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Groundwater isotopic data as potential proxy for Holocene paleohydroclimatic and paleoecological models in NE Brazil

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ABSTRACT

Holocene paleoclimatic patterns in NE Brazil are recognized to present singular characteristics when compared with the remaining tropical South-America. In particular, isotopic variations in speleothem calcite highlight that in contrast to the rest of tropical SA, NE Brazil experienced humid conditions during lower summer insolation, i.e. throughout the Early-Mid Holocene, and aridity when, as nowadays, summer insolation was high. In parallel, paleobotanical and palynological investigations suggest that these wetter conditions, also associated with colder climate, could have promoted the setting of ecological corridors between the current Amazonian (continental) and Atlantic (littoral) forests. In this context, this work aims at showing how groundwater isotopic data could be used as a complementary proxy to further explain these Holocene paleohydroclimatic and paleoecologic processes. By comparing $\delta^{18}O$, δ^2H and d-excess of modern waters with Early-Mid Holocene groundwater in Recife (Pernambuco state, NE Brazil), differences in recharge patterns and moisture origin can be constrained. We find that Early-Mid Holocene waters present higher d-excess than the modern groundwater. Given that the Early-mid Holocene colder and wetter conditions (higher relative humidity) should lead to a reverse trend, i.e. lower d-excess, we hypothesize that the groundwater moisture sources was heavily recycled. Such a hypothesis would be consistent with the presence of a rainforest-type ecosystem, similar to the present Amazonian forest, in the currently arid NE Brazil. These observations highlight the potential added value of the groundwater isotopes proxy to discuss the interrelationships of paleohydrological and paleoecological patterns during the Early-Mid Holocene. These new proxies might allow the spatio-temporal extent of the above-mentioned ecological corridors to be discussed.

1. Introduction

Over the last two decades, the Holocene climate reconstructions for South-America Monsoon System (SASM) historically poor, have been subject to increasing investigation (Vimieux et al., 2009; Vuille et al., 2012; Prado et al., 2013a; Baker and Fritz, 2015). These reconstructions are based on combination of large-scale numerical models (e.g., IPSL-CM5A-LR, Kageyama et al., 2012 and references therein; MIROC-ESM, Watanabe et al., 2011; CNRM-CM5, Voldoire et al., 2013, FGOALS-s2, Bao et al., 2013; BCC-CSMI.I, Xin et al., 2013) calibrated and controlled by various local proxy data.

These proxies include dated pollens records (e.g., Oliveira et al., 1999; Auler et al., 2004), lake sediment geochemical analyses (e.g., Viana et al., 2014), terrigenous pulses in ocean cores (e.g., Arz et al., 1999), travertine deposits (e.g., Wang et al., 2004), tree rings (e.g., Ferrero et al., 2015), ice core $\delta^{18}O$ variability investigations (mainly in the Andes; e.g., Thompson et al., 2013) and speleothem $\delta^{18}O$ analyses (e.g., Cruz et al., 2005; 2009; Novello et al., 2012, 2016; Cheng et al., 2013). However, despite the

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current increasing interest in the South America (SA) paleoclimatic reconstruction, available proxies are still considered to be sparse for the area if they are compared to records from Northern Hemisphere (Vuille et al., 2012; Prado et al., 2013a,b).

Moreover, at the continent scale, the repartition of the proxies is heterogeneous. Multi-proxy reconstruction syntheses (e.g., Villalba et al., 2009; Prado et al., 2013a,b), have highlighted that the Brazilian North-East (referred to "Nordeste" hereafter) is still very poorly documented. This scarcity of paleodata for Nordeste is probably due to the current geologic and climatic contexts of the area. From a climatic point of view, Nordeste is nowadays mainly an arid region featuring caatinga vegetation and potential Holocene lacustrine/riverine sediment/pollen data accumulation and conservation are not in optimal conditions. In this area, only few data over the 3 last millenia from lacustrine sediments were investigated through geochemical proxies next to the seashore (Sifeddine et al., 2011; Zocatelli et al., 2012). In parallel, investigation of speleothem isotopic records necessarily implies to find carbonated contexts with access to developed and unflooded karstic network, such geological conditions being not frequently found in Nordeste.

The few available data for the Nordeste for the whole or portions of the Holocene are nevertheless considered of good quality. Although calibration (against modern hydrometeorological data) and corrections (of long-term isotopic effects on moisture sources) are still discussed (Baker and Fritz, 2015; Moquet et al., 2016), these proxies are relevant, in term of time resolution, for detailed multidecadal and millenial variations of the SASM over the Nordeste (Cruz et al., 2009; Novello et al., 2012; Cheng et al., 2013), and contributed to describe the large scale drivers of SASM changes during the Holocene and the complexity of their interactions.

These indicators have allowed for rainfall intensity patterns to be delineated and forcing typologies to be produced to explain the "mosaic response" of the SA throughout the Holocene (Sylvestre, 2009). The major driver of the SAMS circulation is the land–sea temperature gradient (Vera et al., 2006; Marengo et al., 2012; Cruz et al., 2009; Prado et al., 2013a,b). During the Early-Mid Holocene, lower austral insolation in the Southern Hemisphere induced a less effective land–sea contrast than nowadays, combined with a lower moisture ascendant motion and rain cloud formation leading to a drier climate in the SAMS area. In addition, the latent heat released by the cloud formation was lower, and as this controls the high level circulation through the Bolivian High-Northeast Trough linkage, the subsidence over the Nordeste was lower than nowadays. This allowed for incursions in the area of both the Inter Tropical Convergence Zone (ITCZ) from the North and of the South Atlantic Convergence Zone (SACZ) from the South (Silva Dias et al., 2009), producing more precipitation in this zone while the rest of the SAMS zone was drier (Valdes, 2000; Cruz et al., 2009; Silva Dias et al., 2009; Cheng et al., 2013). Numerical simulations with general circulation models that incorporate basic atmospheric water isotope physics (^{18}O and/or ^{2}H) support this pattern by simulating the amount effect, as well as the link to insolation-driven monsoon activity (Cruz et al., 2009).

In parallel, a temperature cooling of the region during Early-Mid Holocene has been documented, although at a coarser time resolution, through pollen, oceanographic and noble gas data (e.g., Behling et al., 2000; Bush et al., 2007; Ledru et al., 1996, 2009; Stute et al., 1995; Wang et al., 2004; Santos et al., 2014). Despite of remaining uncertainties, it is now broadly accepted that this cooling ranged between 4 and 8 °C over SA in comparison to the Late Holocene, and around 5° in Nordeste (Farrera et al., 1999; Stute et al., 1995; Chatton et al., 2016).

Finally, palynological and paleobotanical records argued for the existence of ecological corridors between the Amazonian Forest and the coastal Atlantic Forest of NE Brazil, an area nowadays featuring an arid caatinga phytogeographical domain (Oliveira et al., 1999; Auler et al., 2004; Cheng et al., 2013 and references therein). These resulting vegetation changes were partially modeled in climatic simulations by Silva Dias et al. (2009).

Nevertheless, two main gaps have been identified in the understanding of the Holocene climatic trends of Nordeste, which still preclude a comprehensive scheme of the SA response to insolation driven patterns. First, more proxy data are still necessary for evaluating the magnitude and impacts of the SAMS variability over the Nordeste precipitation patterns. Second, the possible vegetation changes and their dynamics during this period still need to be clarified, as vegetation-based modeling requires proxies of vegetation impacts on hydroclimatological processes (Silva Dias et al., 2009). In addition, although the ecological corridor theory is supported by paleobotanical clues, the hypothesis of a more widespread hydro-ecological connection between Amazonian basin and Nordeste (Oliveira et al., 1999; Auler et al., 2004), which would have strong consequences on rainfall nature and distribution, has yet to be strengthened.

To address this, our work aims to present insights about the potential for water isotope proxies (deuterium, oxygen-18 and deuterium excess referred to d-excess in the following) from ^{14}C dated groundwater sampled in Nordeste in the perspective of evaluating the vegetation impacts on hydroclimatological processes and reciprocally, the hydrological changes to Holocene ecological variability. Our findings are based on dated paleogroundwater isotopic data primarily acquired in the purpose of hydrogeological investigations (2012–2015 Coqueiral project ; Cary et al., 2015; Chatton et al., 2015, 2016; Bertrand et al., 2016) but whose the patterns were significantly different from the expected trends, in comparison to Holocene paleogroundwater isotopic records found elsewhere in subtropical conditions. On the basis of these observations, we present new hypotheses regarding Holocene potential paleoecological and paleohydrological trends of the Nordeste.

2. Site description

The studied system, known as the Recife sedimentary aquifer system (Fig. 1), is located in the Pernambuco state in Brazil (8°04′03″S, 34°55′00″ W, $z_{mean} = 5$ masl). The studied area is urbanized and contains numerous surficial channels. The upstream area corresponding to the regional substratum, is, as the whole continental Nordeste, an arid to semi-arid area similar to Caatinga or Cerrado systems (Powell and Still, 2009; Cheng et al., 2013), comprised of a low arboreal deciduous scrubland where the vegetation is dormant and leafless for much of the year (Auler et al., 2004). On the seashore, Atlantic forest and mangrove ecosystems stands are found. The aquifer system lies over the Pernambuco and Paraíba basins, separated by the regional transverse structure of the Pernambuco Lineament (Fig. 1). It is composed by the deep systems Cabo and Beberibe of Cretaceous age, reaching a maximum depth of 250 m in the studied area (Cary et al., 2015; Bertrand et al., 2016). These two systems are overlaid by Tertiary and Quaternary sediments forming the superficial aquifers Boa Viagem and Barreiras. Details on the geological and environmental settings may be found in Cary et al. (2015).

The hydrogeological pattern consists in flowlines following the general hydrographic gradient from the western part of the area to the coastline on the east (Cary et al., 2015; Chatton et al.,2016, Fig. 2). The recharge of the modern groundwater mainly occur both vertically from the surface and horizontally from hydraulic connection with the regional substratum. Deep aquifer are mainly fed through to the recharge over the regional substratum, although punctual hydraulic connections occur with the shallow systems next to the seashore due to intensive exploitation pumping. For the deep groundwater systems (Cabo and Beberibe), investigations on recharge temperatures (reported in Table 1) through noble gas (Ar/Ne) analyses suggest a mean recharge temperature around 5 degrees below the current mean air temperature (Chatton et al., 2016). According to Stute et al. (1995), such recharge temperatures are in agreement with a recharge during the Last Glacial Maximum or Early Holocene. These authors found similar recharge temperature for 7–20 kyrs old groundwater in the Maranhão Basin, Piaui state (7°S, 41,5°W). In contrast, the shallow groundwater system of Recife (Boa Viagem and Barreiras) showed an inferred recharge temperature similar to the current mean annual air temperature of 25 °C in the area (WMO, 2013; Chatton et al., 2016).

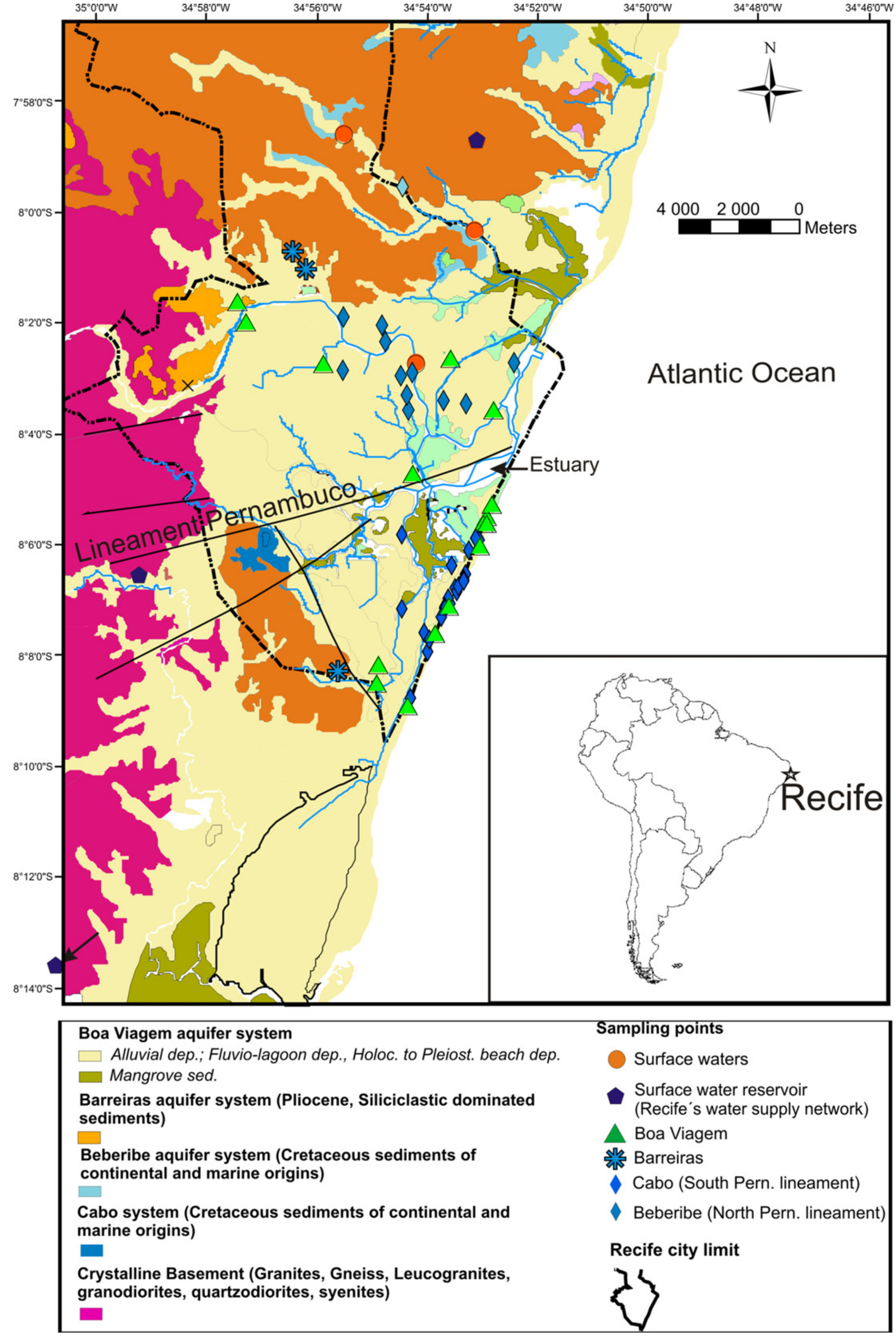

Fig. 1. Localization and geological map of the area.

3. Methodology

Significant differences in recharge temperature suggest distinct recharge periods between the deep and the superficial systems (Chatton et al., 2016), and motivated further dating and analyses of stable isotopes described in the rest of this paper. We performed sampling and data acquisition in March 2013 and March 2014, at the end of the rainy period (September–March), in production wells of the 4 main aquifers (deep aquifers Cabo and Beberibe; shallow aquifers Barreiras and Boa Viagem). Surface water was sampled upstream and downstream in the Beberibe

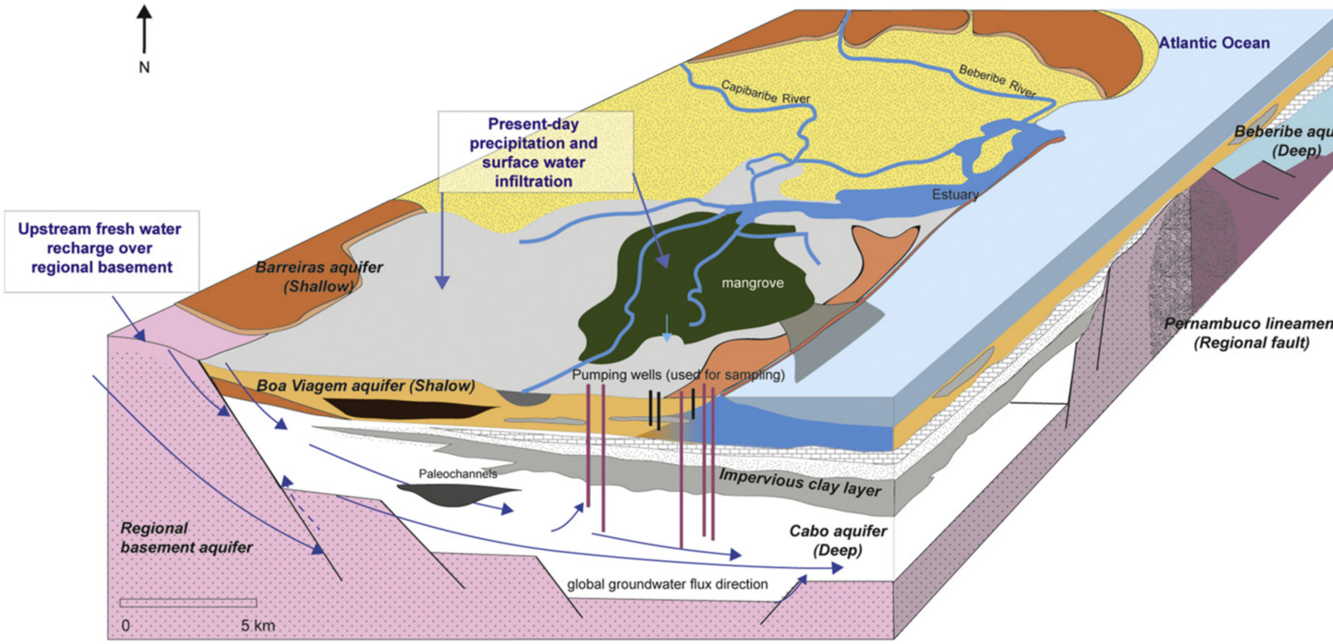

Fig. 2. Conceptual sketch of the aquifer systems (adapted from Cary et al., 2015).

River, close to the estuary, in the Capibaribe river, as in the COMPESA (Pernambuco State Water and Sanitation Agency) drinking water treatment plants (Table 1).

Deuterium and oxygen-18 of water were measured on raw water using a Picarro Laser spectrometer L2130i at USP and reported on the usual δ-scale in ‰ relative to V-SMOW standard, according to Eq. (1):

$$\delta_{sample}(‰) = (R_{sample}/R_{standard}) * 1000 \quad (1)$$

where R is the $^{2}H/^{1}H$ and $^{18}O/^{16}O$ isotope ratios. Our analytical uncertainty is $\pm 0.1‰$ for $\delta^{18}O$ and $\pm 0.9‰$ for $\delta^{2}H$. We post-processed all the measurements according to IAEA and USGS (2013).

For ^{14}C dating, we collected a 1 L aliquot in high-density plastic bottles and we analyzed the sample by accelerator mass spectrometry at the BRGM (French Geological Service, Orléans, France). We measured $\delta^{13}C_{TDIC}$ according to the procedure of Kroopnick et al. (1970). We obtained a carbonate precipitation by adding NaOH (pH[12) and $BaCl_2$ in water samples. A precipitate of $BaCO_3$ was then obtained and dried. We added phosphoric acid to the dry $BaCO_3$ sample inside a vacuum line, and we purified and trapped the evolved CO_2 with liquid nitrogen in a glass tube. Then, we measured the isotopic composition of this gaseous CO_2 with a dual inlet mass spectrometer.

The ^{14}C activity was measured relative to the modern carbon reference and expressed in % of modern carbon (pMC). The calibration of ^{14}C age of groundwater is usually subject to various assumptions depending on the studied groundwater system geological characteristics (see e.g., Fontes and Garnier, 1979; Cheng, 1992). These assumptions may imply possible influence of dead carbon through to carbonated matrix dissolution, carbon isotope exchanges between the various C phases along the groundwater flowpath in open and/or closed system (both estimated measuring ^{13}C and dissolved inorganic carbon speciation), initial activity soil $^{14}CO_2$ which entered the aquifer at the time of recharge. In the context of this study, we hypothesized a very limited influence from carbonated matrix i.e. no ^{14}C dilution, as the deep aquifers mainly consist in siliciclastic sediments (Cary et al., 2015; Bertrand et al., 2016), and that groundwater flows mostly in closed conditions, similarly to the empirical Vogel's (1970) approach. In such a conceptual framework, the ^{13}C variability of dissolved inorganic carbon is only attributed to changes in soil $^{13}CO_2$, depending on the plant type over the recharge area and C speciation (see e.g., Bertrand et al., 2013 and references therein). For this study, considering the suspected changes in vegetation type during the Holocene (Powell and Still, 2009; Oliveira et al., 1999), the equilibrium $^{13}C_{CO2}$ variability may be resulting from changes from C4 plants ($\delta^{13}C_{CO2} = -10$ to $-15‰$ vs PDB) to C3 plants (around $-25‰$ vs PDB) respiration, and therefore has not been used for ^{14}C age calibration. This does not impact age calculation given that matrix carbonate influence is neglected considering the geological context of the aquifers.

In contrast, we took into account the specific correction for South Hemisphere atmosphere ^{14}C production SHcal13 (Hogg et al., 2013) through the Calib program (Stuiver et al., 2005). The uncertainties σ calculated according to Scott et al., (2007) and the SHcal13 curve allowed for an evaluation of age ranges with a 2σ uncertainty (95% confidence; Table 2).

4. Results and discussion

4.1. Isotopic patterns of groundwater in the Recife aquifer system: differences between modern and paleo recharges

The ^{14}C dating performed for the deep groundwater samples in Recife allowed for a recharge period to be estimated ranging from −4.6 kyrs to −20 kyrs BP, with the greatest proportion corresponding to −6 to −13 kyrs B.P, i.e. largely during the Early-Mid Holocene (Table 2). Conversely, the shallow groundwater systems (Boa Viagem and Barreiras) contain CFC's and SF6 concentrations suggesting a modern components of their recharge (Supplementary material Table S1). At a first insight, the large range of ages in paleogroundwater highlight their potentiality for Holocene climate reconstruction, although the coarse time resolution still preclude a detailed evaluation of paleoclimatic processes, and that only low frequency processes should be addressed through these data.

Concerning the stable isotopes of water, shallow groundwater plot along a "modern groundwater line" (MGL; $\delta^{2}H = 4,5\delta^{18}O + 5,7$) indicating recharge by modern precipitation, represented by the Local Meteoric Water Line built from 1 year sampling (LMWL; $\delta^{2}H = 7,4\delta^{18}O + 11,1$; Fig. 3A; Table 3) and the Ceará Mirim (located 300 km northern Recife) MWL built from 3 years monitoring (between 1973 and 1975 through the IAEA/WMO-GNIP network, 2016), followed by secondary evaporation processes. This indicates infiltration of the

Table 1
Groundwater data: Stable isotopes of water, d-excess and recharge temperature

Sample	X (m) [WGS 84; 10S]	Y (m) [WGS 84; 10S]	Type of sample	$\delta^{18}O$ (‰ vs VSMOW)	δ^2H (‰ vs VSMOW)	d excess	Temp (°C) (Chatton et al., 2016)
ALM 73	287507	9109986	Deep Gw	−1,4	0	10.8	19.7
TTD94	289358	9102059	Deep Gw	−1.5	0	11.96	14.8
TTD110	289358	9102059	Deep Gw	−1.5	0	11.58	18
CAB2	290567	9100530	Deep Gw	−1,3	3	12,7	16.8
CAB3	291286	9102344	Deep Gw	−1,2	2	11,82	14.8
CAB4	291499	9102653	Deep Gw	−1,3	1	11,88	15.7
CAB5	289684	9104426	Deep Gw	−1,2	2	11,18	
CAB6	291373	9103389	Deep Gw	−1,2	3	12,48	
CAB10	291165	9102037	Deep Gw	−1,2	3	11,8	18.6
CAB11	291135	9101975	Deep Gw	−1,2	3	12,46	17.4
CAB12	289992	9099014	Deep Gw	−1,3	2	12,72	17.3
CAB13	290468	9101191	Deep Gw	−1,2	2	12,22	
CAB17	291806	9103117	Deep Gw	−1,1	3	12,06	14.3
CAB20	290617	9100953	Deep Gw	−1,5	0	12,12	17.9
CAB22	291014	9101692	Deep Gw	−1,3	2	12,2	
CAB23	291922	9103914	Deep Gw	−1,2	3	12,44	19.4
CAB24	292190	9104320	Deep Gw	−1,3	2	12,4	20.6
CAB26	291545	9102585	Deep Gw	−1,2	2	12,22	14.8
CAB27	291630	9102732	Deep Gw	−1,2	3	12,52	14.4
CAB36	290069	9106520	Deep Gw	−1,1	4	12,66	18
CAB 101	291746	9102955	Deep Gw	−1,2	3	12,66	
CAB102	291746	9102887	Deep Gw	−1,2	3	12,6	14.2
CAB114	289726	9101999	Deep Gw	−1,2	3	11,96	14.8
BEB131	289150	9111308	Deep Gw	−1,2	2	11,46	
BEB132	289753	9115980	Deep Gw	−1,7	−2	11,8	
BEB47	287812	9111792	Deep Gw	−1,5	1	12,38	
BEB50	291777	9108799	Deep Gw	−1,1	4	12,72	14.1
BEB51	289907	9109036	Deep Gw	−1,4	1	12	18.6
BEB52	289195	9110846	Deep Gw	−1,3	2	12,44	
BEB57	291029	9108891	Deep Gw	−1,3	3	12,6	14.5
BEB59	289781	9109798	Deep Gw	−1,4	0	11,66	22.2
BEB60	290047	9109897	Deep Gw	−1,3	1	12,12	25.1
BEB62	293372	9110177	Deep Gw	−1,1	4	12,86	15.4
BAR120	287167	9102952	Sup. Gw	−1,5	0	11,84	
BAR121	291089	9110512	Sup. Gw	−2,0	−3	13,06	19
BAR124	287964	9099662	Sup. Gw	−1,6	−1	11,82	
BAR64	287013	9105315	Sup. Gw	−1,0	2	9,48	
BAR068B	282201	9106787	Sup. Gw	−1,4	0	11,34	
BOV100	292531	9104842	Sup. Gw	−0,6	2	6,32	17
BOV110	292677	9105500	Sup. Gw	−0,4	4	6,98	21
BOV111	289909	9098783	Sup. Gw	−0,8	3	8,94	
BOV112	290790	9101194	Sup. Gw	−1,0	1	8,84	21
BOV113	291257	9102098	Sup. Gw	−0,5	4	8,56	23
BOV115	288908	9100152	Sup. Gw	−1,5	−1	10,96	36
BOV116	288833	9099503	Sup. Gw	−1,5	−1	11,26	
BOV130	291341	9110333	Sup. Gw	−1,5	0	11,56	27
BOV14	292544	9105097	Sup. Gw	−1,0	1	9,26	30
BOV30	287081	9110200	Sup. Gw	−1,2	0	9,04	25
BOV33	284227	9112236	Sup. Gw	−1,8	−2	11,8	19
BOV46	292757	9108650	Sup. Gw	−1,2	1	10,68	
BOV34	284484	9111567	Sup. Gw	−1,2	−1	8,48	21
BOV19	292400	9104840	Sup. Gw	−0,6	4	8,46	23
RIVBEB1	292132	9114584	Surf. Wat.	−1,7	−2	11,72	
RIVBEB2	287787	9117827	Surf. Wat.	−1,2	2	11,06	
RIVCAP	290170	9110195	Surf. Wat.	0,6	8	3,3	
ETA200	291493	9113938	Surf. Wat.	−1,8	−3	11,64	
ETA201	280903	9106726	Surf. Wat.	1,7	14	−0,26	
ETA202	274279	9085417	Surf. Wat.	0,1	7	5,98	

numerous channels featuring the area (Cary et al., 2015). In contrast, the deep groundwater tends to slightly plot above the LMWL and presents richer signatures than modern groundwater, with a trend suggestive of recharge similar to the current Manaus meteoric water line (LMWL; $\delta^2H = 8{,}1\delta^{18}O + 13{,}5$; Gat and Matsui, 1991) within the Amazonian basin (03°06′S 60°01′W) (Fig. 3A), and argues, in addition, for the absence of significant evaporation of the water entering the deep aquifers.

These differences can be further examined through the analyses of the deuterium excess ("d-excess") (Dansgaard, 1964; Eq. (2)). This parameter is primarily, in atmospheric waters, inversely proportional to the relative humidity (RH) in the evaporation area further providing the moisture leading to cloud formation and rainfall (Dansgaard, 1964; Clark and Fritz, 1997). d-excess can then be altered by evaporation (Rozanski, 1985).

$$d = \delta^2H - 8\delta^{18}O \tag{2}$$

In precipitation, the d-excess$_{mean}$ at Recife (March 2013–Feb 2014) is 11.8‰. This value is a bit higher than the range from 10.3 to 11.2‰ observed by Gat and Matsui (1991), through to IAEA-GNIP network, for rainy season on the coastal cities of Nordeste around Recife (Fortaleza, Natal, Salvador). This latter is however probably more representative of infiltrating waters over the last decades in the area. Similarly the average of d-excess in precipitation for 3 entire hydrological years (1973–1975) at Ceara Mirim is lower with a mean value of 9.8‰.

Table 2
Geochemical and isotopic data for the dated paleogroundwater and calculated ^{14}C age ranges. Dissolved element concentrations are expressed in mg/L.

Well	O_2	Conductivity (µS/cm)	pH	T°C	Ca	Mg	Na	K	Cl	HCO_3	SO_4	NO_3	NO_2	$\delta^{13}C$ (TDIC) (‰)	Calculated $\delta^{13}C(eqCO_2)$ (‰)	a_C14 (pmC)	σ a_C14	Lower range age C14 cal age (kyrs BP)	Upper range C14 cal age (kyrs BP)
BEB57	2.2	824	5.9	31.3	41.33	28.62	57.33	24.53	204.58	35.28	32.52	0.17	0.08	−19.7	−21.0	30.30	0.19	10.68	11.14
BEB59	2.43	945	6.09	29.7	19.97	25.34	115.47	30.82	210.93	133.77	11.41	1.03	0.09	−7.2	−9.3	59.10	0.21	4.57	4.85
BEB62	3.03	239	5.86	32.8	3.94	3.60	19.66	11.51	28.72	35.28	11.43	0.16	0.01	−15.6	−16.7	24.40	0.15	13.05	13.28
CAB3	1.01	262	6.25	31.3	3.39	3.31	43.64	6.74	23.49	91.15	8.22	0.18	0.02	−18.8	−14.0	12.80	0.11	19.62	20.10
CAB5	1.06	5063	6.48	30.4	130.55	119.38	589.44	23.66	1402.67	111.73	170.89	0.77	0.11	−14.9	−21.6	27.90	0.10	11.72	12.05
CAB12	0.6	224.3	6	30.5	1.48	1.67	34.80	7.83	17.67	49.99	15.64	0.28	0.03	−11.4	−18.8	34.40	0.10	9.47	9.55
CAB17	1.1	2560	6.1	30.8	60.47	55.34	298.50	20.18	724.13	41.16	88.50	0.58	0.06	−19.5	−13.1	28.90	0.22	7.33	7.57
CAB24	2.68	950	5.99	31.2	25.71	22.71	120.43	19.84	237.65	47.78	41.77	0.33	1.10	−17.7	−21.6	44.00	0.15	10.24	10.52
CAB27	1.09	237	6.3	32.1	3.70	3.47	39.50	6.20	19.57	77.92	10.33	0.15	0.03	−17.1	−19.3	19.30	0.10	15.62	16.05
CAB36	1.25	818	6.2	30	26.54	22.54	84.52	16.58	186.14	47.04	28.91	0.56	0.06	−11.4	−20.1	26.00	0.10	12.66	12.75
TTD94	n.a	2191	6.9	30.5	47.30	61.50	323.00	13.30	537.10	70.80	169.10	n.a	n.a	−19.5	−25.1	28.90	0.10	10.70	11.09
TTD110	n.a	1945	6.6	30.6	47.30	56.40	281.20	13.30	468.00	65.30	142.20	n.a	n.a	−18.1	−22.6	20.90	0.10	14.39	15.11
ALM73	n.a	846	6.8	30.2	44.10	39.90	164.80	21.50	0.00	308.00	2.90	n.a	n.a	−10.1	−15.4	46.20	0.30	6.89	7.25

In aquifers, d-excess for paleogroundwater is higher (d-$excess_{mean}$ = 12,4‰) than for modern groundwater (d-$excess_{mean}$ = 9‰) and recharge (Fig. 3B). This is a pattern that contrasts with the usual paleowaters recharged in colder and wetter conditions as reported in many other areas throughout the world, especially in subtropical environments (Clark and Fritz, 1997; Rozanski, 1985; Rozanski et al., 1997). For instance, in North-Africa, Holocene paleogroundwaters present a mean d-excess of about 5‰ lower than modern precipitations, related to higher RH over moisture source (colder conditions) during that period (Rozanski, 1985). This suggests that the d-excess-shift observed between shallow (modern) and deep (Early–Mid Holocene) groundwater in Recife cannot be attributed to the only increase of rainfall amount and insolation/temperature decreases (Stute et al.,1995; Cruz et al., 2009; Chatton et al., 2016) which should favor depleted $\delta^{18}O$, $\delta^{2}H$ (amount and temperature effects, Clark and Fritz, 1997), higher regional RH and therefore lower d-excess, and suggests that additional processes altering moisture sources occurred between the Early-Mid Holocene and the present day.

These preliminary observations highlight the interest of the groundwater isotopic signatures as a possible complementary tool for paleoclimate studies over the Nordeste region. In this context, a control of the sensitivity of these parameters in comparison to other available and well constrained proxy data is required. In addition the observed d-excess need to be understood in the paleoclimatic context of the area.

4.2. Comparison of regional speleothem $\delta^{18}O$ and ^{14}C-dated groundwater isotopic fingerprints: rainfall amount and moisture source pattern changes during Holocene

In NE Brazil, it was demonstrated that the main factor affecting the temporal isotopic signatures variability of precipitation is the amount effect (Cruz et al., 2009; Baker and Fritz, 2015, and references therein). On this basis, speleothem $\delta^{18}O_{carbonate}$ which follows the average $\delta^{18}O$ variability of drip water entering the karstic systems (Rainha, Furna Nova and Abissal caves, located at 05°36′ S, 37°44′ W at 100 masl and at 100 km distance from the Atlantic coast in the Rio Grande do Norte; Fig. 3) was extensively used as a proxy of precipitation amount variation in the area (Cruz et al., 2009; Cheng et al., 2013). This proxy was shown, especially for the Early-Mid Holocene period, to capture shifts in the location of the ITCZ related to austral summer insolation (Fig. 4A).

By assuming isotopic equilibrium between the drip water supplying the speleothem and carbonate at the time of precipitation (using Eq. 3; Böhm et al., 2000; Affek et al., 2008; Kluge et al., 2013), we compared $\delta^{18}O_{H2O}$ inferred from $\delta^{18}O_{carbonate}$ and the isotopic signatures of our groundwater samples.

$$\delta^{18}O_{carbonate} - \delta^{18}O_{H2O} = 1000 \ \ln\alpha_{carbonates-H2O} = 18.03\left(1000T^{-1}\right) - 32.17 \quad (3)$$

Calculated $\delta^{18}O_{H2O}$ range (from −7 to −0,9 ‰ vs VSMOW) is significantly different (usually lower) from the measured $\delta^{18}O_{groundwater}$ (varying from −1,5 to −1,1‰ vs VSMOW) (Fig. 4B). These differences may be the result of hydrogeological and/or physical and chemical processes. From a hydrogeological point of view, the more depleted signature of drip water fed by karstic system can be explained by a rapid infiltration of water within large fissures featuring karst in some places, limiting previous isotopic enrichment through to evaporation effect near the surface, which would conversely give increased $\delta^{18}O$ values in deposited calcite (Fairchild et al., 2006; Baker and Bradley, 2010). Depending on the geometry of the system and the degree of connection between the surface and the percolation pathway feeding the speleothem, huge $\delta^{18}O_{H2O}$ differences from a speleothem to another may occur, even in the same network. This leads to high variability of the equilibrated $\delta^{18}O_{carbonates}$ between speleothem from neighboring

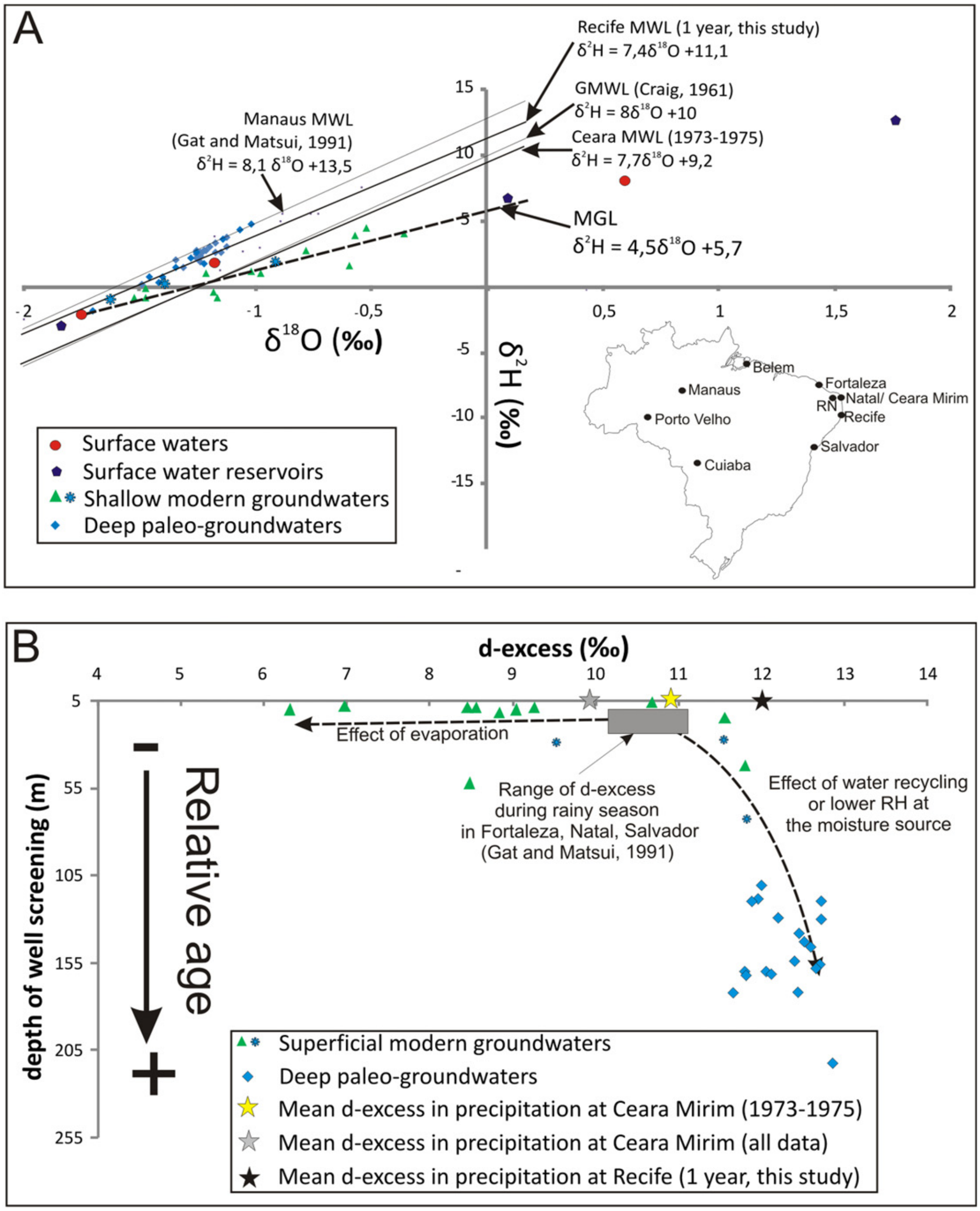

Fig. 3. A.δ^{18}O vsδ^{2}H diagram. Shallow (Boa Viagem/Barreiras) and deep (Cabo/Beberibe) groundwater samples are reported as well as The Global Meteoric Water line (Craig, 1961), the Local Meteoric Water Line performed during the hydrogeological study (Cary et al., 2015) and the Manaus water line reported by Gat and Matsui (1991). Modern Groundwater Line corresponds to the shallow groundwater affected by kinetically evaporated source which are attributed to the local channel infiltration. Note that the deep groundwater plot above the LMWL. B. Deuterium excess d vs well screening depth.

or even identical caves (Ford and Williams, 2007, and references therein). Consistently, Sereffiddin et al. (2004) pointed out a difference of 5‰ for $\delta^{18}O_{carbonates}$ for speleothems spanning the same periods and from neighboring caves fed by two distinct karstic networks. In addition, beyond the likely different recharge conditions occurring in Recife (featured by crystalline and sedimentary lithologies) isotope ratios in groundwater we measured at our site may be buffered by hydrogeological processes. Groundwater circulation is constrained by potentiometric heads organized as equipotentials in aquifer, resulting in a nested organization of parallel flowlines between which mixing is limited (Toth, 1963): local flow systems occur relatively close to the surface, i.e. from a higher elevation recharge area to a directly adjacent discharge area such as a stream or spring, whereas intermediate and regional flows reach to a greater depth in the aquifer. However, the recharge processes (e.g., mixing in the soil zone) buffer precipitation variability (including δ^{18}O), and limits time resolution. Therefore the resulting δ^{18}O of the sampled groundwater could show a lower sensitivity than $\delta^{18}O_{carbonate}$ to high frequency isotopic variability of precipitation. From a physical and chemical perspective, it is also possible that isotopic equilibrium and carbonate saturation within the drip water supplying the speleothem are only reached after the latest fractions of rain events, usually more depleted than the bulk rain water reaching the groundwater system. In spite of these differences whose specific reasons are out the scope of this paper, a co-variation of $\delta^{18}O_{carbonate}$ and $\delta^{18}O_{groundwater}$ is observable for the Early-Mid Holocene (Fig. 4B). This suggests that dated groundwater could be a possible amount effect

Table 3
Stable isotopes data (‰ vs VSMOW) of precipitations in Recife (Monthly sampling, 2013–2014 period). Comparison with the average of regional IAEA stations (IAEA/WMO, 2016). The continental effect on isotopic signatures appears to be mostly true all the year long.

	Recife (Hydrological year March 2013–February 2014)		Belem (1965–1990 averages)		Manaus (1965–1990 averages)		Porto Velho (1965–1983 averages)	
Sample -month	$\delta^{18}O$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{2}H$	$\delta^{18}O$	$\delta^{2}H$
March	−1,0	3	−3.77 ± 2.31	−23.98 ± 17.09	−6.32 ± 2.16	−38.69 ± 18.23	−7.30 ± 1.51	−48.52 ± 12.67
April	−2,0	−3	−5.08 ± 3.45	−30.10 ± 27.94	−7.03 ± 2.61	−43.49 ± 21.53	−7.70 ± 3.91	−50.22 ± 30.44
May	−1,5	−1	−3.17 ± 2.54	−18.56 ± 18.47	−7.18 ± 3.43	−42.52 ± 30.79	−5.25 ± 3.95	−37.84 ± 28.32
June	−2,0	−4	−1.42 ± 1.52	−0.27 ± 9.54	−3.70 ± 2.18	−15.16 ± 17.65	−4.23 ± 2.78	−28.56 ± 23.11
July	−1,2	4	−1.12 ± 1.63	−2.34 ± 8.64	−2.96 ± 1.44	−8.59 ± 14.24	−2.56 ± 2.98	−15.22 ± 24.98
August	−0,9	6	−0.39 ± 1.46	7.50 ± 7.65	−1.80 ± 1.63	−4.04 ± 14.84	−4.39 ± 2.66	−24.92 ± 23.55
September	−0,5	8	−0.22 ± 1.16	4.95 ± 9.24	−1.85 ± 1.40	−1.34 ± 8.78	−1.24 ± 3.26	4.10 ± 16.18
October	−0,8	6	−0.28 ± 1.63	3.53 ± 10.19	−1.93 ± 1.22	−3.63 ± 9.43	−3.45 ± 2.08	−17.40 ± 20.87
November	−0,7	6	−1.02 ± 1.25	−3.75 ± 11.68	−3.54 ± 1.91	−12.81 ± 10.34	−4.92 ± 3.06	−25.54 ± 22.72
December	−1,2	1	−1.33 ± 1.93	−4.73 ± 13.97	−3.30 ± 1.27	−16.46 ± 7.97	−4.11 ± 1.16	−25.34 ± 9.19
January	−1,1	3	−2.32 ± 1.78	−11.02 ± 11.86	−4.14 ± 1.29	−20.50 ± 10.39	−6.49 ± 3.50	−42.73 ± 30.53
February	−0,9	5	−3.07 ± 2.08	−14.61 ± 13.89	−5.08 ± 2.20	−26.76 ± 16.26	−9.56 ± 2.86	−65.83 ± 23.94

proxy in complement to speleothems, although it is buffered and of lower resolution.

In parallel and although the number of dated groundwater data is limited to 13, d-excess appears to be related to the insolation (Fig. 4C). The insolation decrease, while associated with increase in precipitation in the area, seems to be followed by a d-excess increase trend, after a time-lag. This trend strengthens the idea, as mentioned previously, that regional moisture origin has changed between the Early-Mid Holocene and today. This can reflect a temporal modification of the RH over a unique moisture source, spatial modifications of moisture origin and/or a higher recycling of local precipitations, providing a kinetically fractionated vapour (Salati et al., 1979; Rozanski, 1985; Rozanski et al., 1993; Gat and Matsui, 1991; Clark and Fritz, 1997). We discuss these possibilities below.

4.3. Spatio-temporal changes in moisture sources: paleoecological shifts over Nordeste during the Holocene

The current spatial moisture pattern over northern tropical SA is mainly driven by the SAMS circulation which transports, during austral summer, tropical Atlantic moisture that is largely recycled over the Amazon basin westward toward the Andes. The warm and humid air masses are then deflected southward by the Andes through to the Andean low-level jet, transporting moisture towards southeastern SA (Cheng et al., 2013).

The westward Atlantic- Amazon basin moisture transport trend was firstly assessed by Salati et al. (1979) and analyzed by Gat and Matsui (1991) along a transect across northern Brazil, from Belem to Santarem and Manaus (Fig. 3A), yielding an overview of isotopic variability in precipitation. These authors primarily highlighted a shift to more negative δ data values toward inland stands. This is related to the expected continental effect, describing the impoverishment trend in heavy isotopes in precipitation between littoral and continental stands resulting from rainout advancement (Clark and Fritz, 1997). However, the most prominent characteristic of rainfall precipitation signatures was the increase in d-excess from 7,5‰ near the coast in Belem to about 13‰ at Manaus, as in other inland cities such as Porto Velho, Cuiaba and Brasilia. This spatial pattern was attributed to evaporation from open water bodies and from the large rainforest canopy interception (Fig. 5). While transpiration by plants does not lead to isotopic fractionation (Zimmerman et al., 1967), re-evaporation from open water bodies and interception leads to the production (F_{evap}) of a kinetically fractionated vapor (δ_{evap}). This re-evaporated flux mixes with the long-range moisture transport corresponding, after a progressive Rayleigh's distillation equilibrium fractionation of the Atlantic moisture (F_{vap1}; δ_{vap1}), to the remaining cloud water (F_{vap2}; δ_{vap2}) (Fig. 5A). Such a mixing leads to an increase of the d-excess in the resulting moisture and precipitation ($\delta_{vap3,}$ δ_{P2}) (Fig. 5B). In the Amazonian basin, open water and canopy interception re-evaporation (F_{evap}) potentially accounts for 35 % of the total evapotranspiration ($F_{evap} + F_{transp}$) (Gat and Matsui, 1991). Various estimations of the portion of the total evapotranspiration then participating to the local precipitation ($F_{evap\_rec} + F_{transp\_rec}$) were proposed (reviewed in Rocha et al. (2015) and Eltahir and Bras (1994)) and range from 16 % in eastern border of the Amazon basin (Lettau et al., 1979) to 56% (Marques et al., 1977).

To account for this additional processes, an analytical steady-state evapotranspiration isotopic model was proposed and tested by Gat and Matsui (1991). to evaluate the sensitivity of d to the RH and runoff ratios vs rainout ratio. According to these tests, the 3‰ difference between coastal and inland d-excesses would be consistent with a recycling of half the precipitation, of which 20 to 40% would be from open water bodies in an environment featured by a mean RH of 75%.

In this context, the d-excess differences between deep paleogroundwaters and modern recharge and groundwater in Recife could be explained either by the past influence of a distant moisture source similar to the present central Amazon basin, or by a local change in ecosystem type. Indeed, a tropical rain forest like in the Amazon basin does not exist in Nordeste nowadays, this area being arid to semi-arid. Forest stands are limited, and exist only from the seashore to the coastal Atlantic forest. The only relatively large water bodies are located along the seashore and consist in estuary and mangroves, i.e. presenting similar isotopic features as seawater. Nevertheless, Silva Dias et al. (2009) suggest, through modeling approaches that Early-Mid Holocene rainfall increase in Nordeste and related processes such as ITCZ southward shift and SACZ northward displacement, could be accompanied by a positive vegetation feedback, implying a potential role for paleoecological conditions at the continental scale (Fig. 5C;D).

Consistently, the paleobotanical and palynological investigations in Nordeste for the Early-Mid-Holocene argued for the existence of transitional ecological corridors between the present Amazonian rain forest and the Coastal Atlantic Forest. This hypothesis was first suggested by floristic disjunctions revealed by studies of humid forests enclaves in high elevations within the semi-arid region of the caatinga phytogeographical domain (Andrade-Lima, 1966, 1982; Rizzini, 1967; Oliveira et al., 1999). These studies show that Tropical forest taxa are well represented throughout the Holocene in Nordeste such as in Icatu River Valley (10°24′ S 43°13′ W, z = 400 m) which was dominated by gallery forest taxa from 10,060 to 6790 yrs B.P.

Hence, the reported d-excesses in Early–Mid Holocene paleogroundwaters in Recife (Fig. 3B and 4C) strengthen the hypothesis of the existence of such a paleoecological shift in NE Brazil during the Early-Mid Holocene. The rainfall increase coupled with a mean temperature cooling alone does not explain the recycling signature of the Recife's paleogroundwater. Our observation rather involves an alternative explanation: the Gat and Matsui scheme (1991) (Fig. 5C) could have occurred closer to the Nordeste coast (Fig. 5D). Such a hypothesis is strengthened by the time lag of temporal d-excess variation in paleogroundwater compared to insolation and precipitation changes (Fig. 4C). This lag could result from the dynamics of ecological processes, i.e. the time required for the rain forest ecosystem settlement, necessary to trigger significant moisture recycling, a process that seems to be optimal after the maximum insolation phase. Our data suggest that such shift could have occurred, in Recife area earlier than e.g., Icatu River valley , as highest d-excess values are found at about 13100 yrs B.P in Recife. These findings need however to be further comfirmed by more detailed investigations.

In this context, it should be noted that although the concept of a more forested Nordeste and the existence of migration routes have been hypothesized for decades, the location of such routes and the timing of forest expansion phases remained unclear (Auler et al., 2004). Our hypothesis is in agreement with at least one of the hypothesized routes (Auler et al., 2004; Cheng et al., 2013; Oliveira et al., 1999), connecting hydro-ecologically the Recife area to the Amazon basin (Fig. 5C). Nevertheless, the significant d-excess shift observed in the long-term for the deep groundwater system rather argues for more widespread ecological changes leading to the formation of an extended regional rain forest ecosystem (Fig. 5D), as suggested by Auler et al., (2004). Such widespread shift provided the conditions to deeply recycle local moisture, portion of which then entered the aquifers.

5. Concluding remarks on future challenges and use of isotopic proxy data in Nordeste groundwater

The use of d-excess is already largely implemented in dated ice cores to evaluate past moisture source relative humidity conditions (e.g., Steffensen et al., 2008) and/or location changes due to modification in atmospheric circulations (e.g. Masson-Delmotte et al., 2005) and is increasingly monitored in global precipitation and groundwater to validate Global Climate Model simulations (Pfahl and Sodemann, 2014). Our findings should encourage new validation exercises for isotope-enabled GCMs or Earth System Models of Intermediate Complexity (EMICs). Specifically, the modules related to soil-atmosphere interactions could be better constrained by integrating changes in recycling processes from continental surface water evaporation, which seem of great importance in intertropical zones like in Nordeste. Usually, incorporation of water isotopes in GCMs or EMICS (see the Stable Water Isotope Intercomparison Group projects, e.g., Kurita et al. (2011); Risi et al. (2010)) implies to incorporate soil hydrology and atmospheric postcondensation exchanges in the model physics. Such efforts are currently made (e.g., Dee et al., 2015) and highlight the importance of the knowledge of the ecosystem type to better constrain proportion of evaporation versus transpiration recycling processes through d-excess (Jasechko et al., 2013; Dee et al., 2015). This is yet challenging for present day modeling but can be constrained thanks to observational network (e.g., IAEA/WMO, 2016). For paleoclimatologic studies, such calibration is difficult as d-excess, requiring combined ^{18}O and ^{2}H data, is only sparsely available over glacial-interglacial time scales, and mainly in ice cores (Werner et al., 2016). As it is illustrated in this study, paleogroundwater data could provide a valuable help to integrate the dynamic behavior of ecosystem settlements through modifying land/soil modules over large time scales and calibrate these models in mid-latitude areas.

Nevertheless, it should be noted that isotope variability, as evaluated in groundwater, suffers limitations. Due to the integrative reservoir function of such large aquifers, and although nested organization of

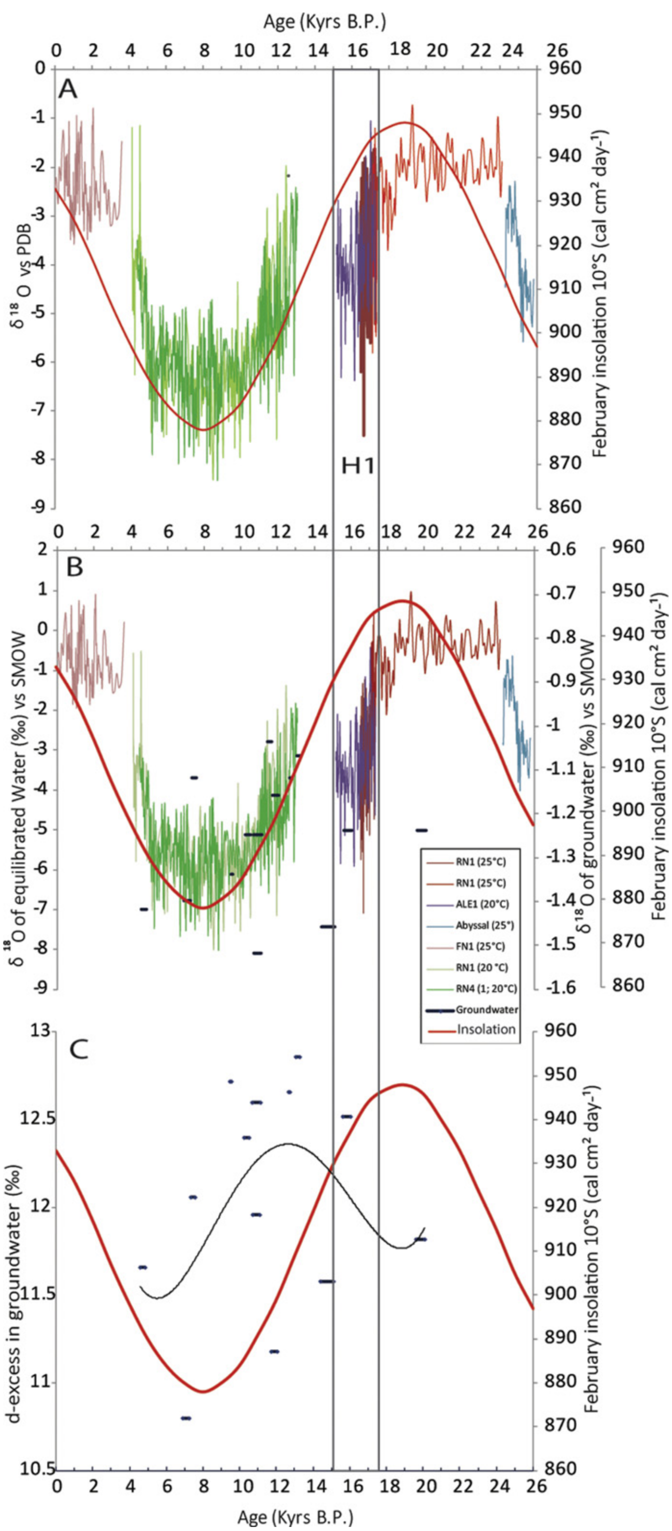

Fig. 4. Comparison of $\delta^{18}O$ trends between Rio Grande do Norte cave calcite (Cruz et al., 2009) and Recife dated deep groundwaters (Cabo/Beberibe). A. Original Cruz et al.'s $\delta^{18}O$ speleothem records in Rio Grande do Norte (note that $\delta^{18}O$ are expressed vs PDB). B. Calculated $\delta^{18}O$ of drip water assuming an isotopic equilibrium between carbonate and drip water (using equation reported in Kluge et al. (2013) and assuming an equilibrium temperature of 25 °C between 0 and 12,5 kyrs B.P (corresponding to the mean annual temperature in Rio Grande do Norte; Cruz et al., 2009). and of 20 °C between 12,5 and 26 kyrs accordingly with the 5 °C difference between these two period suggested by Stute et al. (1995). Comparison with ^{14}C dated Recife's deep groundwater (note that all $\delta^{18}O$ are expressed vs SMOW; $\delta^{18}O$ (vs VSMOW) = 1.03092[$\delta^{18}O$ (VPDB)] + 30.92; Coplen, 1995). C. Corresponding d-excess for the ^{14}C dated Recife's deep groundwater. Note that although the number of data is limited and that few outlier are identified, possibly linked with high frequency and temporary ecological shifts (Oliveira et al., 1999), d-excess seems to reversely follow the insolation pattern with a time-lag. More data would be necessary to confirm this general trend. H1 refers to the Heinrich event 1 characterized by depleted $\delta^{18}O$ in the Rio Grande do Norte cave calcite.

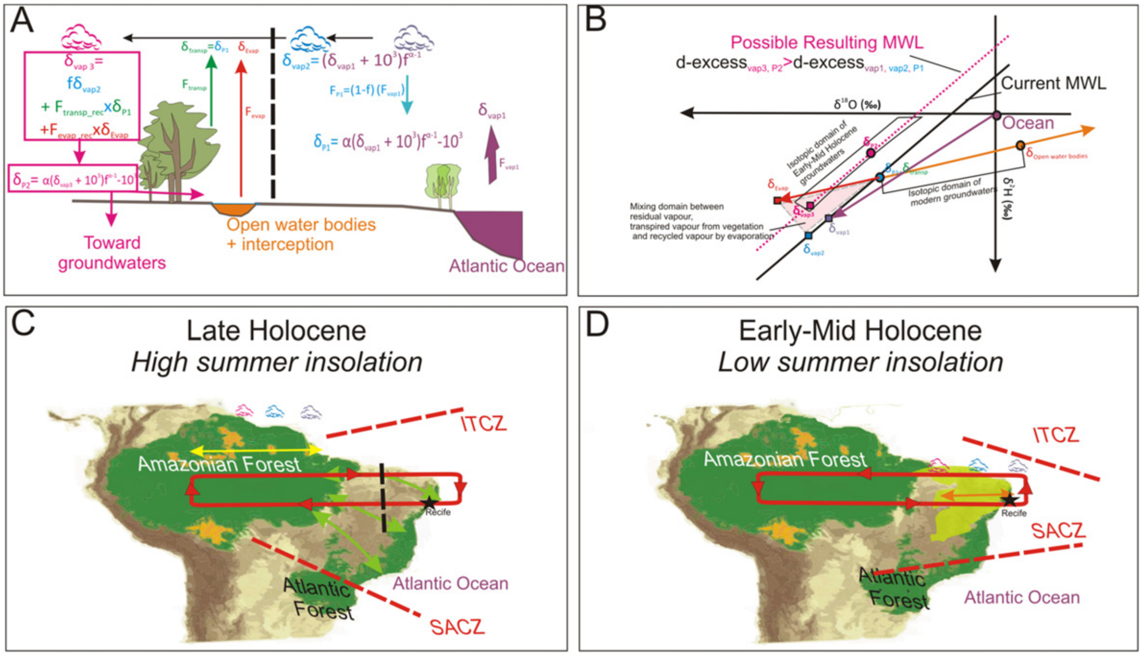

Fig. 5. A. Conceptual scheme of moisture and isotopic patterns for northern tropical SA, and potentially occurring during early-Mid Holocene period (modified after Dansgaard, 1964; Gat and Matsui, 1991). α represent fractionation factor between vapor and liquid. f represent the remaining fraction of the initial content of vapor in the air-mass (Rayleigh distillation model) B. Same processes represented in the $\delta^{18}O$ vs $\delta^{2}H$ domain. C and D. Conceptual schemes of (paleo)climatological and ecological process during Late and Early-Mid Holocene (adapted from Cruz et al., 2009 and Auler et al., 2004). In a context of increased rainfall due to ITCZ location shift, the setting of transitional ecosystems (firstly hypothesized as narrow corridors represented by lime green arrows, but possibly widespread according to Auler et al. (2004)) between Amazonian Forest and Atlantic Forest, favoring open water bodies and interception evaporation, could have promoted recycling of water, what leads to a modified meteoric water line and higher d-excess. Symbols: α: isotopic fractionation factor; F: fraction of contribution from evaporation or transpiration to the clouds. f: remaining fraction of water within the clouds according to the Rayleigh distillation model (cf. Clark and Fritz, 1997).

flow lines following equipotential downgradients (Toth, 1963) rather ensures temporal segregation from shallow to deeper aquifer layers, time resolution can be lower than for other proxies, e.g., speleothems, lake sediment cores (Rozanski, 1985; Corcho Alvarado et al., 2011; Jiráková et al., 2011; Jasechko et al., 2013). In addition, groundwater exploitation through to extensively screened wells (over several meters), such as in Recife may lead to mixing of water of various ages and alter the resolution of the recorded isotopic signatures.

Despite these limitations, however, the presented results illustrate the usefulness of our approach through further strategic sampling. This sampling should be performed on specifically designed low pumping rate wells to limit mixing processes potentially altering isotopic signals and time resolution. Another advantage is that d-excess data in groundwater can be simultaneously investigated with recharge temperature inferred from noble gas (e.g., Stute et al., 1995; Chatton et al., 2016) to complete rainfall amount information obtained from e.g., speleothems and obtain a more comprehensive overview of climatological parameters at the moment of the recharge. In addition, it should be noted as well that the potential timescale for paleoclimate reconstruction in the Recife area is much higher in the south of the city than in the zone investigated for the present study. The depth of the Pernambuco basin Piedade's Graben much less exploited for groundwater pumping, is deeper than 3000 m (Cary et al., 2015), and therefore has the potential to contain older paleowaters, especially next to the seashore according to the regional general flowpath (Fig. 2). Consequently, both better adapted sampling and investigations at greater depths should provide a valuable support for our findings regarding paleoclimatological patterns in Nordeste and NE South-America, especially by tracing the recycling effects in regional moisture patterns. This should help to reciprocally diagnose a more detailed spatio-temporal typology of Holocene ecological changes, which appear, thanks to the reported new isotopic proxies, to be likely much more widespread than narrow ecological corridors between Amazonian basin and the Atlantic forest.

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