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# Glacial recharge, salinisation and anthropogenic contamination in the coastal aquifers of Recife (Brazil)



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# HIGHLIGHTS

# GRAPHICAL ABTRACT

- Study of anthropogenic impacts on the dynamics of coastal aquifers in urban areas.
- A multi-tracer approach was used to assess processes potentially affecting groundwater residence times and flow paths.
- Natural dynamics of deep groundwater systems were reconstructed showing large residence times and paleoclimate characterisation.
- These deep aquifers show a Pleistocene seawater intrusion.
- Present-day mixing with saline surface water and contaminated shallow groundwater has been identified in the deep aquifers.

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# ABSTRACT

Implying large residence times and complex water origins deep coastal aquifers are of particular interest as they are remarkable markers of climate, water use and land use changes. Over the last decades, the Metropolitan Region of Recife (Brazil) went through extensive environmental changes increasing the pressure on water resources and giving rise to numerous environmental consequences on the coastal groundwater systems. We analysed the groundwater of the deep aquifers Cabo and Beberibe that are increasingly exploited. The processes potentially affecting groundwater residence times and flow paths have been studied using a multi-tracer approach (CFCs, SF6, noble gases, 14C, 2H and 18O). The main findings of these investigations show that: (1) Groundwaters of the Cabo and Beberibe aquifers have long residence times and were recharged about 20,000 years ago. (2) Within these old groundwaters we can find palaeo-climate evidences from the last glacial

Abbreviations: BP, Before present; EA, excess air amount; GMWL, global meteoric water line; LMWL, local meteoric water line; LGM, last glacial maximum; MAT, mean annual temperature; NGT, noble gas temperature; pMC, percentage of modern carbon; RMR, Metropolitan Region of Recife; RT, residence time; SST, sea surface temperature; STP, Standard Temperature and Pressure; UA, Unfractionated excess Air; ΔT, cooling estimate.

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Residence time Salinisation Contamination Palaeoclimate Noble gases Chlorofluorocarbons Radiocarbon Stable isotopes.

# 1. Introduction

Accounting for approximately 10% of the Earth's surface the coastal zones host more than half of the world population and human activities. In coastal zones, the social and economic development relies heavily on the availability of water resources for drinking water, agriculture and industry. In many countries, coastal water resources are limited and when surface water fails to meet the demand in terms of resource quality or quantity, groundwater turns out to be a valuable alternative. However, the rhythm at which human activities develop i.e. at which the water demand increases is usually much faster than the renewal times associated to the groundwater cycle and makes groundwater systems particularly vulnerable to environmental changes and human pressure.

Deep coastal groundwater systems are of particular interest as they usually imply large residence times and complex water origins that make these aquifers remarkable archives of climate, water use and land use changes (Edmunds and Milne, 2001). Furthermore, these aquifers are also highly sensitive to salinisation due to their proximity to the ocean and salinisation may be emphasised by aquifer exploitation. Therefore, the study of deep coastal aquifers allows the analysis of the link between anthropogenic pressures and hydrogeological processes which is critical to understand the dynamics and the resilience of coastal groundwater systems for a sustainable management of coastal groundwater resources (Araújo et al., 2015; Vengosh and Rosenthal, 1994).

In order to study groundwater dynamics and anthropogenic impacts for a given aquifer system, the combined use of environmental tracers is usually a fruitful strategy. Atmospheric tracers such as the CFCs and SF<sub>6</sub> are commonly used to study modern groundwater dynamics (<60 yr) and mixing processes as well as the impacts of environmental changes on groundwater systems (Ayraud et al., 2008; Bohlke and Denver, 1995; Cook et al., 1995; Koh et al., 2006). These anthropogenic gases have been released in the atmosphere since the 1950's and are subsequently found in natural waters through atmospheric equilibria that allow dating groundwater by the means of their atmospheric concentrations chronicles. In addition to tracers of modern recharge, radiocarbon dating is a valuable tool to assess slower groundwater dynamics associated with larger residence times (1000 to 40,000 yr) which are found in many aquifers (Corcho Alvarado et al., 2007). To understand the resilience of groundwater systems, impacts of changes in the climate and recharge conditions have been commonly assessed using dating tools combined with noble gases and/or stable isotopes  $\delta^2 H$  and  $\delta^{18}$ O (Aeschbach-Hertig et al., 2002; Beyerle et al., 1998; Castro et al., 2012; Corcho Alvarado et al., 2011; Gastmans et al., 2010; Plummer et al., 2012; Stute et al., 1995). Finally, processes of mixing and salinisation have been largely investigated using conservative geochemical tracers such as chloride and bromide (Aguilina et al., 2015; Cary et al., 2015; Vengosh et al., 1999).

In a context of declining precipitation and increasing demographic pressure the dry North-East of Brazil has been identified as an area of particular interest for the study of climate change and its effects on hydrological services (Bates et al., 2008). Over the last decades, the Metropolitan Region of Recife (RMR, Pernambuco, Brazil) underwent remarkable water and land use changes increasing the pressure on

period at the tropics with lower temperatures and dryer conditions than the present climate. (3) Recently, the natural slow dynamic of these groundwater systems was significantly affected by mixing processes with contaminated modern groundwater coming from the shallow unconfined Boa Viagem aquifer. (4) The large exploitation of these aquifers leads to a modification of the flow directions and causes the intrusion through palaeo-channels of saline water probably coming from the Capibaribe River and from the last transgression episodes. These observations indicate that the current exploitation of the Cabo and Beberibe aquifers is unsustainable regarding the long renewal times of these groundwater systems as well as their ongoing contamination and salinisation. The groundwater cycle being much slower than the human development rhythm, it is essential to integrate the magnitude and rapidity of anthropogenic impacts on this extremely slow cycle to the water management concepts. © 2016 Published by Elsevier B.V.

water resources and giving rise to numerous environmental consequences (Melo, 2013). Over the last three decades, the insufficient public water supply and repeated droughts (1998–1999 and 2012–2013) led to the development of a large and uncontrolled groundwater abstraction with 13,000 private wells (Costa et al., 2002). Recently, the dramatic decline of water tables and the ascertainment of local groundwater salinisation and contamination initiated the abandonment of shallow wells drilled in the superficial aquifers and the construction of new wells in the deep aquifers (Costa et al., 2002; Costa Filho et al., 1998). Despite the limited information about hydraulic connections between aquifers, the ongoing excessive groundwater exploitation is expected to induce significant aquifer exchanges (Costa Filho et al., 1998).

This work aims to address the need for a better understanding on groundwater systems in coastal population growing areas. This study will focus on the investigation of the processes potentially affecting groundwater flow paths and residence times in the deep aquifers of the RMR using a multi-tracer approach (noble gases, CFCs, SF<sub>6</sub>, <sup>14</sup>C,  $\delta^2$ H,  $\delta^{18}$ O and Cl<sup>-</sup>).

# 2. Materials and methods

#### 2.1. Study area

The RMR is an urban area located on the Atlantic coast of the Pernambuco State in north-eastern Brazil with a population of 1.538 million inhabitants (IBGE and E., 2011). The city of Recife was built on the estuary of the Capibaribe River that comprises smaller rivers and a mangrove threatened by recent urbanisation (Melo, 2013).

The RMR knows a hot and humid tropical climate with a mean annual temperature (MAT) of 25.5 °C and an average rainfall of 1600 mm/yr (Silva and de P.R., 2004). While temperatures show low seasonal variations, precipitations are characterised by two distinct seasons: a dry season (September–February, <100 mm/month) and a rainy season (March–August, >200 mm/month).

Surrounded by hills of about 100 m above sea level, the Recife coastal plain is located on two major Mesozoic sedimentary basins divided by an E-W structure called the Pernambuco Lineament. As shown in Fig. 1, the Pernambuco and the Paraíba sedimentary basins are found respectively south and north of the lineament and are underlying Cenozoic sediments that occur all across the plain of Recife.

The Pernambuco basin has a graben and horst structure (de Lima Filho et al., 2006; Maia et al., 2012) and hosts the Cabo Formation (Aptian–Albian) that overlies the crystalline basement of gneisses and granites. The Cabo Formation has mainly a continental origin (de Lima Filho, 1998) and consists of conglomerates of 90 m of average thickness. This formation is topped by arkosean sandstones alternating with discontinuous clay layers that separate the lower Cabo from the sandy upper Cabo. Then a marine transgression led to the formation of limestones deposits of the Estiva Formation (Late Cretaceous).

At the bottom of the Paraíba basin, the Beberibe Formation (Santonian–Campanian) overlies a crystalline basement of highly fractured granites, gneisses, schists and migmatites (de Lima Filho et al., 2006). With an average thickness of 200 m, the Beberibe Formation



Fig. 1. Geology and hydrogeology of the study area.

consists of continental sandstones and argillaceous deposits (Beurlen, 1967) that are underlying the Campanian–Maastrichtian estuarine and lagoonal deposits of the Itamaracá Formation and the limestones with thin interbedded clays of the Gramame Formation (Barbosa et al., 2003). Then a marine transgression led to the formation of Palaeocene and Eocene limestones deposits of the Maria Farinha Formation (Mabesoone et al., 1968).

Finally, fluvial deposits of the Barreiras Formation (Plio-Pleistocene) and the quaternary sediments cover the two Mesozoic sedimentary basins. With an average thickness of 40 m, the Boa Viagem Formation consists mainly of Pleistocene and Holocene marine terraces originating from the last transgression episodes at 123,000, 5100, 3600 and 2500 yr BP (Dominguez et al., 1990; Martin et al., 1996). It also includes tidal lagoon and alluvial deposits, sandstone, reefs, freshwater swamps and mangroves.

In Recife, the public water supply relies mainly on surface waters and dams. Nevertheless, the contemporaneous rise in water demand due to population growth and the repeated droughts led to an increase in groundwater abstraction.

The coastal plain of Recife hosts three main aquifers: the shallow unconfined Boa Viagem aquifer and two deep confined aquifers within the Beberibe and Cabo formations. The Boa Viagem aquifer is the most vulnerable water resource in terms of pollution due to its connection to the mangrove, the estuary and urbanised areas (Leal, 1994). Over the last decades, the dramatic decline of piezometric levels and groundwater quality induced the abandonment of some wells of the Boa Viagem aquifer and led to the drilling of numerous private wells in the deep aquifers (Cabo and Beberibe).

According to the lithological description of the wells, the Cabo and Beberibe aquifers are confined by several clay layers of spatially varying thickness (Cary et al., 2015). However, this aquitard gives locally way to sandy levels where the two deep aquifers are consequently locally unconfined. Despite the limited information about hydraulic connections between aquifers, the ongoing excessive groundwater exploitation is expected to induce significant aquifer exchanges (Costa Filho et al., 1998).

#### 2.2. Sampling and analyses

Forty wells were sampled in the three aquifers (Boa Viagem, Cabo and Beberibe) during a sampling campaign that took place after the rainy season in March 2013 (except 3 samples in September 2013). All the samples were analysed for dissolved gases, chemistry and the stable isotopes <sup>18</sup>O and <sup>2</sup>H. Some samples of the Cabo and Beberibe aquifers were selected for radiocarbon analysis according to their hydrochemical characteristics and spatial distribution.

Stable isotopes (<sup>18</sup>O and <sup>2</sup>H) and anion analyses were performed respectively at the University of São Paulo and BRGM laboratory (Orléans, France) following the procedures detailed in Cary et al. (2015). The uncertainty is  $\pm 0.09\%$  for  $\delta^{18}$ O and  $\pm 0.9\%$  for  $\delta^{2}$ H.

The SF<sub>6</sub> and CFCs (CFC-11, CFC-12 and CFC-113) were sampled in steel ampoules (300 mL and 40 mL respectively) and analysed quickly after the sampling campaign using a Purge-and-trap GC-ECD (Perkin-Elmer) at Geosciences Rennes gas laboratory (Rennes, Brittany, France). An uncertainty of 3% applies to the values above 0.1 pmol/kg for CFCs and 0.1 fmol/kg for SF<sub>6</sub> and rises to 20% for lower values (Labasque et al., 2014). The detection limits are 0.06 fmol/L for SF<sub>6</sub>, 0.05 pmol/L for CFC-11, 0.02 pmol/L for CFC-12 and 0.015 pmol/L for CFC-113.

Major and noble gases were measured throughout the sampling campaign using a GC-TCD (Agilent 3000A Micro-GC) after headspace extraction following the Sugisaki and Taki method (1987) with an analytical precision of 2.5% for Ar, 4% for  $N_2$  and 10% for Ne.

# 2.3. Noble gas temperature modelling

Based on the work of Aeschbach-Hertig et al. (1999) an inverse model was developed to infer the recharge conditions of the aquifers. This model has been adapted to use the available dissolved Ne, Ar and N<sub>2</sub> concentrations in cm<sup>3</sup>STP/g (Standard Temperature and Pressure) to model the noble gas temperature (NGT) and the amount of excess air (EA) that is commonly used to correct atmospheric tracer concentrations (CFC-12 and SF<sub>6</sub>).

Conceptual models have been proposed to describe the excess air component in order to infer recharge conditions from the dissolved noble gas concentrations (Aeschbach-Hertig et al., 2000; Aeschbach-Hertig and Solomon, 2013; Freundt et al., 2013; Stute et al., 1995). Given the limited number of available dissolved gases (Ne, N<sub>2</sub> and Ar) and their related analytical uncertainty this study considers a simple model of excess air formation to determine the recharge conditions of the aquifers of Recife.

Among these simple conceptual models, the Unfractionated excess Air model (UA model) assumes a total dissolution of unfractionated excess air. In the UA model, the dissolved noble gas concentrations are assumed to depend only on the recharge temperature (also called noble gas temperature, NGT), the volume of unfractionated excess air (EA), the altitude of recharge (H) and the recharge salinity (S). Since H and S are well known only two free parameters (NGT and EA) remain to be determined using the inverse model with a degree of freedom v = 1.

The UA model has already been implemented with  $N_2$  and Ar concentrations measured in gas-chromatography by Plummer et al. (2012) to infer the recharge conditions of an old groundwater system in the Atlantic Coastal Plain, USA. As Plummer et al. found  $N_2$ —Ar recharge temperatures in good agreement with NGTs predicted with the full suite of noble gases using a more complex conceptual model, the UA model appears to be a suitable choice for the determination of the recharge conditions of the aquifers of Recife.

The uncertainties associated with the model predictions are given by Monte-Carlo simulation that takes into account the analytical uncertainties to derive the model uncertainties on each NGT and EA. For the described configuration (3 noble gases to infer the NGT and EA of the UA model), the typical calculated uncertainties  $\sigma_{NGT} = 2.5$  °C and  $\sigma_{EA} = 0.0013$  cm<sup>3</sup>STP/g are significant and were balanced by the large number of samples collected on the field.

The average NGT calculated for the Boa Viagem aquifer NGT<sub>BOV</sub> = 22.6  $\pm$  0.6 °C is slightly lower than the MAT (25.5 °C) and was considered as the current recharge temperature for the region. In the following sections the calculated  $\Delta T$  of a sample represents the temperature difference between the apparent modern recharge temperature (NGT<sub>BOV</sub>) and the sample NGT.

### 2.4. Radiocarbon dating

Radiocarbon analyses were performed on selected samples of the Cabo and Beberibe aquifers. This selection was mainly based on the distribution of NGTs and chloride concentrations as well as the spatial distribution of the samples.

The preparation and measurements of the <sup>13</sup>C/<sup>12</sup>C ratio and <sup>14</sup>C activity were performed by Beta Analytic Inc. The dissolved inorganic carbon was extracted by acidification (with H<sub>3</sub>PO<sub>4</sub>) under vacuum and then cryogenically purified. An aliquot was used for the measurement by mass spectrometry of the  $^{13}$ C/ $^{12}$ C ratio. The CO<sub>2</sub> was reduced to graphite to be analysed. The  $^{14}$ C activity was measured by Accelerator Mass Spectrometry. The <sup>14</sup>C activity was measured relative to the modern carbon reference and is expressed in % of modern carbon (pMC) and normalised taking into account the value of  $\delta^{13}$ C. Radiocarbon dating was performed through the software NETPATH (Plummer et al., 1994) using the revised Fontes and Garnier model (Han and Plummer, 2013) to derive <sup>14</sup>C ages expressed in years before present (yr BP). The uncertainty associated to the radiocarbon age of each sample is calculated as the standard deviation of the radiocarbon ages given by different radiocarbon dating models available in NETPATH: Vogel, Tamers, Eichinger, Mook, Ingerson, Fontes and Garnier. These uncertainties vary between 500 and 1500 yr.

As in the case of many studies the  $\delta^{13}$ C of rock matrixes were not available. Therefore, the commonly used value of 1‰ has been selected in NETPATH for  $\delta^{13}$ C of the rock matrix. Similarly, there is no information on  $\delta^{13}$ C of the soil CO<sub>2</sub> and this value is often guessed by the authors. Usually, the soil CO<sub>2</sub> is fractionated by the soil plants and thus shows the isotopic signature of either C<sub>4</sub> plants (-10 to -15%) or C<sub>3</sub> plants (around -25%). Nowadays, C<sub>4</sub> plants are very abundant in Northeastern Brazil (Powell and Still, 2009) however, low  $\delta^{13}$ C of the DIC have been measured in sample of the RMR (most are found between -15% and -20%) indicating that at the time of the recharge the  $\delta^{13}$ C of the soil CO<sub>2</sub> was probably more influenced by C<sub>3</sub> plants than it is now. Therefore the value of -25% was selected in NETPATH for the  $\delta^{13}$ C of the soil CO<sub>2</sub>.

### 2.5. Interpolations

The two-dimensional interpolations used in this article are based on a biharmonic spline interpolation implemented in the software MATLAB® (griddata v4 method).

#### 3. Results

# 3.1. Noble gases and NGTs

Noble and major gas analysis shows a clear distinction between the shallow aquifer Boa Viagem and the two deep underlying aquifers Cabo and Beberibe. Fig. 2a shows that the Boa Viagem aquifer presents low concentrations in Ne, Ar and N<sub>2</sub> while Cabo and Beberibe have significantly higher gas concentrations.

Groundwaters may show *in-situ* production of  $N_2$  through denitrification processes (Boisson et al., 2013). Such activity usually induces high contents of NO<sub>2</sub>, N<sub>2</sub>O when the reaction is not complete or high N<sub>2</sub>/Ar ratios when the reaction is total. In this study, no evidences of



Fig. 2. Measured N<sub>2</sub> and Ar concentrations (2a) and modelled NGTs (2b) for the Boa Viagem (BOV), Cabo (CAB) and Beberibe (BEB) aquifers.

non-atmospheric sources of N<sub>2</sub> were found in the deep aquifers (Cabo and Beberibe). Fig. 2a shows that Cabo and Beberibe aquifers have relatively low N<sub>2</sub>/Ar ratios and their N<sub>2</sub> contents are proportional to Ar contents ([N<sub>2</sub>] = 45.98-[Ar]; R<sup>2</sup> = 0.85). This trend is characteristic of physical processes defining gas concentrations in groundwater such as solubility and excess air. Therefore, the observed N<sub>2</sub> concentrations of the deep aquifers will be assumed to originate only from the atmosphere and hence reflect the characteristics of the aquifers recharge.

The concentrations in Ne, Ar and N<sub>2</sub> were implemented in the inverse model described earlier in order to derive the recharge temperature (NGT) and the amount of excess air (EA) for each sample. The results presented in Fig. 2b show that the NGTs are inversely proportional to Ar contents according to the laws of gas solubility. On the one hand, the Boa Viagem aquifer displays high NGTs (with low Ar concentrations) with an average recharge temperature of 22.6  $\pm$  0.6 °C. On the other hand, the Cabo and Beberibe aquifers show low recharge temperatures (with high Ar concentrations) with an average value of 17.1  $\pm$  1.2 °C. However, the Cabo and Beberibe samples cannot be distinguished on the basis of their noble gas contents or NGTs.

Since the noble gases Ne and Ar only have negligible non-atmospheric sources and N<sub>2</sub> production has been excluded in the deep aquifers, the high dissolved gas concentrations observed in the Cabo and Beberibe samples as well as their corresponding low NGTs have to be explained by other processes.



Thirteen samples from the Cabo and Beberibe aquifers were analysed for radiocarbon and provided <sup>14</sup>C residence times (RTs) for groundwater. The results presented in Fig. 3 show that the RTs of the deep aquifers vary over a large time period ranging from 2000 to 16,500 yr BP.

Fig. 3 also shows that the NGTs of the deep aquifers decrease with increasing RTs. Hence, the lowest recharge temperatures are measured for the samples with the largest RTs while the "modern" ones provide warmer NGTs close to the current recharge temperatures (NGT<sub>BOV</sub>). Between 16,500 and 11,500 yr BP the NGTs remain relatively stable close to the value of 15.0 °C. Then, from 11,500 yr BP and present time the NGTs continue to increase slowly to reach the current recharge temperature (NGT<sub>BOV</sub> =  $23.0 \pm 0.6$  °C).

# 3.3. Stable isotopes of water

Stable isotopes of water were analysed for the Boa Viagem, Cabo and Beberibe aquifers. The results presented in Fig. 4 show that all the samples present a trend similar to the global meteoric water line (GMWL:  $\delta^2 H = 8.0 \times \delta^{18}O + 10.0$ , Rozanski et al., 1993) indicating a meteoric origin. Regarding each aquifer, two main trends may be delineated. On the one hand, the Cabo and Beberibe samples gather along a line which is slightly steeper than the modern local meteoric water line (LMWL:



**Fig. 3.** Evolution of the NGTs with residence times (<sup>14</sup>C ages) in the Boa Viagem (BOV), Cabo (CAB) and Beberibe (BEB) aquifers.



Fig. 4. Measured  $\delta^2 H$  and  $\delta^{18} O$  for Boa Viagem (BOV), Cabo (CAB) and Beberibe (BEB) aquifers.



**Fig. 5.** Measured SF<sub>6</sub> and CFC-12 concentrations for Boa Viagem (BOV), Cabo (CAB) and Beberibe (BEB) aquifers. The red lines show the equilibrium concentrations of each tracer with the atmosphere of the Southern Hemisphere 2010.

 $\delta^2 H = 7.4 \times \delta^{18} O + 11.1$ , Cary et al., 2015). On the other hand, samples from the Boa Viagem aquifer clearly plot along the dotted line that characterises evaporation processes or mixing with evaporated surface waters (Cary et al., 2015). Once again, there is a distinction between shallow Boa Viagem samples affected by evaporation and the deep Cabo and Beberibe samples plotting along a meteoric water line thus showing no evaporation influence.

# 3.4. CFCs and SF<sub>6</sub>

Chlorofluorocarbon and sulphur hexafluoride analyses were performed on 40 samples of the Boa Viagem, Cabo and Beberibe aquifers. Fig. 5 shows that for the Cabo and Beberibe aquifers, the results are relatively homogeneous with very low CFCs and low SF<sub>6</sub> concentrations. On the contrary, Boa Viagem samples show a large variability of CFC contents which are generally greater than the deep aquifers values and sometimes exceed atmospheric equilibria (especially for CFC-113) represented by red lines in Fig. 5. The SF<sub>6</sub> concentrations show less variability than CFCs in the Boa Viagem aquifer but remain higher than the values observed for the Cabo and Beberibe.

According to the previous sections, the Cabo and Beberibe aquifers do not clearly differ on the basis of their NGTs, RTs, stable isotopic signatures and atmospheric tracer contents. Therefore, we will consider in the following sections that these two deep aquifers behave similarly and record the same physical processes.

# 4. Discussion

#### 4.1. Quantification of mixing processes

The different tracers used in this study give complementary information that can be combined to understand the mixing processes occurring in the deep aquifers of Recife.

 Table 1

 End-members characteristics considered for the ternary mixing problem.

End-member	<sup>14</sup> C activity (pMC)	$Cl^{-}$ (mg/L)
Boa Viagem aquifer	90	30-150
Capibaribe River	90	2500
Pleistocene Seawater	0	19,000
Palaeo-recharge	To be inferred	10

#### Table 2

Palaeo-recharge residence time and mixing extents inferred for each end-member for Cabo and Beberibe samples. The saline components percentages refer to mixing processes occurring either with Pleistocene Seawater (P-S) or Capibaribe River (C-R).

Sample	Modern component (%)	Saline component (%)	Palaeo-recharge component (%)	Palaeo-recharge <sup>14</sup> C age (kyr BP)				
CAB-002	10.0	0.0	90.0					
CAB-003	5.0	0.0	95.0	19.5				
CAB-004	9.0	1.0 (P-S)	90.0					
CAB-005	19.0	7.0 (P-S)	74.0	14.8				
CAB-010	11.0	1.5 (P-S)	87.5					
CAB-011	7.0	0.0	93.0					
CAB-012	5.0	0.0	95.0	8.7				
CAB-013	7.0	2.5 (P-S)	90.5					
CAB-017	11.0	4.0 (P-S)	85.0	6.7				
CAB-020	16.0	0.0	84.0					
CAB-022	9.0	0.0	91.0					
CAB-023	38.0	2.0 (P-S)	60.0					
CAB-024	30.0	9.0 (P-S)	61.0	20.0				
CAB-026	19.0	0.0	81.0					
CAB-027	11.0	0.0	89.0	17.8				
CAB-101	25.0	0.0	75.0					
CAB-102	19.0	0.0	81.0					
CAB-114	16.0	2.5 (P-S)	81.5					
TTD-094	9.0	3.0 (P-S)	88.0	11.1				
TTD-110	7.0	2.5 (P-S)	90.5	14.3				
BEB-047	22.0	0.0	78.0					
BEB-050	21.0	8.0 (C-R)	71.0					
BEB-051	35.0	8.0 (C-R)	57.0					
BEB-057	10.0	8.0 (C-R)	82.0	13.5				
BEB-059	12.0	8.0 (C-R)	80.0	4.6				
BEB-060	93.0	7.0 (C-R)	0.0					
BEB-062	12.0	1.0 (P-S)	87.0	14.5				
BEB-036	17.0	1.0 (P-S)	82.0	16.0				
ALM-073	17.0	6.0 (C-R)	77.0	8.4				

On the one hand, considering the large RTs (beyond the CFCs and SF<sub>6</sub> dating range) deduced from <sup>14</sup>C measurements in the Cabo and Beberibe aquifers, such "old" groundwater should not contain any tracer of modern recharge or at least only close to the recharge areas. However, the Cabo and Beberibe aquifers show CFCs and SF<sub>6</sub> contents all over the plain of Recife. Furthermore, the presence of these atmospheric tracers is not a punctual phenomenon as they are spatially distributed in the deep aquifers. Therefore, it is reasonable to assume that the CFCs and SF<sub>6</sub> concentrations observed in the Cabo and Beberibe aquifers originate from mixing with the Boa Viagem shallow groundwater rather than from direct exchanges with surface sources (atmosphere or urban contamination).

On the other hand, some chloride concentrations measured in the deep aquifers exceed the maximum concentrations observed in the



**Fig. 6.** Evolution of the temperature cooling ( $\Delta T$ ) with residence time (<sup>14</sup>C age).

![](_page_6_Figure_1.jpeg)

**Fig. 7.** Evolution of the  $\delta^{18}$ O as a function of the NGT.

Boa Viagem aquifer. Therefore, the chemical composition of the Cabo and Beberibe aquifers cannot be explained by a single binary mixing with the Boa Viagem aquifer. Accordingly, the quantification of the mixing processes that takes place in the deep aquifers of Recife consists in solving a ternary mixing between a palaeo-recharge, a saline endmember and a modern end-member (Boa Viagem aquifer).

In order to characterise the modern end-member, we considered local averages of the Boa Viagem samples for each deep aquifer (BOV-113 for the southern Cabo aquifer, an average of BOV-014, BOV-019, BOV-100 and BOV-110 for the northern Cabo aquifer and an average of BOV-030, BOV-033, BOV-034, BOV-046 and BOV-130 for the Beberibe aquifer). Samples presenting signs of lithogenic production of SF<sub>6</sub> or punctual extreme values of one of the CFCs were excluded from the average Boa Viagem composition. Then, a binary mixing problem between

an "old" end-member (free from CFCs and SF<sub>6</sub>) and the local averages of the Boa Viagem was solved to derive the proportions of modern groundwater in the deep aquifers. For each Cabo and Beberibe sample, the percentage of modern end-member varied from a tracer to another, however, when at least 3 tracers provided mixing values with a standard deviation <0.1, an average mixing percentage was considered. This first step allowed quantifying the proportion of modern groundwater (<60 years old) in the Cabo and Beberibe aquifers. The next steps consisted in identifying older end-members (free from CFCs and SF<sub>6</sub>) involved in the mixing processes according to their chloride contents and radiocarbon activity.

Given the existing saline bodies in the RMR and the transgressionregression history of the region, several saltwater sources are likely to affect the groundwater chemistry in Recife. Considering the assumptions formulated by Cary et al. (2015) based on chemical and isotopic data and allowing for the spatial distribution of salt concentrations in the deep aquifers, a salinisation by modern seawater was excluded and two saline end-members have been considered: the Capibaribe River and the palaeo-seawater from the Pleistocene transgression (123,000 yr BP) recorded in the Boa Viagem Formation (Dominguez et al., 1990; Martin et al., 1996).

Table 1 shows the characteristics of the different end-members considered in the ternary mixing problem. Chloride contents were measured by Cary et al. (2015) except the palaeo-seawater that was assumed to have a chloride composition close to the modern seawater. The radiocarbon activity was assumed to be 90 pMC for modern endmembers and 0 pMC for the Pleistocene seawater.

At this stage, the information given by the partial identification of the palaeo-recharge (radiocarbon activity is still unknown), the complete identification of the other end-members and the determination of the modern end-member proportions allows solving the ternary mixing problem. In a chloride versus radiocarbon activity diagram,

![](_page_6_Figure_9.jpeg)

Fig. 8. Spatial interpolation of residence times (<sup>14</sup>C ages) in the Cabo and Beberibe aquifers. Black arrows show natural flow directions coming from the edge of the plain to the estuary and the Atlantic Ocean. Black dots show the location of sampled wells used for the interpolation.

setting the known characteristics of each end-member and the percentage of modern component enables to determine by trial and error the radiocarbon activity of the palaeo-recharge and the two last mixing proportions. Table 2 summarises the mixing extents of the considered endmembers for each Cabo and Beberibe samples. In the end, the resolution of the mixing problem enables to study independently the three components involved in the mixing processes.

# 4.2. Climate reconstruction

#### 4.2.1. Recharge temperatures

This part of the discussion focuses on the palaeo-recharge component inferred in the previous section. Fig. 6 shows the evolution of the cooling estimate ( $\Delta T$ ) as a function of the residence time of the palaeo-recharge i.e. the radiocarbon age of the sample calculated from the radiocarbon activity corrected from mixing (using RT = 5730/ln(2) × ln(90/a<sub>corrected</sub>)). Contrary to radiocarbon activities, the inferred NGTs have not been corrected from mixing as the corrections on gas concentrations seem uncertain and risk to alter the information of the dataset. In Fig. 6, two outliers have been removed from this figure due to either an excessive mixing extent affecting the sample NGT (CAB-024) or a radiocarbon dating bias (incoherence with the neighbouring samples) that underestimated the sample RT (CAB-017).

The palaeo-recharge component shows RTs ranging from 4600 to 19,500 yr BP that are somewhat larger than the modelled <sup>14</sup>C ages of the deep samples before correction for mixing (results section). These differences do not affect the general trend observed earlier between recharge temperatures and residence times. Once more, there is an increase in  $\Delta$ Ts (decrease in NGTs) with increasing RTs, starting from 0.4  $\pm$  2.9 °C at 4600 yr BP to 8.0  $\pm$  2.7 °C close to the last glacial maximum (LGM around 18,000 yr BP). Fig. 6 also shows that the transition between Late-Glacial and present day recharge temperatures is a

relatively rapid process (1  $^\circ\text{C}/1000$  yr) that takes place between 13,500 and 5000 yr BP.

The residence times observed in the Cabo and Beberibe aquifers refer to Late-Pleistocene and Holocene periods. Over the last decades, the temperature cooling of the region during this period has been documented in the literature including noble gas data, pollen data, speleothem data and oceanographic data (Aeschbach-Hertig et al., 2002; Behling, 1995; Behling and Lichte, 1997; Behling, 1998; Behling et al., 2002; Bush et al., 2007; Ledru et al., 1996; Ledru et al., 2009; Santos et al., 2013; Santos et al., 2014; Stute et al., 1995; Wang et al., 2004). These studies observed that the Late-Pleistocene and Holocene periods recorded a dry and cold phase at the LGM in north-eastern Brazil and a global warming towards the present day warmer and wetter climate. Therefore, this study produces a temperature trend over time that is consistent with the previous observations.

The beginning of the recharge temperatures transition described earlier is also consistent with a previous palaeoclimate data review (Bush et al., 2007). These authors highlight the persistence and, in some cases, the peak abundance of cold resistant taxa in eastern Amazonia and coastal Brazil until 14,000 yr BP while western Amazonia and the Andes were already recording a considerable warming of the climate (Bush et al., 2007). However, the rapidity and time of the transition has not yet been precisely documented for the region (Behling, 1995; Ledru et al., 1996). Nevertheless, the recorded NGT transition period (Fig. 5) concurs with the short time gap in the NGT record published by Stute et al. (Stute et al., 1995) that separates cool Pleistocene recharge temperatures (24.2 °C) from warm Late-Holocene NGTs (29.6 °C) measured in the Piaui province, Brazil.

Another synthesis of terrestrial palaeoclimate data was carried out for tropical climates at the LGM (Farrera et al., 1999). These authors show that over the past two decades many studies have attempted to produce regional cooling estimates at the LGM. If the  $\Delta$ Ts differ from a

![](_page_7_Figure_10.jpeg)

Fig. 9. Spatial interpolation of the percentage of saline component (Capibaribe River or Pleistocene Seawater) in the Cabo and Beberibe aquifers. Black dots show the location of sampled wells used for the interpolation.

study to another depending on the site location and the palaeoclimate proxy, the values suggested in the literature lie in a range of 4 °C to 7 °C (Farrera et al., 1999). In the plain of Recife the predicted cooling estimate reach the value of 8.0  $\pm$  2.7 °C that slightly exceeds the values reported for tropical Brazil. These cooler recharge temperatures carry substantial uncertainties and might reflect the limits of the simple method employed here that seems to underestimate the NGTs.

# 4.2.2. Precipitation pattern

The predicted temperature change at LGM ( $\Delta$ T) does not seem to be recorded by the stable isotopes of water as shown in the Fig. 7. In the case of a large cooling, the samples of the deep aquifers would have undergone a stronger fractionation and would appear more depleted in heavy isotopes than the shallow aquifer (Jasechko et al., 2015). On the contrary, Fig. 7 shows that the oldest and coldest samples of the deep aquifers show less isotopic fractionation ( $\delta^{18}$ O varying from -1.25 to -1.05%) than the youngest and warmest ones ( $\delta^{18}$ O varying from -1.34 to -1.52%). The reasons of these discrepancies can be explained by the following: (1) There is a lack of correlation between  $\delta^{18}$ O and temperature when the MATs ( $\approx$ NGTs) are larger than 20 °C because of the amount effect observed in the tropics (Rozanski et al., 1993). (2) The sea surface temperatures (SST) of the region documented for the Late-Pleistocene and Holocene periods did not vary as much as in the continent ( $\Delta T = 2$  °C, Santos et al., 2013). Since the plain of Recife is a coastal area and receives its precipitation directly from the ocean, the stable isotopic signatures would just reflect the Rayleigh distillation happening at the sea surface at a quasi-non-contrasted temperature. (3) Another possibility would be that the ocean water presented higher isotopic values during the LGM. The global cooling led to ice formation and subsequent higher <sup>16</sup>O sequestration in continental ice, favouring therefore <sup>18</sup>O enrichment in the remaining ocean water by a range of about 1‰ for  $\delta^{18}$ O (Baker and Fritz, 2015). Such a change in the oceanic source of vapour would lead, despite of the regional air cooling, to richer isotopic signatures of the resulting precipitation.

### 4.3. Assessment of natural dynamics and anthropogenic impacts

Apart from palaeo-climate record, the study of the palaeo-recharge component informs on the natural flows occurring in the deep aquifers of Recife. Fig. 8 shows that the RTs increase from 4000 yr BP close to the high topographic areas surrounding the plain to 20,000 yr BP on the coastline. Hence, the study of the palaeo-recharge evidences natural flows starting from recharge areas located at the edges of the plain that are moving slowly ( $\approx$  0.7 m/yr) to the estuary and the sea (discharge areas).

With a better understanding of the natural dynamics of the deep aquifers of Recife, this section will now consider the impacts of the saline and modern components involved in the mixing processes shown respectively in the Figs. 9 and 10.

In the southern part of the plain, most of the wells located close the Atlantic Ocean (East of the plain) show very low chloride contents while the salinised samples can be found further inland to the West. This observation supports that a modern seawater intrusion is not directly involved in the ongoing salinisation of the Cabo aquifer. Considering the geological and climate history of the region as well as the assumptions made by Cary et al. (2015) based on Sr and B isotopic data, the salty groundwater found in the Cabo aquifer and in some wells of the Beberibe aquifer (BEB-036 and 062) most probably originates from the Pleistocene marine transgression that occurred at 123,000 yr BP. As shown in Table 2 and Fig. 9, this old saline component affects a dozen of wells of the Cabo and Beberibe aquifer that show between 1 and 9% mixing with the Pleistocene seawater.

In the northern part of the plain of Recife, the Fig. 9 shows that most of the samples of the Beberibe aquifer are affected by infiltration of 6 to

![](_page_8_Figure_11.jpeg)

Fig. 10. Spatial interpolation of the percentage of Boa Viagem component leaking in the Cabo and Beberibe aquifers. Black dots show the location of sampled wells used for the interpolation.

8% of salty water coming from the Capibaribe River (BEB-050, 051, 057, 059, 060 and ALM). Recently drawn by large groundwater abstraction, these saline waters reach the deep aquifer system using the presentday Capibaribe River channel and the palaeo-channels that were evidenced by Cary et al. with boron isotopes (Cary et al., 2015).

In addition to salinisation processes, Table 2 and Fig. 10 highlight the presence in variable proportions (5 to 93%) in the deep aquifers of Recife of a modern component i.e. shallow contaminated groundwater from the Boa Viagem aquifer. Fig. 10 also shows that these leakages from the Boa Viagem aquifer are the largest in the high well density areas (in the Madalena neighbourhood for the Beberibe aquifer and on the coastline for the Cabo aquifer) where flow direction measurements carried out in March 2014 evidenced downward flows around the mangrove (CAB-005 and 006) and in the Boa Viagem neighbourhood (coastline). These observations support the assumption that large drawdowns related to important deep groundwater abstraction and associated with the construction of improperly sealed wells induced a significant modification of groundwater flows.

As a result, the Cabo and Beberibe aquifers have become more vulnerable to contamination and salinisation and the ongoing mixing with contaminated shallow groundwater (Boa Viagem aquifer) and saline surface water (Capibaribe River) is severely threatening the quality of the groundwater resource of Recife.

#### 5. Conclusion

Over the last decades, the Metropolitan Region of Recife went through remarkable water and land use changes increasing the pressure on water resources and giving rise to numerous environmental consequences on the coastal groundwater systems.

We analysed the groundwater of the deep aquifers Cabo and Beberibe that are increasingly exploited. The processes potentially affecting groundwater residence times and flow paths have been studied using a multi-tracer approach (CFCs, SF<sub>6</sub>, noble gases, <sup>14</sup>C, <sup>2</sup>H and <sup>18</sup>O). The main findings of these investigations show that:

(1) Groundwaters of the Cabo and Beberibe aquifers have long residence times and were recharged about 20,000 years ago.

- (2) Within these old groundwaters we can find palaeo-climate evidences from the last glacial period at the tropics with lower temperatures and dryer conditions than the present climate.
- (3) Recently, the natural slow dynamic of these groundwater systems was significantly affected by mixing processes with contaminated modern groundwater coming from the shallow unconfined Boa Viagem aquifer.
- (4) The large exploitation of these aquifers leads to a modification of the flow directions and causes the intrusion through palaeochannels of saline water probably coming from the Capibaribe River and from the last transgression episodes.

These observations indicate that the current exploitation of the Cabo and Beberibe aquifers is unsustainable regarding the long renewal times of these groundwater systems as well as their ongoing contamination and salinisation. The groundwater cycle being much slower than the human development rhythm, it is essential to integrate this extremely slow cycle to the water management concepts. Finally, if the magnitude of environmental changes is comparable to the anthropic pressure exerted on natural systems, the contrasting rapidity at which such large and permanent changes can occur in slow dynamic systems has to be emphasised.

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# Appendix A

#### Table A

Summary of the SF<sub>6</sub>, CFCs, noble gas and chloride concentrations as well as the  $\delta^{18}$ O and  $\delta^{2}$ H measured in the Boa Viagem, Cabo and Beberibe aquifers. Recharge conditions modelling (NGT and EA) is based on the UA model that uses either Ne, Ar and N<sub>2</sub> concentrations (UA3) or only Ne and Ar concentrations (UA2). The error is 3% on CFCs and SF<sub>6</sub>, 2.5% on Ar, 4% on N<sub>2</sub>, 10% on Ne, 0.09‰ on  $\delta^{18}$ O and 0.9‰ on  $\delta^{2}$ H.

	SF <sub>6</sub>	CFC-12	CFC-11	CFC-113	Ne	Ar	N <sub>2</sub>	Model	NGT	$\sigma_{\text{NGT}}$	EA	$\sigma_{\text{EA}}$	ΔΤ	Cl <sup>-</sup>	$\delta^{18}$ O	$\delta^2 H$
Units	fmol/L	pmol/L	pmol/L	pmol/L	$\times 10^{-7}$ ccSTP/g	$\times 10^{-4}$ ccSTP/g	$\times 10^{-2}$ ccSTP/g		°C	°C	$\times 10^{-3}$ ccSTP/g	$\times 10^{-3}$ ccSTP/g	°C	mg/L	‰ V-SMOW	‰ V-SMOW
BOV-014	2.53	14.39	0.28	0.31	2.58	3.02	1.76	UA2	29.9	3.5	4.73	1.49		267.2	-1.02	1.1
BOV-019	2.85	0.37	0.22	0.30	2.34	3.21	1.63	UA2	22.8	3.1	3.01	1.5		62.3	-0.57	3.9
BOV-030	1.62	1.29	0.46	0.11	2.74	3.29	1.64	UA2	25.7	3.8	5.43	1.75		70.5	-1.18	-0.4
BOV-033	1.16	0.73	1.07	0.07	2.71	3.54	1.61	UA2	20.0	3.1	4.84	1.69		18.3	-1.75	-2.2
BOV-034	1.06	0.44	0.11	0.19	2.8	3.67	1.82	UA3	21.2	3.0	7.38	1.28		14.5	n.a.	n.a.
BOV-046	2.21	0.05	0.10	0.11	2.68	3.53	1.74	UA3	22.7	3.0	6.83	1.21		110.6	-1.21	1.0
BOV-100	2.63	0.14	0.10	1.48	1.98	3.32	1.79	UA3	21.1	2.5	4.37	1.03		173.6	-0.59	1.6
BOV-110	2.31	0.24	0.11	0.50	2.55	3.37	1.54	UA3	22.9	2.9	4.99	1.13		89.4	-0.36	4.1
BOV-112	1.59	0.37	0.19	0.39	2.42	3.32	1.67	UA2	21.5	3.0	3.38	1.54		2826.8	-0.98	1.0
BOV-113	6.00	2.11	0.89	0.30	2.43	3.27	1.56	UA2	22.6	3.1	3.52	1.54		856.9	-0.52	4.4
BOV-115	2.46	0.07	0.13	0.07	3.56	3.18	1.53	UA3	32.9	2.5	7.75	0.93		17.8	-1.47	-0.8
BOV-130	8.35	2.11	1.74	0.62	2.46	3.08	1.30	UA3	25.8	2.8	3.16	1.00		26.4	-1.47	-0.2
CAB-002	1.06	0.11	0.09	0.03	3.42	4.02	1.82	UA3	16.8	2.8	7.61	1.40	5.9	38.3	-1.25	2.7
CAB-003	0.53	0.07	0.14	0.08	3.52	4.23	1.94	UA3	14.8	2.7	8.36	1.46	7.8	23.5	-1.24	1.9
CAB-004	0.54	0.08	0.13	0.08	3.67	4.22	1.96	UA3	15.7	2.9	9.00	1.50	6.9	206.8	-1.31	1.4
CAB-005	n.a.	0.09	0.35	0.04	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1402.7	-1.16	1.9
CAB-010	0.58	0.10	0.17	0.11	3.50	3.92	1.78	UA3	18.6	3.0	7.76	1.38	4.0	290.0	-1.15	2.6
CAB-011	0.52	0.03	0.11	0.01	4.04	4.16	1.91	UA3	17.4	3.1	9.31	1.50	5.2	28.4	-1.22	2.7
CAB-012	13.21	0.07	0.07	0.01	3.33	4.00	1.85	UA3	17.3	2.9	7.87	1.39	5.3	17.7	-1.34	2.0
CAB-013	n.a.	0.06	0.10	0.02	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	502.3	-1.24	2.3

(continued on next page)

#### Table A (continued)

	SF <sub>6</sub>	CFC-12	CFC-11	CFC-113	Ne	Ar	N <sub>2</sub>	Model	NGT	$\sigma_{\text{NGT}}$	EA	$\sigma_{\text{EA}}$	ΔΤ	Cl-	$\delta^{18}0$	$\delta^2 H$
Units	fmol/L	pmol/L	pmol/L	pmol/L	$\times 10^{-7}$ ccSTP/g	$\times 10^{-4}$ ccSTP/g	$\times 10^{-2}$ ccSTP/g		°C	°C	$\times 10^{-3}$ ccSTP/g	$\times 10^{-3}$ ccSTP/g	°C	mg/L	‰ V-SMOW	‰ V-SMOW
CAB-017	0.52	0.04	0.08	0.07	3.41	4.30	2.04	UA3	14.3	2.7	8.92	1.50	8.4	724.1	-1.12	3.1
CAB-020	1.08	0.42	0.09	0.00	3.10	3.82	1.70	UA3	17.9	2.7	6.28	1.29	4.7	34.4	-1.49	0.2
CAB-022	n.a.	0.05	0.13	0.03	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	23.4	-1.25	2.2
CAB-023	0.93	0.08	0.08	0.51	4.16	4.08	1.90	UA3	19.4	3.3	9.8	1.52	3.3	377.1	-1.23	2.6
CAB-024	0.87	0.06	0.06	0.46	2.61	3.47	1.52	UA3	20.6	2.7	4.49	1.12	2.0	1674.6	-1.25	2.4
CAB-026	1.21	0.07	0.14	0.06	3.33	4.12	1.85	UA3	14.8	2.6	7.25	1.38	7.8	56.4	-1.24	2.3
CAB-027	1.20	0.07	0.09	0.03	3.74	4.36	2.04	UA3	14.4	2.8	9.47	1.55	8.2	19.6	-1.24	2.6
CAB-101	n.a.	0.07	0.21	0.08	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	80.8	n.a.	n.a.
CAB-102	0.88	0.07	0.15	0.08	3.20	4.17	1.90	UA3	14.2	2.6	7.34	1.38	8.4	48.3	-1.20	3.0
CAB-114	1.16	0.09	0.13	0.07	3.26	4.15	1.91	UA3	14.8	2.7	7.62	1.42	7.8	454.4	-1.17	2.6
TTD-094	0.48	0.05	0.13	0.04	2.29	3.36	1.29	UA3	18.0	2.3	1.32	1.00	4.6	537.1	-1.52	-0.2
TTD-110	0.59	0.08	0.09	0.02	2.62	3.70	1.52	UA3	15.6	2.4	3.39	1.15	7.0	468.0	-1.46	-0.1
BEB-036	1.03	0.11	0.13	0.17	3.31	4.11	1.87	UA3	15.1	2.7	7.48	1.42	7.5	186.1	-1.12	3.7
BEB-047	n.a.	1.40	0.27	0.03	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	27.3	-1.46	0.7
BEB-050	1.08	0.12	0.22	0.14	2.86	4.02	1.81	UA3	14.1	2.4	5.92	1.30	8.5	205.8	-1.14	3.6
BEB-051	1.41	65.50	0.10	0.09	2.81	3.73	1.72	UA3	18.6	2.7	6.13	1.25	4.0	219.4	-1.40	0.8
BEB-057	0.66	0.08	0.05	0.07	3.53	4.32	2.05	UA3	14.5	2.8	9.33	1.51	8.1	204.6	-1.25	2.6
BEB-059	0.32	n.a.	0.12	0.04	2.60	3.48	1.65	UA3	22.2	2.9	5.88	1.16	0.4	210.9	-1.42	0.3
BEB-060	0.08	1.12	0.90	0.33	4.30	3.94	1.97	UA3	25.1	3.9	11.89	1.57	-2.5	189.1	-1.34	1.4
BEB-062	0.61	0.12	0.11	0.02	3.26	4.14	1.94	UA3	15.4	2.7	8.12	1.41	7.2	206.6	-1.07	4.3
ALM-073	0.82	0.05	0.04	0.03	2.25	3.25	1.26	UA3	19.7	2.3	1.35	0.98	2.9	170.5	-1.40	-0.4

Table B

Data summary on temperature, pH,  $\delta^{13}$ C, radiocarbon activity as well as major anion and cation concentrations measured in the Boa Viagem, Cabo and Beberibe aquifers

	$\delta^{13}C$	<sup>14</sup> C activity	$\sigma_{14C}$	Т	pН	$HCO_3^-$	Cl <sup>-</sup>	$NO_3^-$	$SO_4^{2-}$	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	$Mg^{2+}$
Units	$\% \text{ PDB} \pm 0.1$	рМС	pMC	°C		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
CAB-003	- 18.8	12.8	0.11	31.3	6.3	74.8	23.5	0.2	8.2	43.6	6.7	3.4	3.3
CAB-005	-14.9	27.9	0.10	30.4	6.5	91.6	1402.7	0.8	170.9	589.4	23.7	130.6	119.4
CAB-012	-11.4	34.4	0.10	30.5	6.0	41.0	17.7	0.3	15.6	34.8	7.8	1.5	1.7
CAB-017	- 19.5	44.0	0.22	30.8	6.1	33.8	724.1	0.6	88.5	298.5	20.2	60.5	55.3
CAB-024	- 17.7	31.6	0.15	31.2	6.0	39.2	1674.6	0.3	41.8	120.4	19.8	25.7	22.7
CAB-027	- 17.1	19.3	0.10	32.1	6.3	63.9	19.6	0.2	10.3	39.5	6.2	3.7	3.5
TTD-094	- 19.5	28.9	0.10	30.5	6.9	70.8	537.1	n.a.	169.1	323.0	13.3	47.3	61.5
TTD-110	- 18.1	20.9	0.10	30.6	6.6	65.3	468.0	n.a.	142.2	281.2	13.3	47.3	56.4
BEB-036	-11.4	26.0	0.10	30.0	6.2	38.6	186.1	0.6	28.9	84.5	16.6	26.5	22.5
BEB-057	- 19.7	30.3	0.19	31.3	5.9	28.9	204.6	0.2	32.5	57.3	24.5	41.3	28.6
BEB-059	-7.2	59.1	0.21	29.7	6.1	109.7	210.9	1.0	11.4	115.5	30.8	20.0	25.3
BEB-062	- 15.6	24.4	0.15	32.8	5.9	28.9	206.6	0.2	11.4	19.7	11.5	3.9	3.6
ALM-073	- 10.1	46.2	0.30	30.2	6.8	308.1	170.5	n.a.	2.9	164.8	21.5	44.1	39.9

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