Relationships of stable isotopes, water-rock interaction and salinization in fractured aquifers, Petrolina region, Pernambuco State, Brazil

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Abstract

The Petrolina County, Pernambuco State, Brazil, presents specificities that make it unique from a hydrogeological point of view. Water resource scarcity is both a quantitative and qualitative issue. The climate is classified as semiarid, having low precipitation, along with high temperatures and evapotranspiration rates. Aquifer zones are related to low connected fractures resulting in a restricted water flow in the aquifer. The recharge is limited and the groundwater salinity is high. Stable isotope analyses of H and O were developed in groundwater samples (with different electrical conductivity) and surface water collected in a bypass channel flowing from the São Francisco River. The results were plotted in a δD ‰ versus $\delta^{18}O$ ‰ graph along with the curves of the global and local meteoric water line. Groundwater samples showed unexpected results showing a lighter sign pattern when compared to the meteoric waters. More negative δD and $\delta^{18}O$ values indicate an enrichment in light isotopes, which show that this process is not influenced by surface processes, where the enrichment occurs in heavy isotopes due to evaporation. The isotopic signature observed is interpreted either as resulting from the water-rock interaction, or as resulting from recharge from paleo rains. The waters are old and show restricted flow. So the water-rock contact time is extended. In the rock weathering processes, through the hydration of feldspars, there is preferential assimilation of heavy isotopes at the expense of the lighter ones that remain in the water. Analyses of the $^{87}Sr/^{86}Sr$ ratio and isotopic groundwater dating assist in the interpretations.

Keywords: $\delta^{18}O$ and δD, Artificial Recharge, Salinization, Cristaline Aquifer.

1. Introduction

Petrolina County is located in the southwestern part of Pernambuco State in the Northeastern region of Brazil (Figure 1). Together with Juazeiro County, it forms one of the most promising irrigation poles in the São Francisco River watershed.

Geologically, the region is located between the boundary of the São Francisco Craton and the Borborema Province which is represented by the Riacho do Pontal Mobile Belt. In the southern region of the county, there are outcrops of the Gavião Block rocks mainly gneiss. In the northern portion, the rocks of the Riacho do Pontal Mobile Belt are exposed and represented mainly by schist and marble. The rocks are dated from the Archean to the Neoproterozoic Eras. Figure 2 presents images from rock outcrops observed during fieldwork in the region.

The soils are not thick and show low pedogenetic evolution. The recent alluvial sediments are observed in the vicinity of the intermittent rivers with thicknesses ranging from 5 to 10 meters. There are literature reports screening the existence of alfisol, aridisol, incepsol, andisol, entisol and vertisol. All these not evolved soils are rich in free ions, mainly in the saprolitic horizons or even in shallow horizons of incepsol, aridisol and vertisol derived from gneiss, granite, granulite, basic, ultrabasic rocks and marble.

The climate in the region is classified as semiarid, which is characterized by spatial and temporal irregular rains. The total mean rain is about 450mm/year and the rains concentrate from January to March. The temperatures and the evapotranspiration are high. The average temperature is 26°C and the evapotranspiration varies from 1,200mm to 1,500mm per year. Relief shows a smooth pattern with isolated sparse hills and flat and shallow valleys.

The northeastern region of Brazil suffers severely from water resource deficit. Rainfall is usually overcome by a high evapotranspiration rate resulting in negative water balance most of the time. The shortage of water resources is stressful in the area and directly affects the population life and its social and economic development.

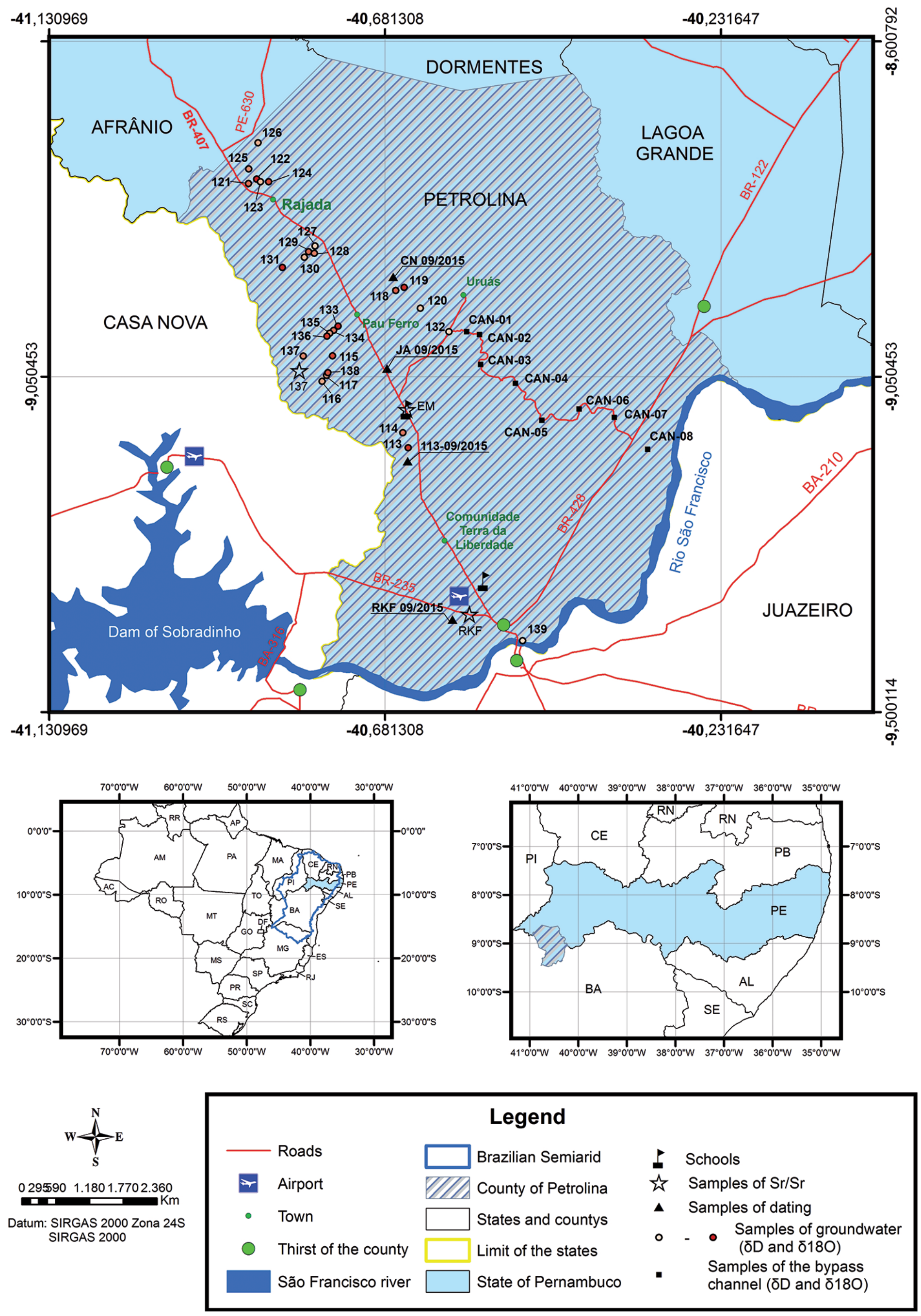

Figure 1
Location map of the study area, Petrolina County, Pernambuco State, Brazil.

The issue of the water resource deficiency is both from a quantitative and qualitative standpoint. Climate, geology and soils control the quantity and the high salinity of groundwater controls the quality. The high salinity of groundwater is given by the joint action of factors such as: climate, soil, high rate of evaporation, plane relief, low connected fractures, restricted circulation of water in the aquifer, and high water-rock time contact. Several authors have presented explanations for the causes of the increasing ion content in the water which are focused on different processes: dry and warm climate conditions, salt enrichment in the soils and water-rock interaction (Silva Junior *et al*., 1999; Santiago *et al*., 2000; Silveira & Silva Junior, 2002; Costa *et al*., 2006; Lima, 2010).

The only perennial stream in the region is the São Francisco River. The aquifers are related to low interconnected fractures zones. Sub horizontal fractures that interconnect the larger vertical fractures were observed serving as preferential flow paths and storage space for water. The flow in these aquifers is restricted and causes the high residence time of water in fractures. The regional flow is rather limited and the water accumulations occur in systems of isolated fractures resulting in wells that are located relatively close to each other, having different hydraulic characteristics and electric conductivity of the water.

In order to extend the knowledge of this area with so many hydrogeological peculiarities, isotopic studies were carried out in the groundwater of the region. The studies aim to contribute to issues not yet studied, such as the recharge conditions, the source of groundwater and the causes of its high salinization.

Banded marble and associated reddish soils.Riacho do Pontal Mobile Belt. Southwest of the of Pau Ferro village. (UTM coordinate: 304357/9003747 zone 24L).

Schist showing low angles foliation. Outcrop of the Riacho do Pontal Mobile Belt rocks. Located in BR-407.

Intersection of vertical and horizontalfractures observed in deactivated quarry located at the margins of BR-407, north of Petrolina. Gavião Block. (UTM coordinate: 328666/8967177 zone 24L).

Banded and folded gneiss. Gavião Block. Campus of the UNIVASF University. (UTM coordinate: 330120/8968855 zone 24L).

Figure 2
Outcrops of typical rocks observed in the Petrolina region.

2. Material and method

Stable isotope δD_{vsmow} and $\delta^{18}O_{vsmow}$ analyses were performed in 24 groundwater samples for isotopic characterization of the regional fractured aquifers. Samples are distributed in the region and were chosen in order to contemplate the waters of different salinities.

The water supply in the rural areas is possible through bypass channels that take water from the São Francisco River to the interior. Complementarily, 8 surface water samples were collected along the bypass channel that connects the São Francisco River to the Uruás Village for δD_{vsmow} and $\delta^{18}O_{vsmow}$ analyses.

Three pairs of samples were taken for $^{87}Sr/^{86}Sr$ ratio analysis. Each pair consists of a sample of groundwater collected in a deep well and a sample of weathered rock collected in the surroundings of the same well.

The analyses were performed at the Geochronology Laboratory of the University of Brasília (UnB), and the water $\delta^{18}O$ and δD were measured in the PICARRO analyzer unit model L2120-i that uses the mass spectrometry method for measurement with laser separation. The values obtained were compared with the VSMOW standard for obtaining the precise results. $^{87}Sr/^{86}Sr$ rates in water and rock were determined using a TIMS (thermal ionization mass spectrometer) spectrometer model Triton Plus.

Water ages were determined by the 14 Carbon and the Tritium methods in groundwater for 4 samples with different electrical conductivity values. The analyses were carried out in the HIDROISOTOP laboratory located in Germany by the Accelerator Mass-Spectrometry (AMS) method. The measurements are expressed in % of Modern 14C with double standard deviation. The raw data obtained from the 14 Carbon analyses were replaced in the equation purposed by Allègre (2008):

$$T = 8033 \ . \ \ln \frac{A_t^{14}}{A_0^{14}} \qquad \text{(Eq. 01)}$$

3. Results

The δDvsmow and $\delta^{18}O_{vsmow}$ analyses of 8 samples collected along the bypass channel that connects the São Francisco River to the Uruás Village were plotted on the graph $\delta^{18}O_{versus}$ δD along with the global meteoric water line (GMWL). The sample CAN-08 is located next to the São Francisco River and as the numbering of the samples decreases as they get close to the Uruás Village. The samples clearly show the influence of evaporation in the isotopic signal with enrichment in positive isotope values as the bypass channel moves away from the São Francisco River (Figure 3).

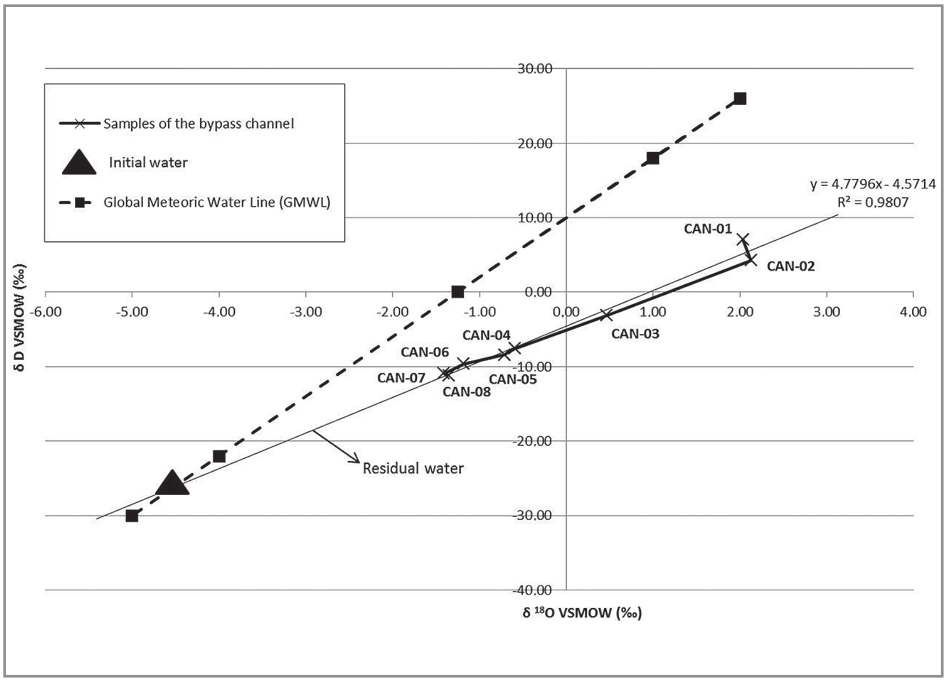

Figure 3
Graph showing the influence of the evaporation process by the isotopic signal of the bypass channel that deviates water from the São Francisco River to the Uruás Village.

The twenty four groundwater samples collected in wells have also been plotted on the $\delta^{18}O$ versus δD graph along with the global and local meteoric water line. The curves of the local meteoric water lines were obtained by the Floresta IAEA GNIP station and by the Salati *et al.* (1979) which drew up a local meteoric water line for the northeastern of Brazil.

Surprisingly, the groundwater samples of the Petrolina region were located above the global and local meteoric water lines. The points of all sampling data align as a curve with R^2 = 75% correlation. In this research, this line is called as the "Petrolina's Groundwater Line" (Figure 4).

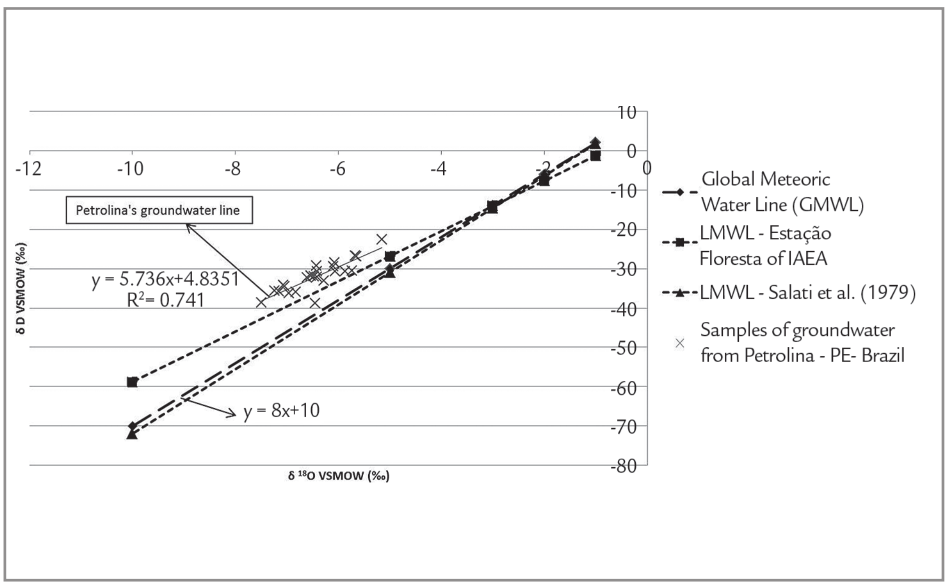

Figure 4
δD versus $\delta^{18}O$ plot showing the isotopic signal of groundwater from Petrolina region. Note that the data align over the local and global meteoric water lines (GMWL and LMWL).

In three pairs of samples collected, an $^{87}Sr/^{86}Sr$ ratio analysis was conducted comparing the ratio between the groundwater and rock samples. In the RKF sample, it was possible also to collect a fresh rock sample that was also used in the comparison. The results are shown in Figure 5.

Due to the little Sr concentration in the groundwater, water-rock interaction can result after a long time in an isotopic equilibrium with respect to Sr. The sample EM shows different values of $^{87}Sr/^{86}Sr$ ratio when comparing the weathered rock and the groundwater. This means that the process of water-rock interaction did not occur for the necessary time to establish the isotopic equilibrium with respect to Sr. Sample 137 shows more similar values of $^{87}Sr/^{86}Sr$ ratio. The groundwater sample RKF shows values of $^{87}Sr/^{86}Sr$ ratio to be very similar to the weathered sample, but with values different from the fresh rock sample. This demonstrates that the action of the water-rock interaction process in the RKF sample, occurs with sufficient time to establish the equilibrium with respect to Sr.

The result of the Tritium and 14 Carbon dating and approximate ages estimated by the % of 14 Carbon data with respect to modern Carbon (Eq. 01) are expressed in Table 1. The ages of samples do not show a correlation with its electrical conductivity (EC), as can be observed in the Figure 6 plot.

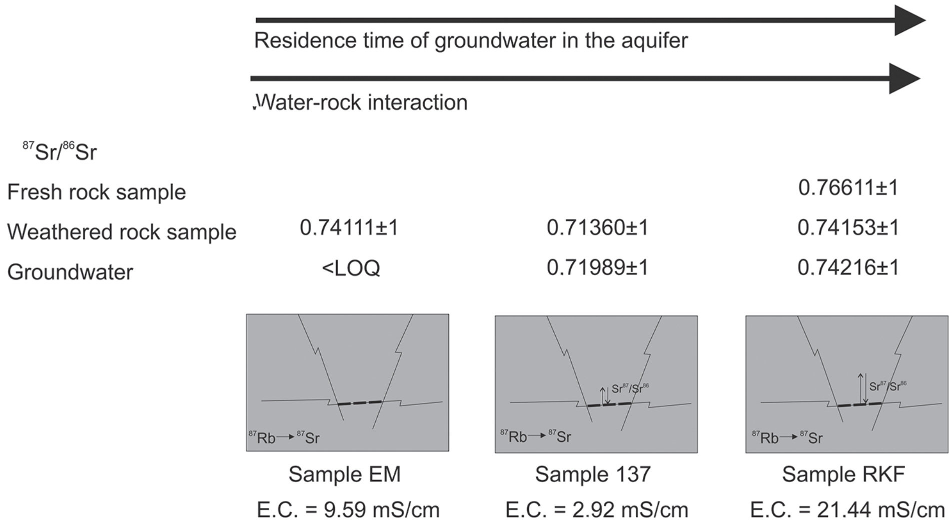

Figure 5
Schematic view showing the analysis of the water-rock interaction process by the $^{87}Sr/^{86}Sr$ ratio values. The proximity of the values of the $^{87}Sr/^{86}Sr$ ratio between the weathered rock sample and the groundwater sample is an indicative of the water-rock interaction process: in the EM sample, the process has a poor performance while in the RKF sample, the process almost achieves equilibrium with respect to Sr. L.O.Q.: Limit of Quantification; E.C.: Electrical Conductivity.

Table 1
^{14}C ages of groundwater from Petrolina region.

Sample	Tritium (H^3)	Carbon 13 ($\delta^{13}C$-DIC) ‰	Carbon 14 (^{14}C-TIC) %-modern	Approximate ages (years)	Electrical Conductivity (µS/cm)
RKF	< 0.6	-11.1	96.55 ± 0.56	282 ± 45	12,630
113	< 0.6	-11.7	93.63 ± 0.54	528 ± 43	3,490
CN	0.6 ± 1.0	-12.3	74.99 ± 0.44	2.312 ± 35	1,876
JA	< 0.6	-13.5	50.13 ± 0.34	5.547 ± 27	2,720

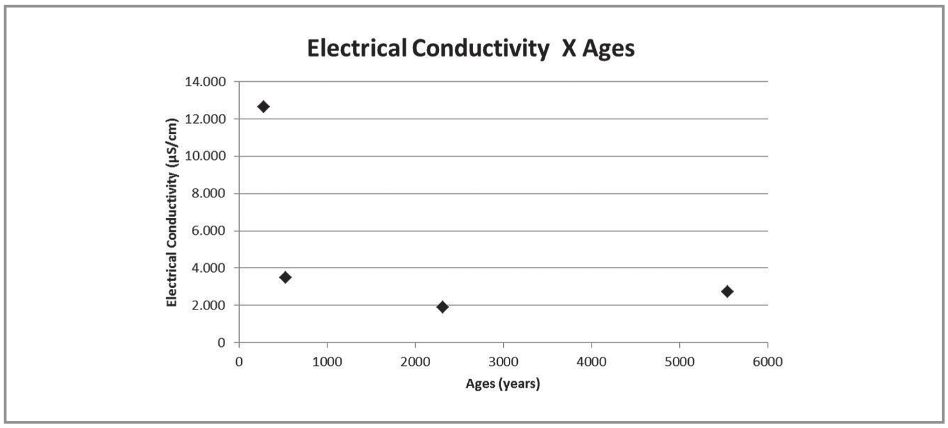

Figure 6
Plot of the electrical conductivity versus water ages, showing no correlation between these parameters.

4. Discussion

The samples collected in the bypass channel show the importance of the evaporation process for surface water in the semiarid northeast of Brazil. Evaporation makes water enriched in heavy isotopes resulting in water samples plotted below the Global Meteoric Water Line – GMWL and Local Meteoric Water Lines - LMWL.

This process, developed in the surface environment, is not observed in groundwater that showed enrichment in light isotopes, since the sampling data are plotted above the Global and Local Meteoric Water Lines (GMWL and LMWL). There are 2 explanations for the enrichment of the light isotopes signal. Either it is related to ancient recharge by paleo rains that occurred in different climatic conditions, or it is due to the water-rock interaction process, or both of them.

Frape *et al.* (1984) describe a similar situation in fractured aquifers in Canada. In the referred to aquifer, fresh water occurs in the shallow parts (depth <650 m) and saline water in the deep parts (depth >650 m). Isotopic studies ($\delta^{18}O$ versus δD) have been done and the fresh water samples are plotted below or on top of the GMWL. However the saline ones are plotted above the GMWL. The authors also made analysis of the $^{87}Sr/^{86}Sr$ ratio and the samples of saline water showing a strong correlation with the samples of weathered rocks showing water-rock interaction. Finally, the authors concluded that the saline waters have undergone an intense process of water-rock interaction and that the isotopic sign observed can reflect either a recharge in a different climate or the process of water-rock interaction (Frape *et al.* 1984).

The first hypothesis suggests the aquifer recharge occurred at lower temperatures to result in enhanced rainfall in light isotopes. Groundwater dating shows approximate ages ranging from 282 to 5,547 years before present. It is known that the Earth is in an interglacial period that started after the end of the last glacial period approximately 10,000 years to 12,000 years, which can corroborate this explanation.

The second hypothesis is that this is due to water-rock interaction during the hydration of silicate minerals in the groundwater contact with rocks, where the fractured rocks would preferentially use heavy isotopes, causing the fractionation of the groundwater and residual water enriched in light isotopes. It's known that igneous and metamorphic rocks and limestones are enriched in heavy isotopes and have positive values of $\delta^{18}O$ and δD (Allégre, 2008).

In the study area, as in the northeastern region of Brazil, the aquifers occur on interconnected fractures with low flow or with many stagnation centers resulting in water being a long time in the aquifer, and allowing the development of water-rock interaction processes that take place during an extended time. In the fieldwork, it was possible to observe that wells located relatively close to each other, can show hydraulic characteristics (yield, static level, specific capacity) and water characteristics (ages, electrical conductivity) quite distinct. This indicates that the aquifers in the area occur in isolated systems of fractures and that there is a not significant regional flow. These systems of fractures would be interconnected by large sub horizontal fractures that serve as major paths to conduct and store water.

Due to little Strontium (Sr) concentration in the groundwater, the water-rock interaction can result after a long time in a isotopic equilibrium with respect to Sr. This process can be analyzed by the comparison of the $^{87}Sr/^{86}Sr$ ratio of the primary rock minerals, the secondary minerals located in fractures pores and the groundwater (Allègre, 2008).

In the case of carbonates, groundwater tends to reflect the $^{87}Sr/^{86}Sr$ ratio of the total rock, because these rocks are essentially homogeneous with respect to Sr. On the other hand, in silicates, the $^{87}Sr/^{86}Sr$ ratio is dominant in the isotopic composition of specific minerals resulting in groundwater with different ratios regarding the total rock, but matching the Sr/Sr of weathered minerals (Montgomery *et al*., 2006).

Groundwater from different sources can show different $^{87}Sr/^{86}Sr$ ratios which make it a good tool in origin, flow groundwater mixture and water-rock interaction studies (Geyh, 2001). Related studies have already been carried out in the Pre Cambrian Shied of Canada, in Mont-Dore region in France (Geyh, 2001) and in England (Montgomery *et al*., 2006), among others.

The data analysis for strontium in 3 pairs of samples allows observing that the process of water-rock interaction in groundwater exists in different intensities. The $^{87}Sr/^{86}Sr$ ratios of the EM sample are not similar when compared with the groundwater and the weathered rocks. However, in Sample 137, they are. Similar to the RKF sample, the $^{87}Sr/^{86}Sr$ ratio for groundwater is close to the weathered rock, but differs from the fresh rock values. The results confirm the process of water-rock interaction into the isotopic equilibrium with respect to strontium in different intensities.

The water dating results show that there is no relationship between the electrical conductivity and the groundwater ages (even considering a small data set, just 4 analyses). The differences in the fracture characteristics (such as geometry and connectivity) and in the dissolution rates of minerals that filled the fractures explain the lack of correlation. In areas where the flow is restricted and has the presence of more soluble minerals, the salinity of the waters is high but not necessarily is it older.

In the region of Petrolina, a set of factors are involved in the high salinity of groundwater, such as: restricted recharge, soils, semiarid climate, plain relief, low connected fractures and process of water-rock interaction. The enrichment in salts in the soils can be a major controller in the groundwater salinization when compared to the water-rock interaction process, which explains the absence of relationship between the E.C. and the groundwater ages. The lack of correlation of the E.C. with the $^{87}Sr/^{86}Sr$ ratio, which is related to the water-rock interaction process, also corroborates this explanation.

5. Conclusions

Groundwater salinization is observed in several fractured aquifers areas of the semiarid region in northeastern Brazil. It is believed that it can be the result of a joint action of several factors and is not being caused by just one aspect alone.

The dating data prove there is no correlation between the electrical conductivity and the groundwater ages. As the water-rock interaction process is slow, the soil's salt enrichment is considered as the most important factor for the water salinization. Additionally, the $^{87}Sr/^{86}Sr$ ratio data and the regional groundwater isotopic characterization show that water-rock interaction does exist in varying degrees, indicating that this process must also contribute to the ion enrichment.

The majority of the soils in the region are poorly evolved, shallow and enriched in alkali and alkaline earth elements. Precipitation waters percolating in the soils reach the crystalline substrate and flow through open fractures transporting the solute. During this process, these may carry soluble elements present in the soils.

Such processes can enrich the waters and increase its salinity before infiltration into the fractures in the rock mass. The plan relief pattern, the crystalline terrain nature, and the thin soil coverage result in high volumes of precipitation waters to remain on the surface as depression storage for a long time where intense direct evaporation (as can be verified by the isotopic signal of the bypass channel) causes the salt enrichment in the recharge water. Subsequently rains can carry the salts accumulated as depression storage into the fractured aquifers.

The low connectivity of the fractures, together with the relief pattern (showing shallow and open valleys), restricts the water velocity circulation, due to the low gradient of the system as a whole. The longer the time the water stays in the fractures increases the water-rock interaction increasing the salinity.

The groundwater $\delta^{18}O$ and δD signals show enrichment in light isotopes. This can be caused by water-rock interaction, or by recharge of paleo rains. The first option occurs by the feldspar hydration processes to form clay minerals (e.g. kaolinite), that preferentially capture the heavy Oxygen and Hydrogen isotopes. The preliminary $^{87}Sr/^{86}Sr$ ratio data confirm the existence of water-rock interaction in the region.

Historic reports of Petrolina residents demonstrate that groundwater quality can be enhanced after continuous pumping for some decades. The pumping activates the water circulation in the aquifer and open space (in the depression cones) so that new recharge water can mix with the old stagnated water or move slowly in the fractures pore space.

Acknowledgments

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