Institute of Geosciences of the Federal University of Bahia (UFBA), and the methodology followed the Standard Methods for the Examination of Water and Wastewater (Rice *et al.*, 2017).

In collection and storage of samples for determination of stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$), amber glass bottles of 50 ml were used. These data were obtained using a mass spectrometer (MAT Delta Plus model, Termo Finnigan), an automatic reactor (H-Device Thermo Quest Finnigan) specific for the D/H ratio analyses, and automatic preparation system of online samples (Gas Bench II Finnigan) specific to the analysis of $\delta^{18}\text{O}$, in the Nuclear Physics Laboratory of the Institute of Physics (UFBA). The oxygen isotopic ratios were analyzed using the water- CO_2 equilibration method, with an accuracy of $\pm 0.1\%$ (Epstein & Mayeda, 1953). Hydrogen isotope ratios were determined by the method of reduction of Cr (Brand *et al.*, 2000), with accuracy of 1%. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values were reported in the delta notation, in part per thousand, and were normalized using the Vienna Standard Mean Ocean Water (VSMOW).

3 Geomorphological and Climatic Characteristics

The rivers located in the studied area make up a drainage system from the left margin of São Francisco river (Figure 1). Altitude varies from 900-1000 in the frontier between Goiás and Bahia to 600-700 m in the

eastern border of the aquifer., where the relief gently slopes to east. This extensive plateau develops an accelerated process of mechanized agriculture with continued irrigation, which results in the almost complete replacement of natural vegetation. These factors have led to an intensive exploitation of water which is collected either directly in the courses of the rivers, or it is extracted from the underground storage via deep wells. Most rivers are perennial and fed by the baseflow. They form broad floodplains with wide

lowlands, sometimes receiving contributions of short pluvial channels. The highest altitudes in the western portion form the drainage divide between São Francisco and Tocantins rivers watersheds. In general, the interfluvies have sandy surface formations that facilitate the infiltration of rainwater. Currently, the most active morphogenetic process is the runoff, with relocation and transportation of sand towards the lower lands.

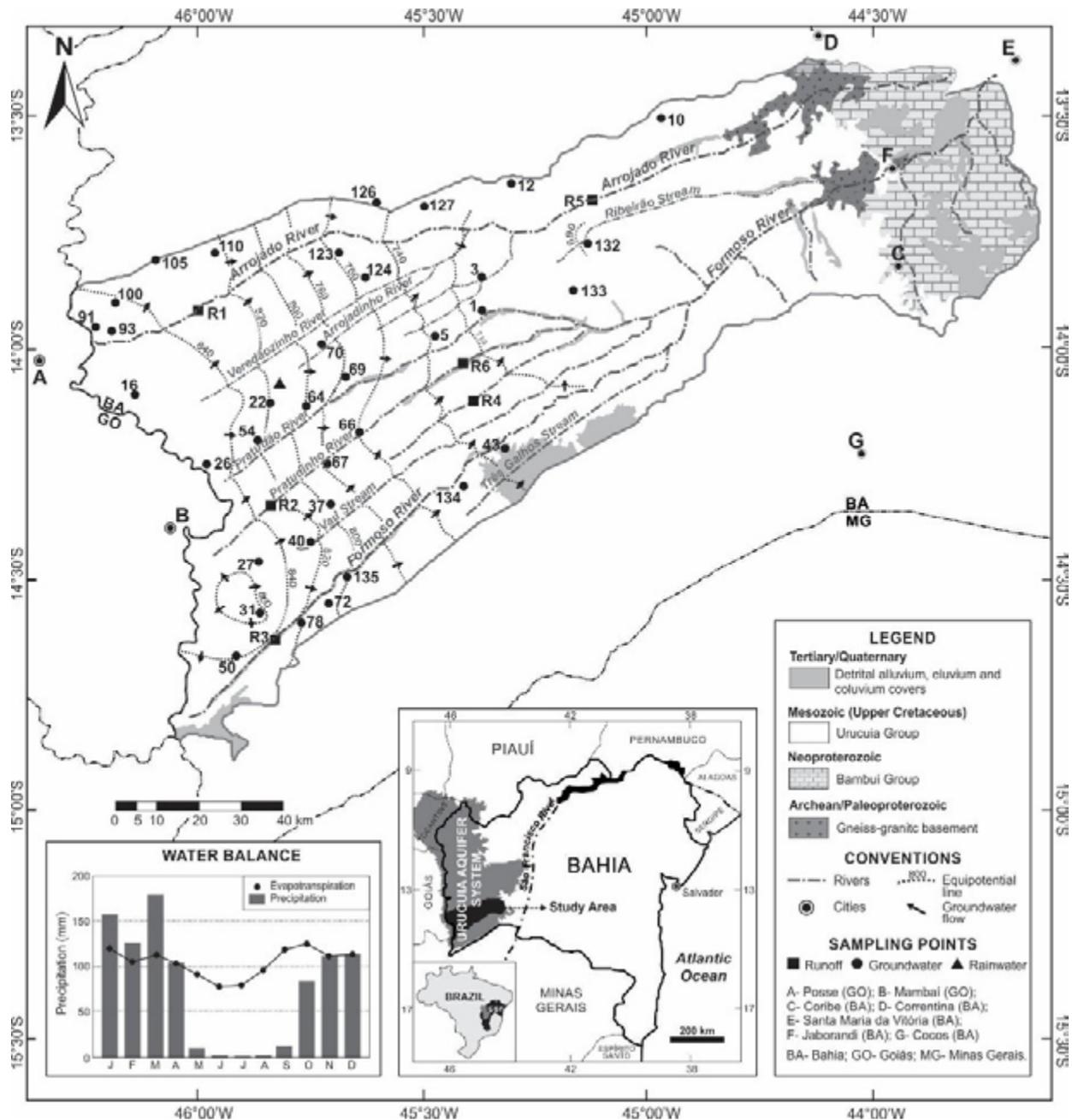


Figure 1 Geologic map of the Formoso and Arrojado rivers watersheds highlighting the sampling points of runoff, groundwater and rainwater, potentiometry and the groundwater flow (water balance for Gatos rainfall station between 1945-1974).

The climate is megathermal - average temperature of the coldest month above 18°C -, and summer rain - less rainy month with precipitation below 60 mm. The precipitation regime comprises isohyetal ranges between 800 and 1,500 mm, and the level of precipitation varies increasingly towards west. The average annual temperature for the studied area is 23.2°C. The average maximum temperature is 32°, and 18°C is the average minimum temperature. The relative humidity has a monthly average ranging from 45% in August to 79% in December, with an annual average of 68%. The rainy season occurs between early October and April, with November to January being the wettest quarter (51% of total precipitation) linked to atmospheric currents of continental nature. From May to September, it gets practically dry (4% of the total precipitation), but the rivers remain perennial due to exudation of UAS.

4 Geological and Hydrogeological Setting

The studied area is located in Formoso and Arrojado rivers watersheds, in Sanfranciscana Basin - São Francisco Craton (CSF). Both areas compose and integrate the southern portion of the UAS, which is an association of aquifers that occur in the Urucuia Group domain. It is the main geological unit in this area represented by a set of siliciclastic rocks of Upper Cretaceous age. In general, the substrate consists of the pelitic-carbonate sequence of Bambuí Group, and Archean-Paleoproterozoic granite-gneiss rocks in the eastern portion. Urucuia Group is divided into two units: the basal unit called Posse Formation and the upper one, named Serra das Araras Formation (Figure 1) (Campos & Dardenne, 1999).

The Posse Formation consists of fine to medium eolian sandstone. It is pinkish to reddish, friable and usually bimodal sediments. It presents large-sized cross-stratification, and minor plan-parallel ones, which is characteristic of a desertic environment of dune fields. The Serra das Araras Formation comprises of conglomerates, sandstones, and mudstones sequences, which have silica cementation and iron oxides as an intense and common process. The sequences represent superimposed sedimentation cycles in river environments developed in wide plains with large range of discharge, probably wadi fans facies. The contact of Posse and Serra das Araras Formations is abrupt, presenting an erosive surface considered as a megasurface associated with climate change in the Urucuia Group depositional environment (Campos & Dardenne, 1999).

At the current state of knowledge, the UAS region is considered uniform and homogeneous (Gaspar & Campos,

2007; Schuster *et al.*, 2010). However, eodiagenetic processes and changes in sedimentation pattern along its extent impart important hydrodynamic changes to the system and, consequently, the differentiation of regional unconfined, perched, unconfined with deep water table, and confined aquifers (Gaspar & Campos, 2007).

The groundwater flow occurs preferably from SSW to NNE, with a compartmentalization of the aquifer by a groundwater divide at the western end, approximately N-S direction, which separates the groundwater flow to east toward the São Francisco River basin and to west toward the Tocantins River basin. This configuration represents an example of asymmetry between hydrogeological and hydrographic basins (Barbosa, 2016).

5 Results and Discussion

5.1 Hydrochemical Characteristics

The statistical summary of the physico-chemical analysis of groundwater and surface water (Table 1) shows a variation in the pH of 4.4 to 7.4, indicating that the UAS waters varies from neutral to slightly acidic. The low electric conductivity (EC) and total dissolved solids (TDS) confirm its poorly mineralized condition. Most of the samples presents values below the limits of detection of the analytical method.

Most of the ions exhibits values within the potability limit according to the ordinance 2914/2011 of the Brazilian Ministry of Health, with the exception of the iron ions with average values above 0,3 mg/L. Given that the UAS groundwater is characterized by abundant CO₂, low pH, and lack of dissolved oxygen, iron appears in the form of dissolved ferrous bicarbonate (Barbosa, 2016).

Piper (1944) hydrochemical diagrams allow the classification of water in terms of its dominant ions expressed as total percentage of cations and anions (Figure 2). The analytical values of the major elements characterize the UAS as a set of interrelated aquifers, and establishes the hydrogeochemical evolution of their natural waters. Shallow groundwater, surface water, and rainwater samples were interpreted and deep groundwater bibliographic reference data were incorporated (e.g., Aquino *et al.*, 2003; Nascimento, 2003).

The analysis generated the identification of three hydrochemical facies: Ca-Cl, Ca-HCO₃, and Na-Cl, corresponding to 52%, 21%, and 27% of the samples, respectively. The hydrochemical results (Figure 2) reflect the existence of aquifer units related to the southern UAS, i.e., regional unconfined aquifer, confined aquifer, and unconfined aquifer with deep water level.

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Item	Groundwater (*)				Surface water (*)				(**)	(***)
	Mean	Min	Max	S.D	Mean	Min	Max	S.D		
pH	5.73	4.37	7.40	0.71	5.13	4.20	6.56	0.51	4.01 – 7.68	6.50 – 8.50
TDS	15.34	<4.00	135.00	24.00	5.29	<4.00	12.00	2.03	4.00 – 164.00	1,000
EC	19.38	3.60	234.00	33.56	5.90	<4.00	13.00	2.56	2.40 – 124.00	1,250
Ca ²⁺	1.80	<0.10	41.00	5.61	0.44	<0.10	4.78	1.00	0.02 – 3.71	200
Mg ²⁺	0.17	<0.02	3.20	0.41	0.71	0.03	13.20	2.86	0.001-1.100	150
Na ⁺	0.33	<0.10	6.60	0.65	0.40	0.11	2.39	0.50	0.009 – 2.400	200
K ⁺	0.28	<0.10	1.20	0.15	0.48	<0.10	4.74	0.98	0.002 – 2.400	10
Fe	0.66	<0.05	7.28	1.13	0.12	<0.05	0.25	0.05	0.014 – 6.420	0.3
HCO ₃ ⁻	8.26	<1.00	122.00	16.26	2.07	2.80	<1.00	0.68	0.36 – 5.27	500
Cl ⁻	3.48	<2.00	20.00	2.77	2.91	<2.00	11.00	2.07	0.07 – 2.99	250
NO ₃ ⁻	0.35	<0.20	4.37	0.48	0.33	<0.20	1.60	0.36	0.012 – 0.139	10
SO ₄ ²⁻	1.91	<1.00	9.30	0.80	1.80	1.10	<2.00	0.37	0.024 – 4.22	250

(*) Sampling campaigns, 1st - 30/09/2005 to 05/10/2005; 2nd - 03 to 14/12/2005; 3rd - 16 to 24/05/2006; 4th - 14 to 29/11/2006; (**) Bibliographic reference value Aquino *et al.*, 2003; (***) Environmental quality standards - Decree 2914/2011 of the Ministry of Health and World Health Organization and the US Environmental Protection Agency (EPA).

Table 1 Statistical summary of the physico-chemical analysis of groundwater and surface water of the Arrojado and Formoso rivers watersheds.

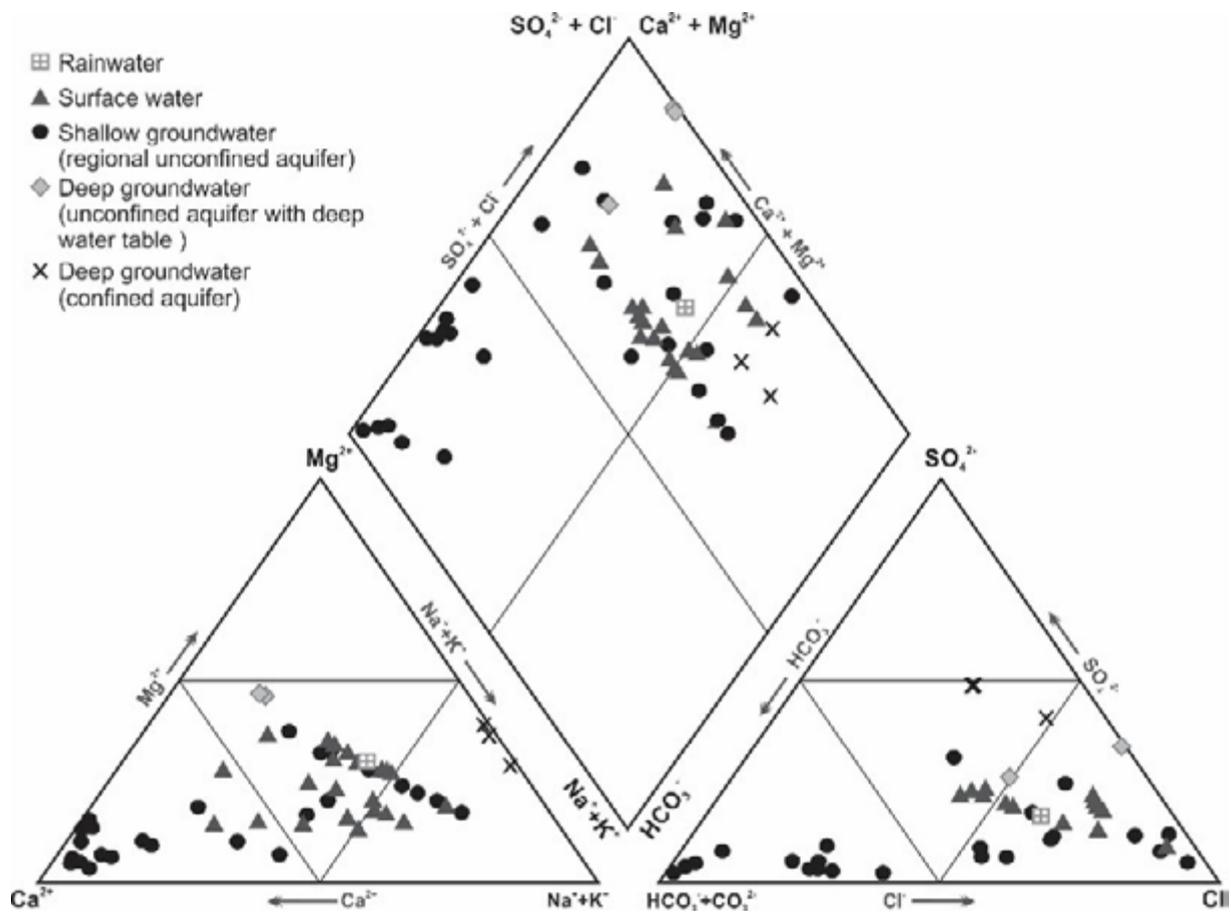


Figure 2 Graph of the classification of shallow and deep groundwater, superficial water and rainwater through the Piper (1944) diagrams.

5.2 Rainwater and Surface Water

The infiltration of rainwater in large areas of the flat relief is primarily responsible for the recharge of the UAS, and the morphology of the relief has a paramount importance for the replenishment of the UAS. Chemically, the recharge waters have a composition of mixed type Na-Mg-Ca-Cl- HCO_3 . The rainfall heights have isohyets typically higher than 1,000 mm per year. However, the expansion of agricultural areas and soil compaction caused by soil management tend to increasingly hinder the recharge process (Gaspar & Campos, 2007).

The main rivers have a composition of Na-Cl and mixed Na-Ca-Cl type.

5.3 Regional Unconfined Aquifer

The regional unconfined aquifer has a large spatial extent and a variable water table. The average value for the regional water table depth is 39 m, obtained by electrical geophysical methods and well data (e.g. Barbosa, 2016). Groundwater is predominantly extracted by wells, which are less than 100 meters deep and commonly located in the headquarters of farms. It is used primarily for domestic supply and as input for dilution and application of pesticides on crops (Gaspar & Campos, 2007). The aquifer displays a great variety of hydrochemical facies (i.e., Ca- HCO_3 , Ca-Na-Cl and Cl-Na), whose progress occurs in local and regional flow systems (Figure 2).

5.4 Confined Aquifers

Confined aquifers occur in depth, underlying the regional unconfined aquifer. It is common in the western-central portions of the study area, where persistent fractured silicified zones are present in different stratigraphic levels. In general, these levels work as aquitards, allowing a vertical leakage between regional unconfined and confined underlying aquifers.

The potentiometric levels are variable with average depth of 20 m in the central portion of the basin. It has a high hydrogeological potential with average specific capacity of 12 $\text{m}^3/\text{h}/\text{m}$. The deep wells are used in irrigation projects through center pivots, with flow rates of exploitation above 300 m^3/h , small drawdown, and long radius of influence (above 2,500 m) (Barbosa, 2016). The water has a great residence time. The composition is of Na-Cl and mixed Na- SO_4 -Cl (Figure 2).

5.5 Unconfined Aquifer with Deep Water Level

The unconfined aquifer with deep water level is situated in the western extreme of the UAS. Its east side is delimited by an N-S groundwater flow divide. The potentiometric surface progressively increases in depth towards the west, where it reaches more than 200 m.

The unconfined condition is characterized by position of these levels above the regional water table. The discharge occurs under conditions of high hydraulic gradient, and determines a relatively rapid flow system. It consists of mixed Ca-Mg-Cl water (Figure 2), which feeds the rivers in the karst-crystalline system of Tocantins river watershed (Gaspar & Campos, 2007).

5.6 Isotope Characteristics

Stable isotopes in water (^{18}O and ^2H), affected by meteorological processes, provide a characteristic “fingerprint” of their origin, and represent a key feature for the investigation of the groundwater origin. In the studied area, the rainfall is progressively depleted in heavy isotopes, with strong seasonal differences (Figure 3). The global meteoric water line (GMWL) is an average of many local meteoric water lines (LMWL) controlled by characteristic climatic factors, including the source of the vapor masses, secondary evaporation, and seasonality of precipitation (Craig, 1961). These local factors affect both the deuterium excess (d) and the line slope (Table 2).

SAMPLE	1ª CAMPAIGN			2ª CAMPAIGN			3ª CAMPAIGN			4ª CAMPAIGN			
	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	d (‰)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	d (‰)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	d (‰)	$\delta^{18}\text{O}$ (‰)	v	d (‰)	
SURFACE WATER	R1	-4.2	-29	4.3	-4.1	-28	5.2	-4.3	-29	5.2	-	-	-
	R2	-4.2	-31	3.2	-4.0	-26	6.3	-4.0	-27	4.9	-3.8	-27	3.3
	R3	-4.3	-30	4.2	-5.6	-38	7.1	-4.4	-31	4.6	-4.4	-30	5.0
	R4	-4.3	-31	3.6	-4.8	-33	5.2	-4.4	-30	5.3	-4.4	-30	4.8
	R5	-4.3	-30	4.2	-5.1	-35	6.1	-4.4	-29	5.4	-4.3	-30	4.8
	R6	-	-	-	-	-	-	-4.5	-29	6.9	-4.5	-32	3.5
	R7	-	-	-	-	-	-	-	-	-	-4.4	-30	5.5

Table 2 $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotope data and deuterium excess (d) of surface water, groundwater and rainwater (*) of southern UAS.

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SAMPLE	1ª CAMPAIGN			2ª CAMPAIGN			3ª CAMPAIGN			4ª CAMPAIGN			
	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	d (‰)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	d (‰)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	d (‰)	$\delta^{18}\text{O}$ (‰)	v	d (‰)	
GROUNDWATER	01	-4.8	-34	4.2	-	-	-	-	-	-	-4.6	-31	6.3
	03	-4.7	-34	3.5	-	-	-	-	-	-	-	-	-
	05	-4.4	-31	3.7	-4.3	-29	6.1	-	-	-	-4.2	-28	5.3
	10	-4.4	-33	2.9	-4.7	-32	5.5	-4.7	-30	8.0	-4.7	-32	6.2
	12	-4.2	-29	4.4	-4.5	-30	6.2	-4.5	-27	8.9	-4.4	-30	5.5
	16	-4.3	-30	4.7	-4.0	-27	5.8	-4.3	-25	9.0	-4.3	-25	10.2
	22	-4.5	-31	4.9	-4.7	-33	5.2	-4.5	-30	6.3	-4.5	-31	4.8
	26	-4.5	-32	3.7	-4.6	-30	6.5	-	-	-	-4.6	-33	4.5
	27	-4.6	-32	4.4	-4.6	-31	6.1	-4.6	-31	5.4	-4.6	-31	5.9
	31	-4.2	-31	2.4	-4.5	-32	4.5	-4.6	-29	7.5	-4.6	-32	5.3
	37	-4.9	-33	5.8	-5.0	-34	5.9	-5.1	-33	8.0	-5.2	-35	6.4
	40	-4.7	-33	5.3	-4.7	-32	5.7	-	-	-	-4.8	-32	6.4
	50	-4.7	-32	5.1	-	-	-	-	-	-	-	-	-
	54	-4.5	-31	5.0	-4.7	-32	5.3	-4.8	-31	6.8	-4.7	-32	5.6
	56	-	-	-	-	-	-	-	-	-	-4.4	-30	4.7
	64	-4.5	-31	5.1	-4.6	-32	4.7	-	-	-	-4.6	-31	5.6
	66	-5.1	-34	6.5	-5.2	-34	7.9	-5.1	-34	7.2	-5.2	-35	6.6
	67	-4.9	-33	6.0	-	-	-	-4.9	-33	6.0	-4.7	-32	5.4
	69	-4.9	-34	5.9	-4.9	-33	6.4	-4.8	-32	6.0	-4.6	-32	5.2
	70	-3.7	-30	-0.8	-4.5	-29	7.2	-	-	-	-4.6	-31	5.8
	72	-4.8	-33	5.6	-4.8	-34	4.6	-4.8	-32	6.4	-4.8	-33	5.9
	78	-4.7	-33	5.3	-4.6	-31	5.6	-4.7	-31	6.3	-4.5	-31	5.4
	88	-	-	-	-	-	-	-	-	-	-4.4	-30	4.8
	91	-4.0	-29	3.6	-4.3	-30	4.7	-4.6	-30	7.2	-	-	-
	93	-4.3	-32	2.5	-4.6	-33	4.0	-4.6	-29	7.8	-4.6	-31	5.8
	100	-3.8	-31	-0.8	-4.5	-30	6.2	-4.5	-29	7.0	-4.6	-31	6.4
	105	-4.2	-29	4.9	-4.1	-28	4.7	-4.2	-28	6.4	-4.2	-30	4.0
	110	-4.3	-31	3.8	-4.6	-32	5.0	-4.6	-29	7.7	-4.7	-32	5.9
	123	-4.1	-32	0.4	-4.8	-32	7.0	-4.8	-33	5.9	-4.8	-25	13.3
	124	-4.5	-32	3.9	-	-	-	-4.6	-30	7.3	-4.6	-34	3.2
	126	-4.4	-30	5.6	-4.5	-29	7.2	-4.4	-29	6.6	-4.5	-32	4.6
	127	-	-	-	-4.4	-28	7.4	-4.3	-29	5.2	-4.4	-33	2.8
	129	-4.2	-30	4.0	-	-	-	-	-	-	-	-	-
	132	-4.5	-30	5.7	-	-	-	-4.4	-30	5.6	-4.5	-31	5.4
	133	-4.6	-33	4.3	-4.6	-31	5.4	-4.8	-33	4.7	-4.8	-35	2.7
134	-4.9	-33	6.0	-4.9	-32	7.1	-	-	-	-4.9	-36	3.5	
135	-4.9	-33	5.8	-4.9	-32	7.1	-5.0	-33	6.7	-4.9	-34	4.9	
*	CH-01	-	-	-	-3.6	-20	8.7	-	-	-	-	-	-
	CH-02	-	-	-	-	-	-	-	-	-	-1.1	1.4	9.8

Table 2 Cont.

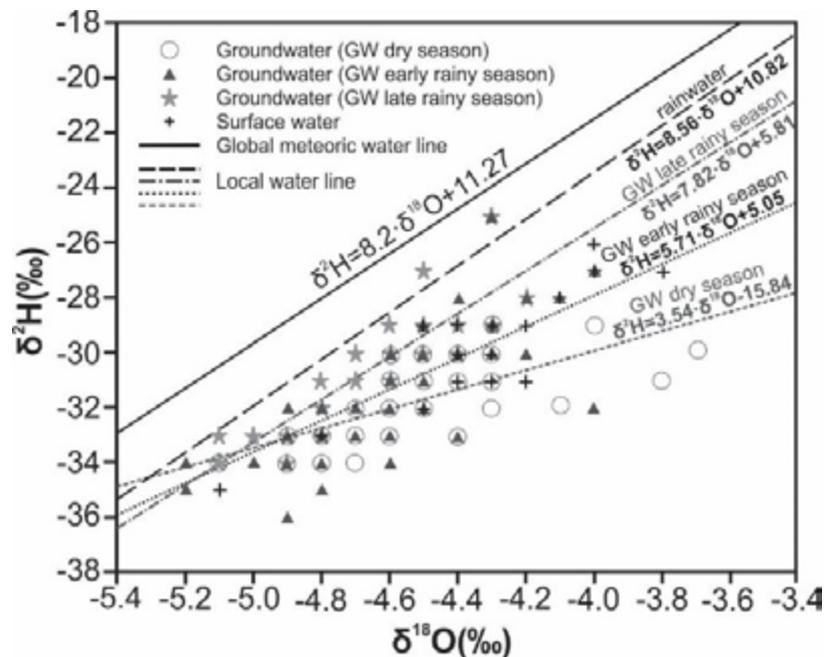


Figure 3 Graphical representation of $\delta^2\text{H}$ - $\delta^{18}\text{O}$ relationships for rainwater, groundwater (dry and rainy seasons) and surface water. Equation of global meteoric water line is extracted from Rozanski *et al.* (1993).

The isotopic composition of the rainwater (Table 2; Figure 3) shows a very close behavior to GMWL, representing the influence of Continental Equatorial humid air masses. It is originated in the western Amazon, and advances towards eastern Brazil, reaching the UAS and causing the so-called “summer rains” (Figure 4).

The recharge of the UAS corresponds to approximately 20% of the average rainfall (Barbosa, 2016); the other 80% is lost as runoff, evaporation, and transpiration by vegetation. While processes of runoff and transpiration have a small participation in the isotopic composition of the groundwater, the evaporation implies a systematic enrichment of the heavy isotopic content. Due to the process of evaporation, most groundwater samples present different isotopic values than the precipitation water (Figure 3).

The surface water and groundwater have isotopic compositions that lie practically in the same range of values (Table 2; Figure 3), which indicates the existence of a connection between the reservoirs, so that more than 90% of the UAS baseflow contributes to the total flow of rivers in the rainy recession. The isotopic signatures of groundwater during the rainy season (Figure 4) tend to approach the GMWL. During this period, the soil profiles probably have a small evaporation, indicating that the groundwater recharge occurs predominantly by direct infiltration of rainfall. In this case, macropores and preferential flow channels in the unsaturated zone allow the rapid movement of the water into the water table.

In the dry season (Figure 3), the isotopic composition of the surface water and the groundwater is significantly modified by rainfall. This is probably caused by strong enrichment due to evaporation shifting the local water line to a slope lower than 8. Thus, as it approaches the rainy season, the atmospheric air column becomes increasingly saturated and the effect of evaporation is significantly reduced (Figures 3 and 4).

5.7 Hydrogeochemistry Evolution Model

The evolution of the chemical composition in southern UAS can be determined by the hydrochemical facies commonly found in the recharge area, in groundwater flow systems path, and in the baseflow or discharge. Recharge is due to rainwater infiltration and occurs at the western end of the study area. In early flow path stage, the water shows a mixed composition of Na-Mg-Ca-Cl- HCO_3 . From this recharge originates the occurrence of local, intermediate, and regional flow systems (Figure 2 and 5).

The local flow system implies that the groundwater moves rapidly and does not undergo pronounced interactions with the substrate. Facies of Ca- HCO_3 are predominant, and provoke the first major chemical transformation of infiltration water. The movement of groundwater is active with very low TDS and acid pH. The water is enriched with the ion HCO_3 along the path in the vadose zone, derived from the dissociation of carbonic acid.

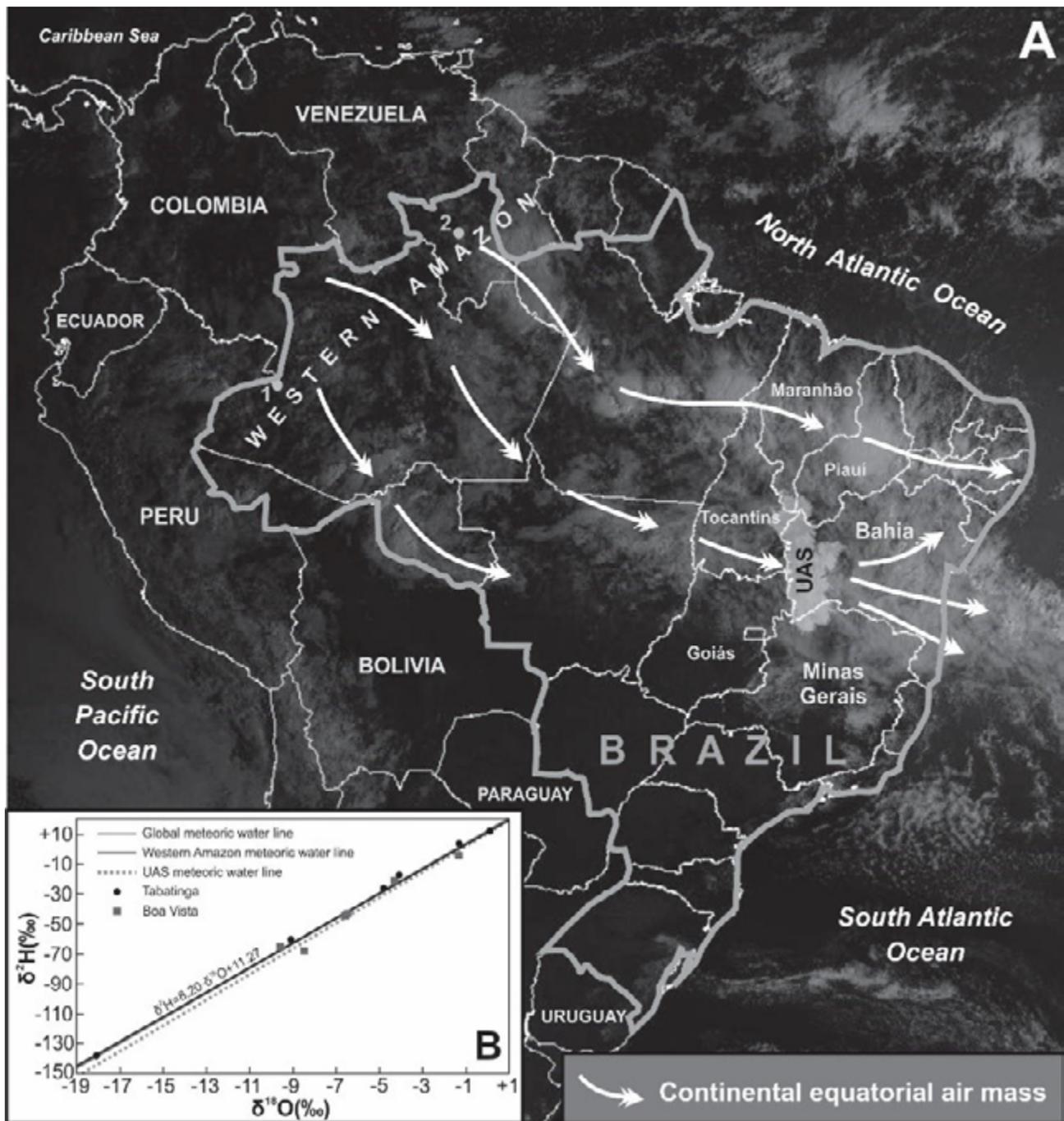


Figure 4 Dynamics of air masses in the atmosphere of South America. (A) Satellite image of the Instituto Nacional de Meteorologia (INMET) in November 2014 and (B) local meteoric water lines ($\delta^2\text{H}$ - $\delta^{18}\text{O}$) for rainwater in the Western Amazon after Honório (2007) and for the southern UAS after Barbosa (2016). Equation of global meteoric water line is extracted from Rozanski *et al.*, (1993).

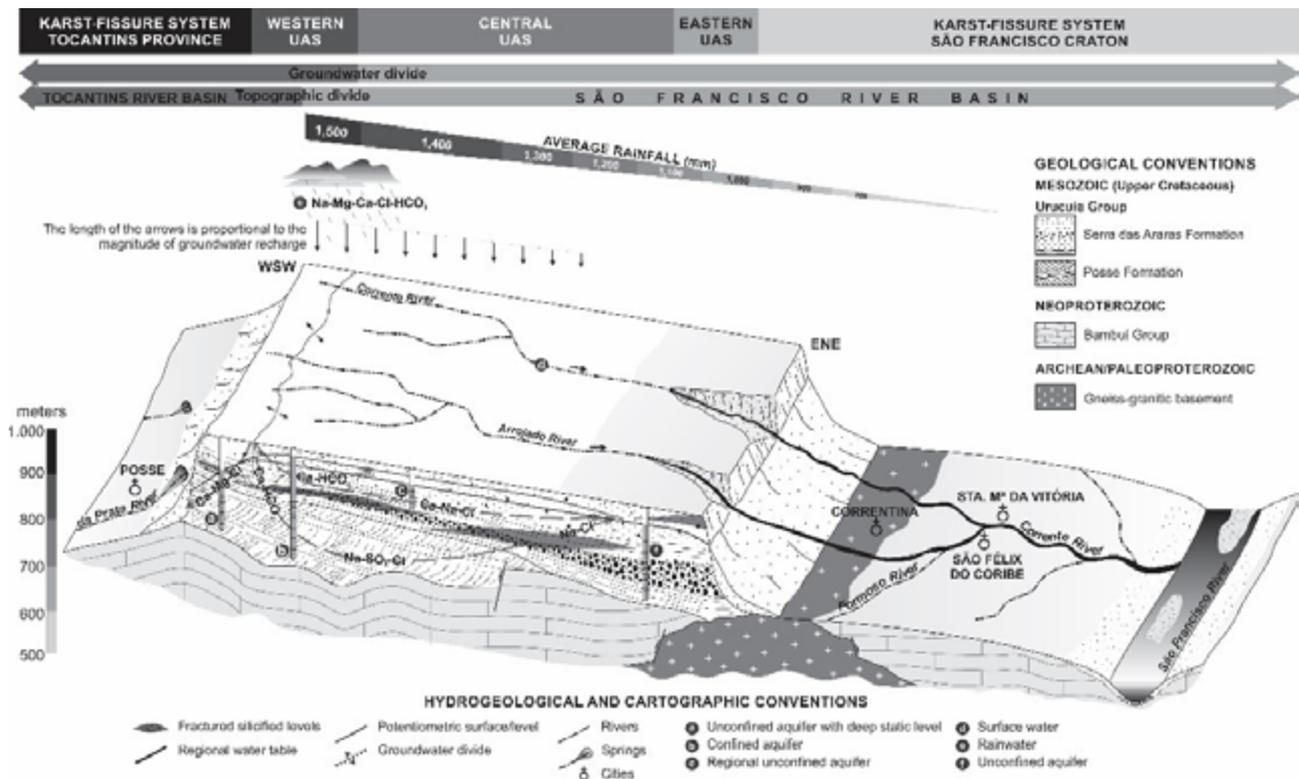


Figure 5 Schematic representation of the hydrogeochemical evolution model of the southern UAS (adapted from Barbosa, 2016).

In the intermediate flow system, the circulation is less active than the local system. The main change is from HCO_3 to Cl anions and Ca to Na cations. It is an evolution of Ca-HCO_3 , Ca-Na-Cl , Na-Ca-Cl , and Na-Cl facies, respectively. In deep and unconfined section of UAS, water moves slowly and it has a longer residence time and higher TDS. Probably, the mixture of water generates $\text{Na-SO}_4\text{-Cl}$ and Na-Cl facies, which characterizes the regional flow system. At the western end, limited by the groundwater divide, there is a progressive increase in the depth of the potentiometric surface. The discharge conditions occur under high hydraulic gradient, featuring a rapid change from Ca-HCO_3 to Ca-Mg-Cl facies.

Either part or all of this classic sequence of hydrochemical change can be a means for the identification of each aquifer type. The silicified and fractured sandstone levels are probably responsible for a vertical leakage between regional unconfined and confined aquifer. This features an interface and mixing zone, which explains the great compositional variability of the UAS waters (Figure 5). Surface water, the main zone of discharge, is composed of Ca-Na-Cl and Cl-Na facies. It largely represents the water volume refunded by the baseflow of the UAS in local, intermediate and regional flow systems.

6 Conclusions

In this study, the hydrochemistry and the signature of stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) in surface, groundwater and precipitation events were analyzed in the western UAS. Groundwater recharge occurs mainly between November and February by direct infiltration of rainwater. It presents mixed hydrochemical composition of Na-Mg-Ca-Cl-HCO_3 , and an isotopic composition very close to the GMWL. During this period, the UAS possesses a higher water table, which favours the renewal of its waters. In dry seasons, from May to October, the UAS presents a lower water table. The isotopic compositions of surface water and groundwater are modified with respect to the rainfall, due to strong enrichment caused by the evaporation process. During this period, the drought induces high pumping rates of deep wells. The seasonal variation of the isotopic composition represents a continuous cycle. In other words, when approaching the rainy season, the atmospheric air column becomes increasingly saturated, and the effect of evaporation decreases considerably.

After being recharged, the groundwater evolves according to local, intermediate, and regional flow systems. The local flow system has an active circulation, low TDS,

and consists of Ca-HCO₃ facies. In the intermediate flow system water evolves from Ca-Na-HCO₃ facies to Na-Cl. In relation to the previous one, there is an increase in TDS, and a less active circulation. Both are found in the shallow groundwater of regional unconfined aquifer. The regional flow system occurs in deep groundwaters with a slow movement, and an increased residence time. It has higher TDS, Na-SO₄-Cl facies, with the dominance of Na-Cl, which is a typical feature of the lower confined aquifer. At the western end, the unconfined aquifer with deep water level (Ca-Mg-Cl facies) is limited by a groundwater divide, with a progressive increase in depth of potentiometric surface in a relatively fast flow system. In this context, the groundwater discharges under conditions of high hydraulic gradient.

The discharge occurs through the baseflow of rivers with a hybrid composition from mixed Na-Ca-Cl to Na-Cl. This indicates that the river is fed by both the regional unconfined aquifer and the confined aquifer. The chemical and isotopic compositions of surface water and groundwater have small differences, which indicates the existence of a connection between the reservoirs. The occurrence of silicified fractured levels determine the existence of the different types of aquifers in UAS, and they probably represent a mixing and interface zones, where a leakage process between the aquifers and the great variability of hydrogeochemical facies may take place.

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