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ORIGINAL PAPER

Groundwater quality in a fraction of the river Brigida hydrographic basin for irrigation

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Abstract: Groundwater quality assessment is essential for the sustainable utilization of water resources for agricultural and domestic purposes. The aim of this study was to determine and map the spatial variations of the chemical attributes of groundwater for irrigation purposes in the municipally of Moreilândia, State of Pernambuco, Brazil. The work was carried out from the collection of 93 water samples in semi-artesian wells and amazon wells, to determine: electrical conductivity (EC), hydrogen potential (pH), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), sodium adsorption ratio (SAR), and hardness (GHF). The data were subjected to multivariate analysis, Pearson correlation, geostatistics and later confection of isoline maps through kriging. The geostatistical tool allowed the creation of unsampled areas that enable decision making for the possible drilling of semi-artesian and Amazon wells. It was verified that there are no signs of sodicity, however, there is a risk of salinization in the waters evaluated, being essential to use specific management of groundwater.

Keywords: Semi-arid, salinity, sodicity, geostatistics.

Introduction

In the Brazil Northeastern semi-arid, the hydrographic basins are characterized by being unities of biodiversity conservation and hydric resources (Araújo et al., 2020). However, the anthropic exploration of this resource has been intensified, due to climatical changes, and by low rainfall indices, consequently, contributing to an uneven distribution of water availability in quantity and quality (Rupias et al., 2021).

The superficial waters availability, in the semi-arid usually is limited, because factors as high temperatures, high thermal amplitude, strong insolation, high rates of evaporation, and lack of planning in the

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construction of tanks, contributing negatively in the marked reduction of stored water volume (Gondim et al., 2017), thus potentializing the utilization of groundwaters, coming from semi-artesian wells and Amazonas.

Characteristics as topographic, soil and lithology are factors that have direct influence in the chemical attributes of groundwaters (Moreira et al., 2020), commonly in the semi-arid regions are found waters with salts concentration above 1 g L^{-1}, being necessary a systematic monitoring due to negatives risks to the soil (salinity and sodicity) and plant (changes in osmotic potential and phytotoxicity) (Tavares Filho et al., 2020).

The groundwater resources need quantitative and qualitative assessment to overcome problems related to water shortages and negative environmental impacts, with interest of preserve the natural resources and secure the sustainability (Torres et al., 2016; Makhlof et al., 2021).

The utilization of geostatistical tools enables the constant evaluation of a large number of variables that occurs vertically and horizontally along the landscape, determining specifics management zones for the correct and safe way of water utilization, without degrading the environment (Moreira et al., 2020). In the light of this, the goal of this study is to determine and map the spatial variations of groundwaters chemical attributes, of the municipality of Moreilândia, State of Pernambuco, Brazil, for irrigation purposes.

Material and Methods

The study was carried out in the municipality of Moreilândia, in the State of Pernambuco, Brazil, located at the geographical coordinates: 07º 37' 51" S and 39º 33' 04" W. The region weather is characterized according Köppen classification, as been Bshw' kind, steppe type, hot semi-arid, with the rainy season late into the fall. The study was performed in the months of June and July 2020, at properties that are utilizing groundwaters, for irrigation purposes, in vegetables and forage plants, for animal feed, mainly cattle, goats, and sheep. Figure 1 describes the municipality location, soil types and geology.

For the map making was utilized the open-source software QGIS 3.16.9 (Quantum GIS 3.16.9 - QGIS Development Team, 2021) utilizing the shapefiles available at the Brazilian Institute of Geography and Statistics. The geological data were obtained from the geological map of the state of Pernambuco, in the 1:500.000 scales of the Brazil Geological System. Furthermore, was utilized the numerical terrain model through SRTM data (Shuttle Radar Topography Mission) with shaded relief (artificial lighting with 350° and elevation 45°). Geographic Coordinate System: SIRGAS 2000.

The water samples were collected manually, packaged at pet bottles (500 mL), in semi-artesian wells and Amazonas where the water was allowed to drain for approximately one minute to avoid residues of other materials, being the semi-artesian ones drilled with perforating machines in soils with the most diverse characteristics, and the Amazonas excavated manually, on the margins and in the middle of intermittent water courses, totaling 93 samples.

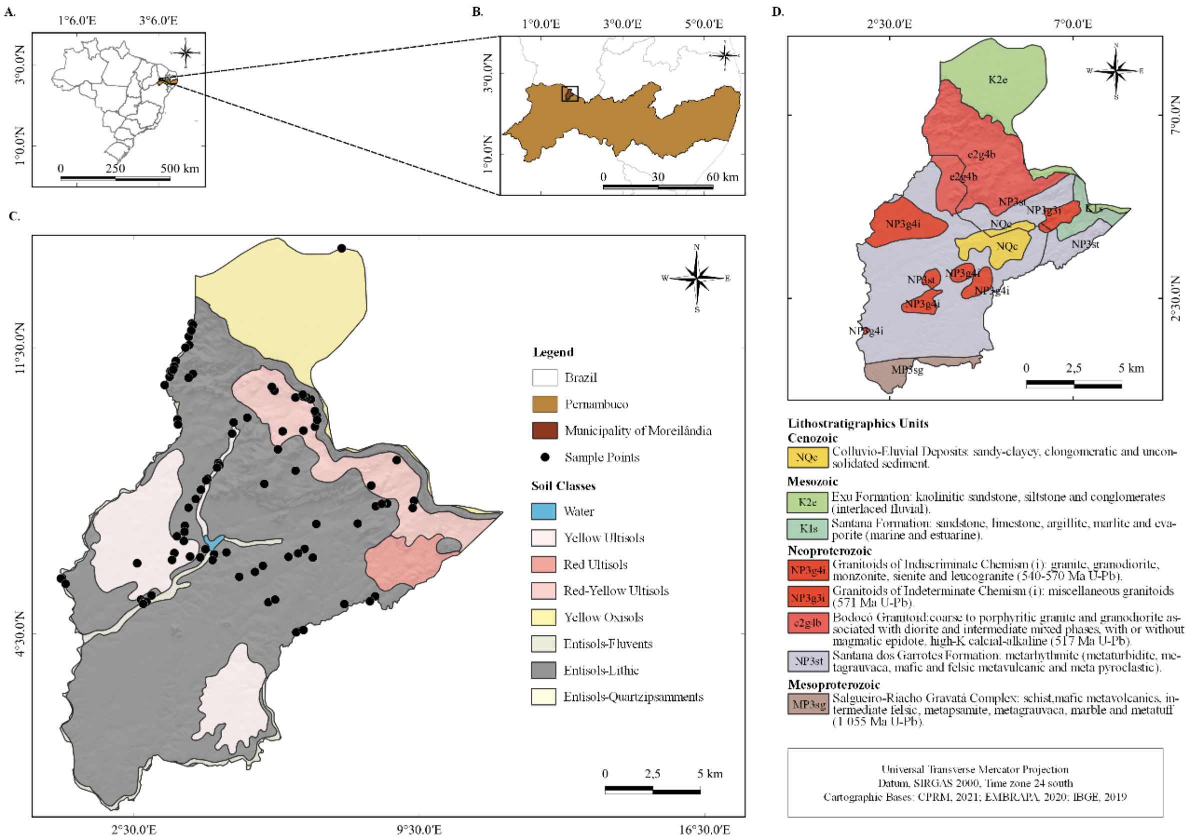

Figure 1: Representation of the groundwater sampling of the municipality of Moreilândia-PE. (A) Brazil map with emphasis on the State of Pernambuco; (B) localization of the municipality; (C) soil maps with the sampling points; and (D) geological map.

After collecting, the samples were forwarded to the Soil and Plant Analysis Laboratory of the Federal Institute of Education, Science and Technology of the Sertão Pernambuco (IF Sertão-PE), located at the municipality of Petrolina-PE. The following water attributes were evaluated: electrical conductivity (EC), hydrogen potential (pH), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), and sodium (Na^+) according to the recommended procedures by Parron et al. (2011). From the results obtained were calculated the sodium adsorption relation (SAR), proposed by Richards (1954) (Equation 1) and the water hardness content, expressed in French hydrometric degrees (GHF), according to Almeida (2010) (Equation 2).

$$\mathrm{SAR}\ (\mathrm{mmol_c\ L^{-1}}) = \frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \qquad (1)$$

$$\mathrm{Hardness(GHF)} = \frac{2.5 \times (Ca^{2+}) + 4.12 \times (Mg^{2+})}{10} \qquad (2)$$

Subsequently, in Tables 1 and 2, the groundwaters were classified as to salinity (Frenkel, 1984), sodicity (Ayers and Westcot, 1999) and hardness grade (Almeida, 2010).

Table 1: Classification of groundwater in the municipality of Moreilandia, State of Pernambuco, Brazil

Salinity[1]	Degree of restriction	Sodicity[2]	Degree of restriction
C1 < 0.75	Low salinity risk	S1 < 13	Lower
C2 0.75 to 1.50	Medium salinity risk	S2 13.1 to 20	Medium
C3 1.51 to 3.00	High salinity risk	S3 20.1 to 30	High
C4 > 3.00	Very high salinity risk	S4 > 30	Very high

[1]Classified according to Frenkel (1984); [2]classified according to Ayers and Westcot (1999); C – electrical conductivity; S – sodium adsorption relation.

Table 2: Classification of groundwater based in French hydrometric degrees (GHF) in the municipality of Moreilândia, State of Pernambuco, Brazil

Water type	GHF
Very sweet	< 7
Sweet	7-14
Moderately sweet	14.1-22
Moderately hard	22.1-32
Hard	32.1-54
Very hard	> 54

Classified according to Almeida (2010).

Statistical analysis was performed by means of an exploratory study of the data using MINITAB® software, been calculated the measures of location (mean, median, minimum and maximum), the measures of variability (coefficient of variation - CV%) and the measures of central tendency (asymmetry and kurtosis) to verify the normality of the chemical attributes evaluated. To the CV analysis, was utilized the Warrick and Nielsen (1980) classification, with low variability for values under 12%, average between 12 and 60%, and high for values over 60%.

Pearson's linear correlation was performed on the analyzed water attributes, classified according to Santos (2007), as follows, values of $r > 0.8$ (strong); $0.5 < |r| < 0.8$ (moderate); $0.1 < |r| < 0.5$ (weak), and $0 < |r| < 0.1$ (very weak). The semi variograms were obtained by the $GS^{+®}$ program (Robertson, 2008) and fitted to the data using spherical, exponential and Gaussian models. By means of these models, the prediction of the attributes in non-sampled zones was made by means of kriging, represented in contour maps, using the SURFER® program.

The choice of theoretical models was made by observing the sum of the squared residuals (SQR), the coefficient of determination (R^2) and, subsequently, the correlation coefficient obtained by the cross-validation technique. The degree of spatial dependence (SDG) was classified based on the nugget effect and the $(C_0/C_0+C_1)*100$ plateau, which considers the degree of spatial dependence to be strong when the $C_0/(C_0+C_1)$ ratio is less than 25%, moderate when the ratio is between 25 and 75%, and weak when the ratio is greater than 75% (Cambardella et al., 1994).

Results and Discussion

The descriptive analysis of evaluated data presents similar values to the results of attributes mean and median, this behavior represents a normal distribution of data, except for Ca^{2+} (Table 3), confirming the not normality by the high standard deviation (159.1). However, the normality or not normality of the data's distribution is not a condition to the use of the geostatistical tool, it is only expected that there will be variation in the data (Moreira et al., 2020).

Table 3: Descriptive analysis of the chemical attributes of groundwater in the municipality of Moreilândia, State of Pernambuco, Brazil

Attributes	Mean	Med	SD	Min	Max	Coefficients			Outliers
						Ass	Curt	CV (%)	
pH	6.9	6.9	0.3	6.4	8.1	0.9	2.3	4.7	8
EC (dS m^{-1})	1.9	1.4	1.5	0.0	6.2	1.3	1.2	79.9	12
Na^+ (mg L^{-1})	49.4	50.0	28.3	3.0	118.0	1.2	-0.7	57.3	2
K^+ (mg L^{-1})	12.5	10.0	10.3	1.0	47.0	0.0	1.1	82.1	4
Ca^{2+} (mg L^{-1})	131.1	84.6	159.1	3.1	682.8	2.1	3.7	121.4	7
Mg^{2+} (mg L^{-1})	1.1	1.4	0.6	0.0	1.4	-0.9	-0.8	56.7	0
Hardness (GHF)	33.6	21.0	42.8	0.7	21.0	2.0	3.4	127.3	7
SAR ($mmol_c$ L^{-1})	1.4	1.3	0.8	0.2	5.1	1.8	5.2	55.8	0

CV – coefficient of variation [CV% = (standard deviation – SD/mean) x 100]; EC – electrical conductivity; hardness – ion content (Ca^{2+} and Mg^{2+}) dissolved in water; SAR – sodium adsorption relation; Med – Median; Max – Maximum values; Min – Minimum values; Ass – Asymmetry; Curt – Kurtosis

The attributes Ca^{2+} and Na^+ presented high mean values and with maximum values reaching 118.0 and 682.8 mg L^{-1}, respectively (Table 2). The high concentration and variation of these chemical elements in the aquifer can be explained by the dissolution and hydrolysis of more soluble minerals that fill fractures and faults in the rocks, such as carbonates and feldspars present in granite (Roisenberg et al., 2003).

The hardness value presented in the samples represents a high total level of alkaline-earth ions in the water, in particular Ca^{2+} and Mg^{2+} salts, being that the degree of hardness is directly proportional to the concentration of these salts. According to Modesto et al. (2020), hard waters provides a risk of clogging of emitters, especially drippers, due to the formation of salt crusts, through decanting, of excess calcium carbonate or magnesium.

Based on the symmetry of the data that show the dispersion around the mean, they can be considered positively asymmetric, except for Mg^{2+} (negatively asymmetric) and based on the kurtosis that shows dispersion in relation to a normal curve (mesocurtic), the data of Na^+ and Mg^{2+} presented a platicurtic distribution and different from the behavior of the other attributes evaluated (leptocurtic) (Betzek et al., 2017).

As for the coefficient of variation (CV%) of the evaluated data, it can be classified as homogeneous variability when the CV% is less than 12%, heterogeneous variability when it is between 12 and 60%, and very heterogeneous if it is greater than 60% (Warrick and Nielsen, 1980). Following this classification line, it was verified that the values of the water attributes (Table 3), present a high heterogeneous distribution, consequently a high variability of the chemical attributes except for pH, which presented a homogeneous distribution. The heterogeneity observed in the CV% values, may be associated with the source material of the region, as well as anthropogenic issues as stated by Matias et al. (2019), studying the variability of chemical attributes in the Brazilian Cerrado.

Checking the linear correlation of the chemical attributes of the water (Table 4), by Person, a positive and significant interaction was found for most variables at $p < 0.05$ probability level.

Table 4: Pearson’s linear correlation between chemical attributes of groundwater in the municipality of Moreilândia, State of Pernambuco, Brazil

	pH	EC	Na^+	K^+	Ca^{2+}	Mg^{2+}	Hardness
EC	-0.24**						
Na^+	-0.06	0.21					
K^+	-0.05	-0.09	0.57**				
Ca^{2+}	-0.15	-0.03	0.67**	0.59**			
Mg^{2+}	0.11	-0.02	0.75**	0.62**	0.52**		
Hardness	-0.13	-0.01	0.69**	0.54**	1.00**	0.52**	
SAR	0.25	0.20	0.15**	0.41*	-0.18**	-0.23**	-0.17

EC – electrical Conductivity; hardness – ion content (Ca^{2+} and Mg^{2+}) dissolved in water; SAR – sodium adsorption relation ;* and ** significant at($p < 0.01$ and $p < 0.05$, respectively, by the F test.

Pearson’s correlation indicated a negative correlation between electrical conductivity (EC) and water pH. In contrast, the positive correlation between Na^+ and the attributes K^+, Ca^{2+}, Mg^{2+}, hardness, and RAS was observed, showing that the attributes had influence of the saline content in the groundwater, showing a strong and significant correlation with each other. When the correlation is positive, it reflects the direct relationship between the two variables, showing that as the content of one variable increases the other tends to increase as well.

The negative correlation between Ca^{2+} and Mg^{2+} with RAS, indicates that the results exert an inversely proportional position, meaning that as one variable increases the other tends to decrease (Torres et al., 2016).

For the semivariograms, the models obtained for the studied attributes were Gaussian for pH, Na^+, Ca^{2+} and Mg^{2+} and spherical for EC, K^+, hardness, and SAR (Table 5). When the semivariograms fit any of the observed models, there is a point from a certain value of the distance between sampled points, in which spatial dependence is no longer observed, this is given by the fact that these models have thresholds (Vicente et al., 2018).

Table 5: Models and estimated parameters of the adjusted semivariograms for the chemical attributes of groundwater in the municipality of Moreilândia, State of Pernambuco, Brazil

Attributes	Model	C_0	$C_0 + C_1$	SDG (%)	Range (m)	R^2	CRVC	
							b	a
pH	Gaussian	0.0647	0.130	49.62	4,087.64	0.67	0.59	2.84
EC	Spheric	1.310	2.635	49.71	7,330.00	0.83	0.58	0.78
Na^+	Gaussian	35.000	617.3	5.67	2,875.20	0.90	1.00	0.21
K^+	Spheric	9.900	95.6	10.36	5,590.00	0.84	0.41	0.99
Ca^{2+}	Gaussian	10.000	178.20	0.06	969.95	0.27	1.04	-1.56
Mg^{2+}	Gaussian	0.075	0.530	14.15	10,981.20	0.88	0.96	0.03
Hardness	Spheric	1.000	2172	0.046	4,600.00	0.51	1.15	0.21
SAR	Spheric	0.094	0.675	13.92	2,454.00	0.98	0.55	0.62

SDG – degree of spatial dependence [DSD% = (C_0/C_0 + C_1) x 100]; R² – coefficient of determination of the model; CRVC – regression coefficient from cross-validation; b – angular coefficient; a – interceptor; EC – electrical conductivity; hardness – ion content (Ca^{2+} and Mg^{2+}) dissolved in water; SAR – sodium adsorption relation.

Regarding the degree of spatial dependence (SDG%) a strong relationship occurred among the evaluated attributes, with the exception of pH and EC that presented moderate spatial dependence (Cambardella et al., 1994).

The strong dependence shows that the distribution of chemical attributes in space is not random, so that the semivariograms explain most of the variance of the experimental data, being intensely influenced by intrinsic soil properties, such as texture and mineralogy, indicating that the model and the sampling density reflect the reality of the area (Carvalho et al., 2018; Matias et al., 2019). The strong spatial dependence of chemical attribute concentration in water has already been observed by several authors (Torres et al., 2016; Lundgren et al., 2017; Rocha et al., 2017; Vicente et al., 2018; Moreira et al., 2020) in different environments, and demonstrates that the geostatistical tool can be used to determine the variability of these attributes in a spatio-temporal variation with accuracy.

The reach between the attributes evaluated presented a variation of values between Ca^{2+} (969.95 m) and Mg^{2+} (10,985.20 m), which correspond to the areas considered homogeneous within the reach limit of each variable analyzed. The reach values are influenced by the source material, in which the Litholic Neosol class represents more than half of the soils characteristic of the evaluated region, and this may be the reason for the homogenization of the area (Figure 1). It is a parameter that should be analyzed for ensuring that all points within a circle, with the radius shown, are so similar that they can be used to reliably estimate values for any point between them (Matias et al., 2019).

The highest values of the coefficient of determination of the model fitted to the semivariogram (R^2) were observed for SAR (98%), Na^+ (90%), Mg^{2+} (88%), K^+ (84%), and EC (83%), respectively. The R^2 shows in percent how much of the variation in the estimated semivariance values are explained by the models, denoting that the semivariogram met the spatial interpolation requirements.

The cross-validation regression coefficient (CRVC) indicates that the model is really expressing the real situation of the site under study when the values are close to one for variable (b) and close to zero for variable (a) of the equation and is directly related to the R^2 values. Thus, SAR, Na^+ and Mg^{2+} showed the highest ratios respectively and therefore have a lower error, making them reliable for the use of kriging (Lundgren et al., 2017).

Based on the results obtained in the semivariograms, spatial distribution maps were made (Figure 2) of the attributes pH, EC, Na^+, K^+, Ca^{2+}, Mg^{2+} and SAR obtained in water. The kriging technique allows to estimate the values of the evaluated attributes in non-sampled points, allowing the definition of specific zones. According to Lundgren et al. (2017), the construction of maps allows the identification of the greatest and least variability in relation to the attributes.

All variables analyzed presented spatial variability and allowed the estimation by the isolation maps prepared by interpolation using the ordinary kriging technique as shown in Figure 2, as a reflection of the correlations obtained in Table 3. The pH values in water were generally classified as neutral, corroborating results obtained by Marques and Lima (2017) and Moreira et al. (2020).

The high concentrations of Na^+, K^+, and Ca^{2+} have a direct reflex on the EC. Thus, the groundwater of the evaluated wells presented medium to high risk of salinization, according to Frenkel (1984), being classified as C2 and C3. When the SAR was estimated, no risk of sodicity was observed (S1), according to the classification proposed by Ayers and Westcot (1999). Therefore, even with high levels of Na^+, the risk of sodification was reduced by the high levels of Ca^{2+} in the samples evaluated. In relation to hardness, it is observed that in the distribution map most areas present GHF from very sweet to medium hard according to Almeida (2010), as a reflection of the low level of Mg^{2+}, which in the proposed equation is equivalent to 1.64 times more than the level of Ca^{2+}.

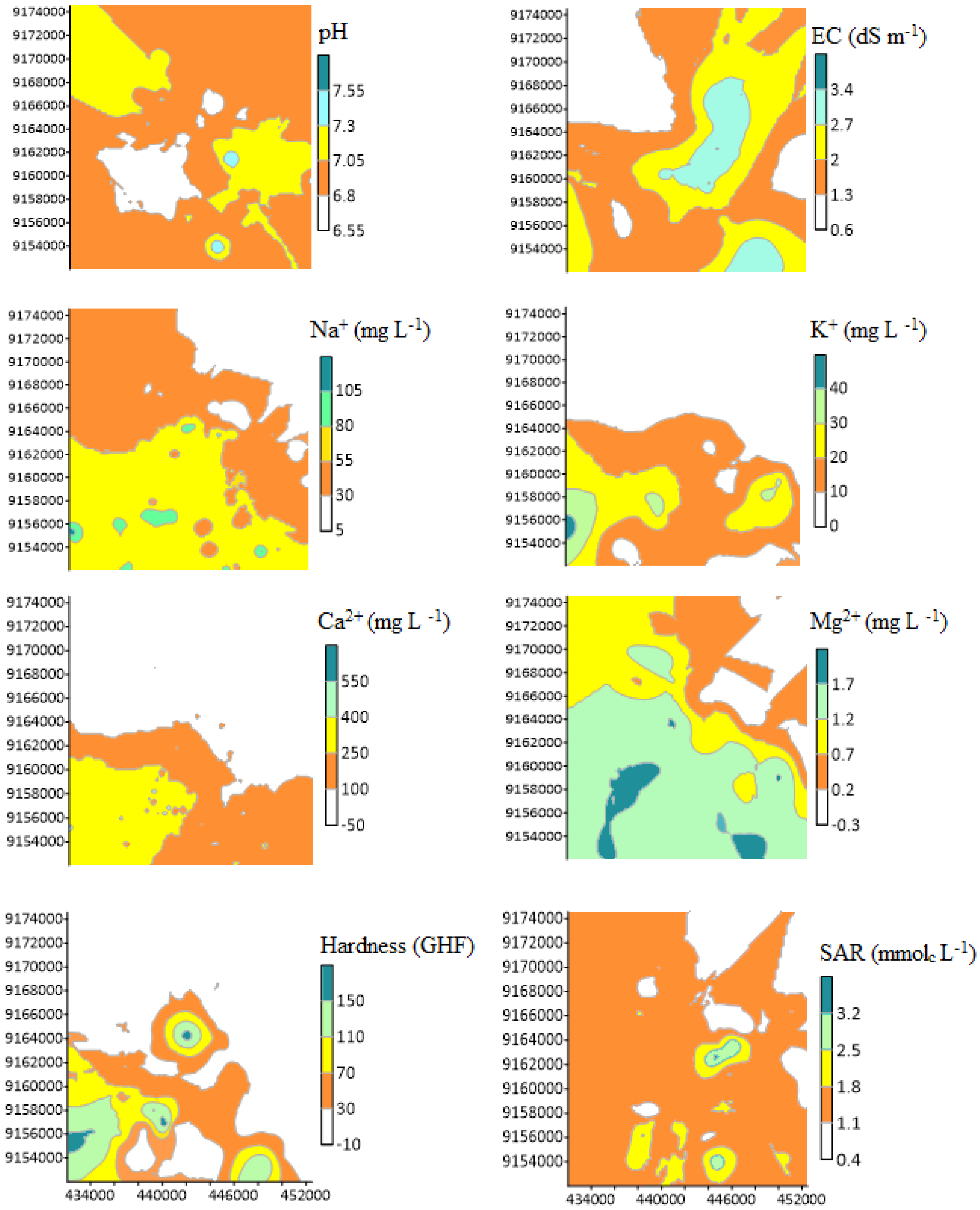

Figure 2: Maps of spatial variability of chemical attributes of groundwater in the municipality of Moreilândia, State of Pernambuco, Brazil.

The study of the relationship between the distribution of water samples collected in the municipality of Moreilândia-PE and the chemical variables analyzed in the groundwater was performed by means of an ordination generated by multivariate principal component analysis, involving the specific collection points of each well and the chemical attributes. The variability retained in principal components 1 and 2 explained 72.14% of the original variability, where CP1 and CP2 each retained 55.06 and 17.08%, respectively, of the original information of the evaluated data (Figure 3).

The association between the contents of K^+, Na^+, Mg^{2+} and the values of EC and SAR obtained, show a direct relationship between these variables that positively influenced, CP 1 and CP 2 (Figure 3). The direct relationship between Ca^{2+} and Hardness values was also observed in Figure 3, showing that the variability of the concentrations of these chemical variables can directly influence the subsurface water quality.

The identification of the variability of the chemical attributes of groundwater allows the evaluation and definition of specific zones of sites with quality water, thus providing the use of these springs for the practice of irrigation in agricultural crops, consequently providing an increase in productivity in the region and efficiency of irrigation systems.

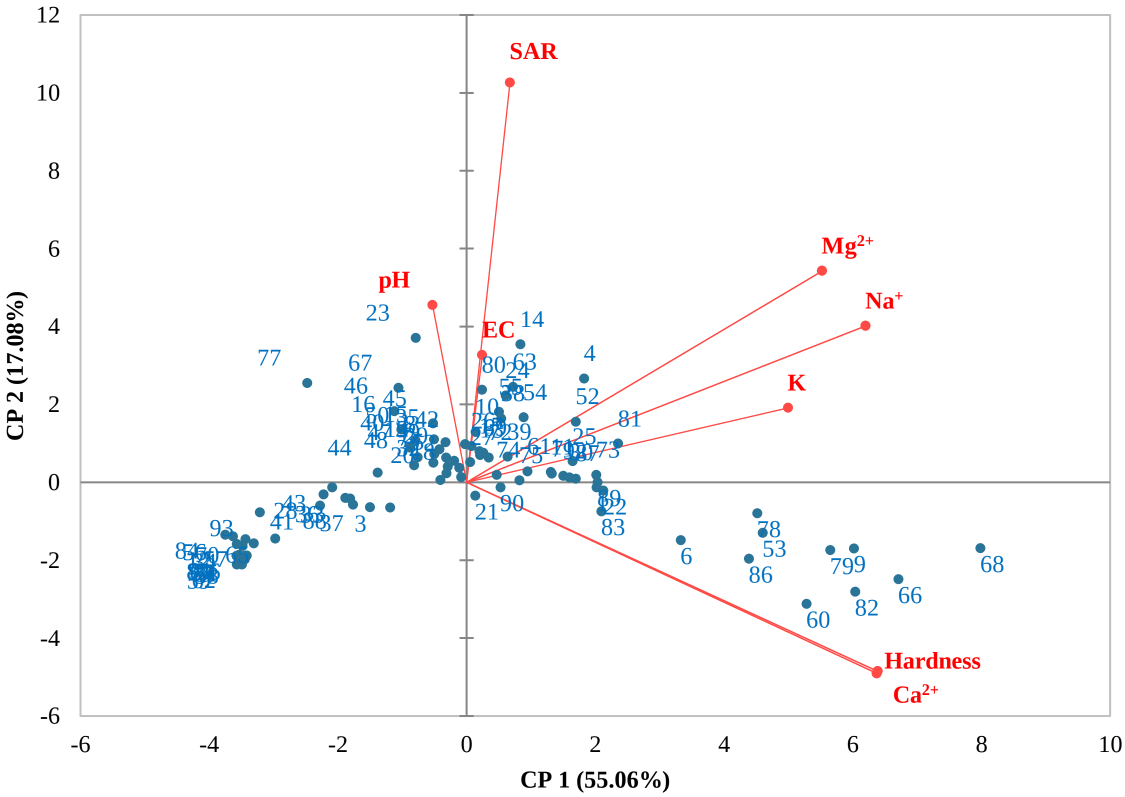

Figure 3: Principal component analysis (PCA) between sample collection points and chemical attributes of groundwater in the municipality of Moreilândia, State of Pernambuco, Brazil.

Conclusions

The magnitude of electrical conductivity values found in the region requires the use of specific management in the use of groundwater for irrigation.

The groundwater showed no evidence of sodicity.

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