Salinization mechanisms of a small alluvial aquifer in the semiarid region of northeast Brazil

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Key words: discriminant analysis, inverse geochemical modeling, groundwater

ABSTRACT

The objective of this research was to identify and quantify the primary processes responsible for the increase in salinity observed in the alluvial aquifer during the dry season. Multivariate statistical analysis and inverse geochemical modeling were used to simulate possible salinization mechanisms in the alluvial aquifer. For this, by quantifying electrical conductivity and the concentrations of the ions Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, Cl$^-$, HCO$_3^-$ and SO$_4^{2-}$ in waters from the crystalline basement near the study area, water reservoirs near the alluvial aquifer and the studied alluvial aquifer, groups were formed and discriminant analysis was applied. Significance tests showed that direct evaporation has not only an influence on the alluvial aquifer, but also a mean volumetric contribution of 15.8% from waters of the crystalline basement, accompanied by processes of salt dissolution and precipitation, which would also justify the increase in salinity observed in the alluvial aquifer in the dry period.

Palavras-chave: análise discriminante, modelagem geoquímica inversa, água subterrânea

RESUMO

Com o objetivo de identificar e quantificar os principais processos responsáveis pelo aumento da salinidade observada durante o período não chuvoso em um pequeno aquífero aluvial localizado no semiárido do Nordeste brasileiro utilizaram-se a análise estatística multivariada e a modelagem geoquímica inversa para simular prováveis mecanismos de salinização no aquífero; para isto e por meio da quantificação da condutividade elétrica e dos íons Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, Cl$^-$, HCO$_3^-$ e SO$_4^{2-}$ em amostras de águas do embasamento cristalino próximo à área de estudo, nos reservatórios próximos ao aquífero aluvial e do aquífero aluvial estudado, foram formados grupos e aplicada a análise discriminante. Testes de significância dos resultados demonstraram que a evaporação direta não apenas exerce influência sobre o aquífero aluvial mas ainda tem uma contribuição volumétrica média de 15,8% de águas do cristalino acompanhada de processos de dissolução e precipitação de sais, o que também justificaria o aumento da salinidade no aquífero aluvial no período seco.
**Introduction**

In the state of Ceará, there are thousands of wells providing water essentially for irrigation and human consumption, which are the main source of water supply in some of these areas. In general, the quality of the water in these wells is directly related to the geological formation of the region. Water with high salt concentration is usually found in areas of crystalline rock formation (Silva Júnior et al., 1999; Lopes et al., 2008), while water with low salt concentration is found in areas of sedimentary rocks (Andrade Júnior et al., 2006; Silva et al., 2007).

Among crystalline areas, along the shore of rivers, streams and in the mouth of water courses, there are recent deposits of unconsolidated sediments called alluvium. From 1998 to 2007, 192 wells with mean depth of 6.8 m were installed in the alluvial aquifer of the Forquilha watershed (Burte, 2008).

Due to its easy exploitation and good quality, when compared with water stored in crevices of crystalline rocks, the water from the alluvial aquifer of the Forquilha River becomes an important source for both human and animal consumption, as well as to irrigate small plantations, such as maize and bean. However, during the dry period, the piezometric level of the wells lowers, while the salinity of alluvial waters increases. The increase of salt contents in the alluvial aquifer by the mixture with water from the crystalline crevices in an interaction of aquifer systems is possible, since the studied alluvial region is totally inserted in fractured crystalline basement. The conservative characteristic of the chloride ion (Svensson et al., 2012) makes its measurement a parameter usually used to identify deterioration in water quality (Richter & Kreitler, 1993; Manwell & Ryan, 2006; Lucas et al., 2010). This ion was used in this study as a tracer of the water from crystalline crevices, which is rich in chloride.

Cruz & Melo (1968) and Costa et al. (2006) show that groundwaters can acquire their composition through the progressive concentration of dissolved ions by evaporation, and studies in nearby regions (Pereira et al., 2006; Machado et al., 2007) pointed out the importance of the contact between water and rock as the origin of the salts dissolved in groundwaters.

Many authors have used multivariate statistical analysis in an attempt to describe the hydrogeological processes with interactions of aquifer systems (Ji et al., 2007; Cloutier et al., 2008; Raspa et al., 2008; Pinto et al., 2012) and inverse geochemical modeling (Parkhurst & Appelo, 1999) aiming to describe and identify the hydrogeochemical processes of water-rock interaction (Uliana & Sharp, 2001; Mahlknecht et al., 2006; Sharif et al., 2008), since the weathering of rocks can play a relevant role in the chemistry of the water (Marković et al., 2013).

Given the above, this study aimed to understand the probable mechanisms of the salinization dynamics of the alluvial aquifer during the dry period of the year, using multivariate statistical analysis and inverse geochemical modeling.

**Material and Methods**

The studied watershed (Figure 1) is located southeast of the municipality of Quixeramobim - CE, Brazil, and extends for 30 km, where 800 families live, a total of 17 communities of small farmers (Jacob & Brandão, 2006). The wells P10, P27, P38, P51, P60, P68, P86, P92, P111, P104, P114, P133 and P136, and the Riacho Verde reservoir, which acts as a recharge source of the alluvial aquifer through small controlled releases during the dry period, were used in the simulations of the salinization dynamics.

The alluvial deposits are scattered in zones of crystalline rocks and represent an area of approximately 5.6 km². The study area is also characterized by the existence of two well defined seasons: the rainy period (from January to June) and the dry period (from July to December), with average rainfall of 594 mm year⁻¹ in the last ten years, and nearly 90% of rain events occurring only in the rainy period.

For the statistical analysis of the Forquilha watershed, 39 hydrochemical analyses were used. The analyses were divided into three primary groups: 1º) waters from the crystalline basement, 2º) waters from the reservoirs and 3º) waters from the wells of the alluvial aquifer. The hydrochemical analyses used in this study reflect the typical values observed in the studied area in the last ten years and have analytical errors less than 10%.

Since the study is based on the process of salinization of the alluvial aquifer, the hydrochemical data of the groups are only from dry periods, in order to avoid the effect of dilution by recharge.

To simulate the increment in salinity by the contribution of water from the fissure aquifer, five water groups were defined for subsequent graphical differentiation. Besides the primary groups (crystalline, reservoirs and wells), two new groups were formed, with mixture ratios of 1:1 and 3:1 between waters from the reservoir and the crystalline basement, respectively.

For the study of direct evaporation in the alluvial aquifer, six different groups were defined for later graphical differentiation. Besides the primary groups, three new groups were formed, referring to concentration factors of 1.5x, 2.5x and 3.5x in the salts of the reservoir waters, which are responsible for the recharge of the aquifer during the dry period, through the release of water from the Riacho Verde reservoir.

Discriminant functions and graphical representations of the groups, formed according to their most representative factors, were generated using statistical softwares for multivariate analysis.

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*Figure 1. Map of the Ceará state and location of the Forquilha River*
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Inverse geochemical modeling was used to characterize the hydrogeochemical behavior of the groundwater in the alluvial aquifer along the Forquilha watershed, identifying and quantifying combined processes that contribute to a change in the chemical composition of the water.

The simulations consisted of finding a group of mole transfers of minerals, gases and metallic ions, through physical and chemical processes (dissolution/precipitation, ionic exchanges and sorption) necessary to reach, from an average ionic composition of the reservoir waters, the ionic composition observed in the wells of the alluvial aquifer.

By adapting the methodology of Uliana & Sharp (2001), the following hypothesis (Figure 2) was considered for the salt increment in alluvial waters during the dry period: the water from the Riacho Verde reservoir is released to initiate the recharge of the alluvial aquifer. Then, it receives a contribution of salt-rich water from the fissure aquifer. Along the flow pathways, it suffers a process of enrichment/depletion of salts through the dissolution and precipitation of the reactive phase, causing the final composition of the water in the wells along the alluvium to be the one observed at the end of the dry period.

Table 1. Values of the variables for the observations used in the discriminant statistical analysis (Electrical conductivity-EC in µS cm⁻¹ and ion concentration in mg L⁻¹)

<table>
<thead>
<tr>
<th>Observation</th>
<th>EC</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>HCO₃⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline 1</td>
<td>4162.0</td>
<td>184.0</td>
<td>189.6</td>
<td>137.5</td>
<td>50.0</td>
<td>721.0</td>
<td>34.1</td>
<td>372.0</td>
</tr>
<tr>
<td>Crystalline 2</td>
<td>5732.0</td>
<td>118.0</td>
<td>159.0</td>
<td>598.0</td>
<td>47.9</td>
<td>1373.0</td>
<td>79.1</td>
<td>49.0</td>
</tr>
<tr>
<td>Crystalline 3</td>
<td>4820.0</td>
<td>181.3</td>
<td>236.8</td>
<td>492.3</td>
<td>2.0</td>
<td>1237.4</td>
<td>170.0</td>
<td>446.9</td>
</tr>
<tr>
<td>Crystalline 4</td>
<td>4246.0</td>
<td>60.0</td>
<td>96.0</td>
<td>168.0</td>
<td>18.4</td>
<td>543.0</td>
<td>10.6</td>
<td>301.0</td>
</tr>
<tr>
<td>Crystalline 5</td>
<td>4880.0</td>
<td>146.0</td>
<td>141.6</td>
<td>442.0</td>
<td>48.9</td>
<td>1092.0</td>
<td>33.5</td>
<td>258.0</td>
</tr>
<tr>
<td>Crystalline 6</td>
<td>2598.0</td>
<td>120.0</td>
<td>103.2</td>
<td>146.0</td>
<td>12.3</td>
<td>456.0</td>
<td>22.6</td>
<td>330.0</td>
</tr>
<tr>
<td>Crystalline 7</td>
<td>2679.0</td>
<td>120.0</td>
<td>127.0</td>
<td>137.5</td>
<td>11.7</td>
<td>409.0</td>
<td>27.4</td>
<td>548.0</td>
</tr>
<tr>
<td>Crystalline 8</td>
<td>4160.0</td>
<td>145.4</td>
<td>224.4</td>
<td>222.0</td>
<td>13.0</td>
<td>768.0</td>
<td>320.0</td>
<td>320.1</td>
</tr>
<tr>
<td>Crystalline 9</td>
<td>3100.0</td>
<td>211.4</td>
<td>165.6</td>
<td>101.9</td>
<td>10.0</td>
<td>801.0</td>
<td>28.0</td>
<td>322.2</td>
</tr>
<tr>
<td>Crystalline 10</td>
<td>4015.0</td>
<td>14.4</td>
<td>314.4</td>
<td>316.0</td>
<td>40.0</td>
<td>1188.5</td>
<td>126.5</td>
<td>362.3</td>
</tr>
<tr>
<td>Crystalline 11</td>
<td>3350.0</td>
<td>109.5</td>
<td>109.6</td>
<td>477.8</td>
<td>19.8</td>
<td>920.4</td>
<td>185.0</td>
<td>84.0</td>
</tr>
<tr>
<td>Crystalline 12</td>
<td>2206.0</td>
<td>128.0</td>
<td>55.6</td>
<td>174.0</td>
<td>12.2</td>
<td>403.0</td>
<td>42.6</td>
<td>172.0</td>
</tr>
<tr>
<td>Crystalline 13</td>
<td>2850.0</td>
<td>204.0</td>
<td>116.0</td>
<td>198.0</td>
<td>20.0</td>
<td>668.3</td>
<td>73.0</td>
<td>353.5</td>
</tr>
</tbody>
</table>

| DF1 | (1.7317E−03×EC)+(7.6729E−03×Ca²⁺)+(−6.1644E−02×Mg²⁺)+(−1.1680E−02×Na⁺)+(−1.1677E−02×K⁺)+(6.0068E−03×Cl⁻)+(2.3053E−03×SO₄²⁻)+(4.0972E−03×HCO₃⁻)+(−3.6396E−00)
| DF2 | (2.1446E−04×EC)+(−2.6114E−02×Ca²⁺)+(−6.3455E−02×Mg²⁺)+(−1.0633E−02×Na⁺)+(6.4705E−03×K⁺)+(1.2349E−02×Cl⁻)+(8.4705E−03×SO₄²⁻)+(1.2287E−02×HCO₃⁻)+(−3.1195E−00)

Results and Discussion

The data of the three primary groups formed from 39 hydrochemical analyses are shown in Table 1.

The discriminant functions generated in the simulation of the mixture between waters from reservoirs and the crystalline basement are presented below:

\[ DF1 = (1.7317E−03×EC)+(7.6729E−03×Ca²⁺)+(−6.1644E−02×Mg²⁺)+(−1.1680E−02×Na⁺)+(−1.1677E−02×K⁺)+(6.0068E−03×Cl⁻)+(2.3053E−03×SO₄²⁻)+(4.0972E−03×HCO₃⁻)+(−3.6396E−00) \]

\[ DF2 = (2.1446E−04×EC)+(−2.6114E−02×Ca²⁺)+(−6.3455E−02×Mg²⁺)+(−1.0633E−02×Na⁺)+(6.4705E−03×K⁺)+(1.2349E−02×Cl⁻)+(8.4705E−03×SO₄²⁻)+(1.2287E−02×HCO₃⁻)+(−3.1195E−00) \]

The functions DF1 and DF2 discriminate 99.52% of the total data variability. Thus, the use of only these two functions is considered sufficient to explain the relationships between the groups (Table 2).

According to the graph DF1 vs DF2, which shows the discriminant functions for the hypothesis of mixture between waters from the reservoir and the crystalline basement for the five groups (Figure 3A), the mixture of reservoir and the crystalline basement waters is not enough to justify the chemical composition of the water of the wells. Despite the increase in the factors 1 of the reservoir waters for the well...
samples, which could be explained by the mixture, the increase of factor 2 is predominant. For a better viewing, the centroids of the five groups are shown in Figure 3B, where it is observed that the mixture by itself does not lead to the quality characteristics of the water from the wells.

The correlations between the variables and the factors are presented in Table 3, where DF1 shows strong correlations between electrical conductivity, chloride, calcium, magnesium and sodium. Waters with high DF1 are rich in dissolved salts and are predominantly chlorinated; as for DF2, it has bicarbonate as the predominant ion. Waters tend to have high DF2 values are classified as bicarbonated, with low electrical conductivity.

The results of the multivariate analysis for the process of mixture do not discard, however, the possibility of salt increment in the alluvial aquifer by the contribution of the crystalline basement, since the complexity of the hydrogeological dynamics allows a hydrochemical evolution through combined processes by a variety of factors (Tóth, 1999; Pereira et al., 2006), such as mixtures of groundwaters, ionic exchanges and salt dissolution in the flow pathways of alluvial aquifers (Machado et al., 2007; Cloutier et al., 2008).

In the study of the effects of evaporation on the alluvial aquifer, the following discriminant functions were determined:

\[
\begin{align*}
\text{DF1} &= (1.57548E-03 \times \text{EC}) + (1.70314E-02 \times \text{Ca}^{2+}) + \\
&+ (9.14626E-03 \times \text{Mg}^{2+}) + (8.71782E-03 \times \text{Na}^+) + \\
&+ (7.62977E-03 \times \text{K}^+) + (2.30689E-03 \times \text{Cl}^-) + \\
&+ (2.00621E-03 \times \text{SO}_4^{2-}) + (1.40769E-00) \\
\text{DF2} &= (-9.49516E-05 \times \text{EC}) + (-1.25839E-02 \times \text{Ca}^{2+}) + \\
&+ (-5.80987E-02 \times \text{Mg}^{2+}) + (-1.02425E-02 \times \text{Na}^+) + \\
&+ (1.61883E-02 \times \text{K}^+) + (1.27350E-02 \times \text{Cl}^-) + \\
&+ (1.07275E-02 \times \text{SO}_4^{2-}) + (1.94963E-02 \times \text{HCO}_3^-) + (-4.39860E+00)
\end{align*}
\]

The discriminant functions DF1 and DF2, for this hypothesis of hydrochemical evolution dynamics of alluvial waters, discriminate together 97.607% of the total data variability. Thus, the use of only these two functions was considered enough to explain the relationships between the groups (Table 4).

The results for water samples from the crystalline basement, reservoirs, wells and reservoir with concentration factors of 1.5x, 2.5x and 3.5x are shown in Figure 4A, where the graph DF1 vs DF2 shows the discriminant functions for the hypothesis of evaporation. According to the graph, when waters from the reservoirs are concentrated, the chemical composition moves upward (in DF2) slightly, proportionally to the concentration factor, and slightly to the right (in DF1).

According to the centroids (Figure 4B), waters from the wells tend to be a group with characteristics very similar to the group of 2.5x concentration factor.
According to Table 5, the Mahalanobis distances between the centroids of the groups well and reservoir with 2.5x concentration factor are very small, while greater distances are observed between the centroid of the crystalline and the centroids of the other groups.

According to the Fisher test (5% significance level), there are two hypotheses: $H_0$ - The intraclass covariance matrices are equal and $H_1$ - The intraclass covariance matrices are different.

In Table 6, it is verified that where the calculated p-value is lower than the significance level ($\alpha = 0.05$), the null hypothesis $H_0$ should be rejected in favor of the alternative hypothesis $H_1$. Thus, the groups reservoir and reservoir with 1.5x concentration factor are from the same group, and the groups reservoir with 2.5x concentration factor and well are also part of the same group, because the null hypothesis for these two cases are accepted.

The statistical arguments confirm the importance of the evaporation effect, which adequately describes the mechanism of salinization of alluvial waters. Other studies on salinization of groundwater by evaporation (Schoeller, 1959; Cruz & Melo, 1968; Silva Júnior et al., 1999; Lopes, 2008) corroborate these results, which are consistent with the study of Robaux (1953) for arid zones, who found that direct evaporation acts up to 2 m deep, but considers that it can reach 22 m in alluvial soils, through the influence of capillarity, promoting a progressive salt concentration.

In the hypothesis that the water in the alluvial aquifer results from a combined process of dissolution/precipitation of salts and mixture between water that infiltrates the alluvial aquifer, from the releases of the Riacho Verde reservoir, and the water that is discharged by the crevices of crystalline rocks near the alluvial aquifer, the contribution of the crystalline basement was quantified considering that the concentrations of Cl$^-$ in the mixture and in the well are equal.

In a simulation for the P10 well, the mixture contains 12.61% of water from the crystalline basement. Then, the inverse geochemical modeling is performed (Parkhurst & Appelo, 1999) in order to obtain the final composition of the water in the well.

In Table 7, where the positive values describe dissolutions and negative values indicate precipitations, the simulation results show that the evolution in salt concentration is due to: dissolution of CO$_2$, which favors the increase of the ion bicarbonate in the waters; dissolution of anorthite and K-feldspar; precipitation of albite and K-mica; a small release of methane gas; and ionic exchanges of the cations Ca$^{2+}$, Mg$^{2+}$ and Na$^+$, through interaction processes with the metallic ions adsorbed to the clays (Machado et al., 2007) present in the sandy clay soils of the alluvial terrain, favoring the absorption of Ca$^{2+}$ and the release of Na$^+$ (Mahlknecht et al., 2006).

The quantified mole transfers are consistent with the ones from other studies (Uliana & Sharp, 2001; Mahlknecht et al., 2006; Machado et al., 2007; Sharif et al., 2008), which
Table 7. Inverse geochemical simulation for the P10 well. Mole transfers of the reactive phases in mmol L\(^{-1}\)

<table>
<thead>
<tr>
<th>Reactive phase</th>
<th>Chemical formula</th>
<th>Mole transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaX(_2)</td>
<td>CaX(_2)</td>
<td>-3.934</td>
</tr>
<tr>
<td>MgX(_2)</td>
<td>MgX(_2)</td>
<td>1.965</td>
</tr>
<tr>
<td>NaX</td>
<td>NaX</td>
<td>3.398</td>
</tr>
<tr>
<td>KX</td>
<td>KX</td>
<td>0.000</td>
</tr>
<tr>
<td>CH(_4)(_g)</td>
<td>CH(_4)(_g)</td>
<td>-1.401</td>
</tr>
<tr>
<td>CO(_2)(_g)</td>
<td>CO(_2)(_g)</td>
<td>4.781</td>
</tr>
<tr>
<td>Sulfur</td>
<td>S</td>
<td>1.868</td>
</tr>
<tr>
<td>Albito</td>
<td>NaAl(_2)Si(_2)O(_8)</td>
<td>-2.315</td>
</tr>
<tr>
<td>Anorthite</td>
<td>CaAl(_2)Si(_2)O(_8)</td>
<td>3.748</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>KAl(_3)Si(_3)O(_10)(OH)(_2)</td>
<td>2.315</td>
</tr>
<tr>
<td>K-mica</td>
<td>KAl(_3)Si(_3)O(_10)(OH)(_2)</td>
<td>-2.499</td>
</tr>
</tbody>
</table>

Also involve simulation of dissolution/precipitation processes of reactive phases in groundwater flows of alluvial zones, evidencing that this model provides plausible results for this type of hydrogeological domain.

For all the other wells, the simulations were performed for the same hypothesis and in all of them the results show mole transfers similar to the ones found for the P10 well, with volumetric contributions of water from the fissure aquifer ranging from 1.53 to 27.99% to the enrichment of salts in the water of the alluvial aquifer.

**Conclusions**

1. Water evaporation in the alluvial aquifer is a relevant factor, and this salt concentration process justifies the salinization of the alluvial aquifer during the dry period, from July to December.
2. The contribution of crystalline crevices to the salinity of alluvial waters is plausible in some points.
3. In the hypothesis of volumetric contribution of waters from the crystalline basement, the mean contribution volume simulated is 15.8%, but it can represent 64% of the salinity found in the alluvial wells.
4. A single contribution of waters from the fissure aquifer is not enough to justify the increase in the salinity of alluvial wells. In order to achieve the final composition of the water in the alluvial aquifer, other sources of salt contribution are necessary, and the dissolution of minerals can be one of them.

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**Literature Cited**


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