

## MECHANISMS CONTROLLING SURFACE WATER QUALITY IN THE COBRAS RIVER SUB-BASIN, NORTHEASTERN BRAZIL<sup>1</sup>

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**ABSTRACT** - Stream water quality is dependent on many factors, including the source and quantity of the streamflow and the types of geology and soil along the path of the stream. This study aims to evaluate the origin and the mechanisms controlling the input of ions that effect surface water quality in the sub-basin of the Rio das Cobras, Rio Grande do Norte state, Northeastern Brazil. Thirteen ponds were identified for study: three in the main river and ten in the tributaries between, thus covering the whole area and lithology of the sub-basin. The samples were collected at two different times (late dry and rainy periods) in the hydrological years 2009 and 2010, equating to total of four collection times. We analyzed the spatial and seasonal behavior of water quality in the sub-basin, using Piper diagrams, and analyzed the source of the ions using Guibbs diagram and molar ratios. With respect to ions, we found that water predominate in 82% sodium and 76% bicarbonate water (cations and anions, respectively). The main salinity control mechanism was related to the interaction of the colloidal particles (minerals and organic sediment) with the ions dissolved in water. Based on the analysis of nitrates and nitrites there was no evidence of contamination from anthropogenic sources.

**Keywords:** Desertification. Semiarid. Salinity.

## MECANISMOS CONTROLADORES DA QUALIDADE DAS ÁGUAS SUPERFICIAIS NA SUB-BACIA HIDROGRÁFICA DO RIO DAS COBRAS DO NORDESTE BRASILEIRO

**RESUMO** - A qualidade da água de um rio dependente de vários fatores, incluindo a origem e quantidade de escoamento e a formação geologia dos solos ao longo do fluxo. Objetivou-se avaliar a origem e os mecanismos controladores da entrada dos íons e, conseqüentemente, da qualidade da água na sub-bacia do rio das Cobras, RN. Foram selecionados 13 açudes, sendo 3 no rio principal e 10 entre os afluentes, abrangendo toda a área e litologias da sub-bacia. As amostras foram coletadas em duas épocas distintas (final dos períodos secos e chuvosos) nos anos hidrológicos de 2009 e 2010, totalizando 4 momentos de coleta. Analisou-se o comportamento espacial e sazonal da qualidade da água na sub-bacia utilizando o diagrama de Piper e a origem dos íons pelo diagrama de Gibbs e razão molar. Constatou-se que em relação aos íons, predominam águas sódicas em 82% e águas bicarbonatadas 76% (cátions e ânions), respectivamente. Os resultados obtidos sugerem que o principal mecanismo controlador da salindade está relacionado a interação das partículas coloidais (sedimentos orgânicos e minerais) com os íons dissolvidos na água. Também não se observou indícios de contaminação antrópica na área, tendo por base a análise de nitratos e nitritos.

**Palavras-chave:** Desertificação. Semiárido. Salinidade.

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<sup>1</sup>Received for publication in 07/31/2014; accepted in 07/18/2016.

Extracted from the first author's doctoral's thesis.

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## INTRODUCTION

The Cobras River sub-basin, Rio Grande do Norte (RN), is located in the Seridó desertification region, and is one of the worst affected desertification areas among the various sub-basins that comprise the Piranhas-Açu basin (RN and Paraíba States) in the northeastern region of the RN. This sub-basin was chosen as a pilot area to test the effectiveness of the actions detailed in the National Plan of Action and Combat to the Desertification (PAN-LCD) drawn up by the Brazilian Government in 2004.

Currently, in state of RN these actions are being implemented via the construction of hydro-environmental works aiming to improve the availability of water for the rural population. However, this work is being carried out without any prior technical study that may assist the choice of the sites and indicate which preventive measures can be taken to prevent the process of salinization.

Studies considering the geochemical evolution of surface water in existing reservoirs are important tools for planning and sustainability in semiarid zone (JALALI, 2007), and provide valuable information on the behavior and seasonal, temporal and spatial variability of ionic compounds dissolved in the water within the river basins and sub-basins, as well as its dynamics in rock-soil-water systems.

Several studies have evaluated the behavior and temporal and spatial variation of ionic water quality in surface reservoirs, especially in arid and semi-arid areas where there is usually a high water deficit (XU et al., 2012; HAYNES et al., 2007; BOWMER, 2011).

The hydrochemistry of surface water is influenced by many factors, such as precipitation, geological context, and anthropogenic action by the inclusion of organic materials (YADANA, 2009) and pollution with chemicals (pesticides and herbicides) used in agriculture. In the case of semi-arid regions, the climate influence is strongly determined by the high evaporation rates and large climate variability over short distances.

Understanding the dynamics between geology, climate and human action is key for determining the mechanisms that will influence decisions regarding proper water resources management at the local level and meeting the demand of diffuse Brazilian semi-arid rural populations. The objective of this paper is to assess the origin and controlling mechanisms of ion input and the surface water quality from the Cobras River sub-basin, in the Seridó desertification region, RN.

## MATERIAL AND METHODS

### Study area

This work was conducted in the Cobras River sub-basin, RN, which is an integral part of the Piranhas-Açu watershed, occupying an area of 159.13 km<sup>2</sup> (Figure 1) and belonging to the cities of Parelhas, Carnaúba dos Dantas and Jardim do Seridó (BRAZIL, 2004).

The rainy period extends from January to May, with an average annual precipitation of 612.4 mm, average, minimum and maximum temperatures of 26.1, 21.2 and 32.0 °C, respectively and, potential evapotranspiration of 1552 mm per year (KÖPPEN, 1948).

This water system, associated with other climatological parameters, provides the region with a drainage network consisting of intermittent rivers where the flow of surface water exists for only a few days within the rainy period. Dams are the most common method of water storage.

The sub-basin is formed by the metamorphic rocks of the crystalline basement of the Seridó, located in the far northeast of the Borborema Province. The Seridó formation occupies the largest portion of the sub-basin, covering an area of 127.81 km<sup>2</sup> (Figure 2), representing 80.9% of the total area according to geological maps (JARDIM DE SÁ, 1998).

### Area and collection of samples

The thirteen sampling points selected for hydrochemistry characterization were located in dams along the sub-basin, with three sampling points along the main river and ten in the tributaries (Figure 2), in order to cover all the lithologies within the study area.

The samples were collected both at the end of the dry periods (December 2009 and 2010) and during rainy days (August 2009 and 2010) of each hydrologic period, thus totaling four sampling times. Some dams dried up at the end of the 2010 rainy season and so it was not possible to sample all points. Fifty analyses were performed in total (Table 1).

The sampling of dams covered the largest part of the area and included all the lithologies of the sub-basin (Table 1). Analysis of Electric Conductivity (EC), Sodium Adsorption Ration (SAR), Total Dissolved Solid (TDS), hardness, NO<sup>3-</sup>, NO<sup>2-2-</sup>, Ca<sup>+2</sup>, Mg<sup>+2</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> were performed via the methods recommended by Embrapa (1999).

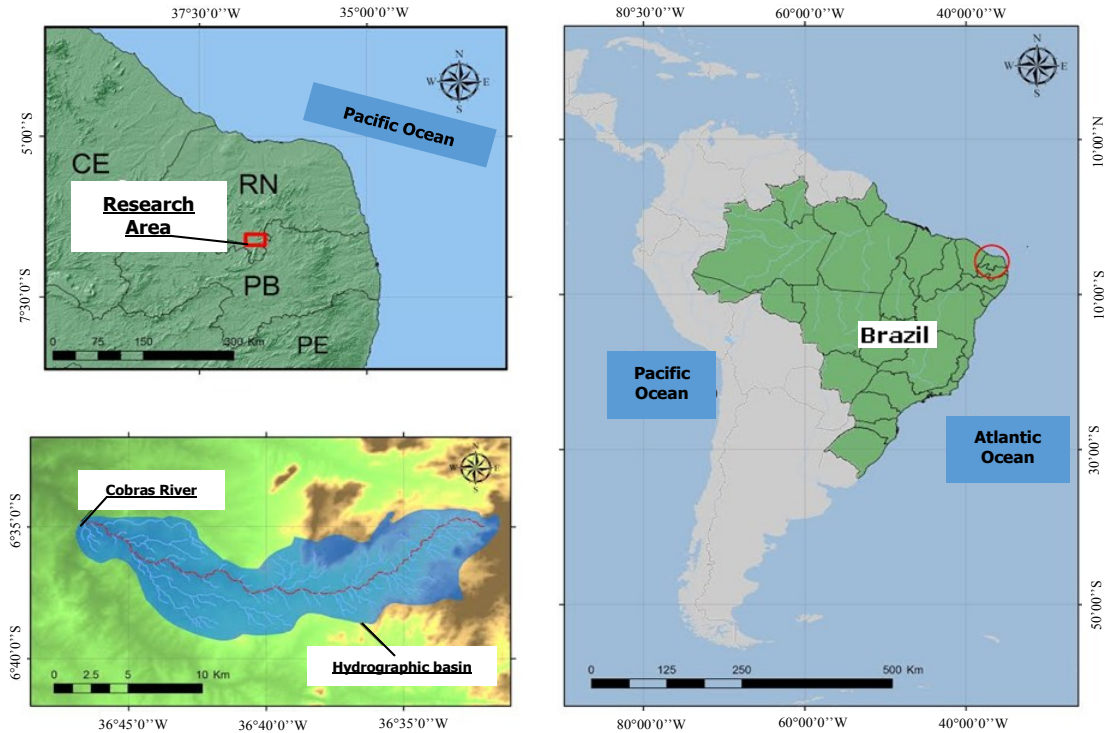


Figure 1. Coverage area in the Cobras River sub-basin, RN State, northeastern Brazil.

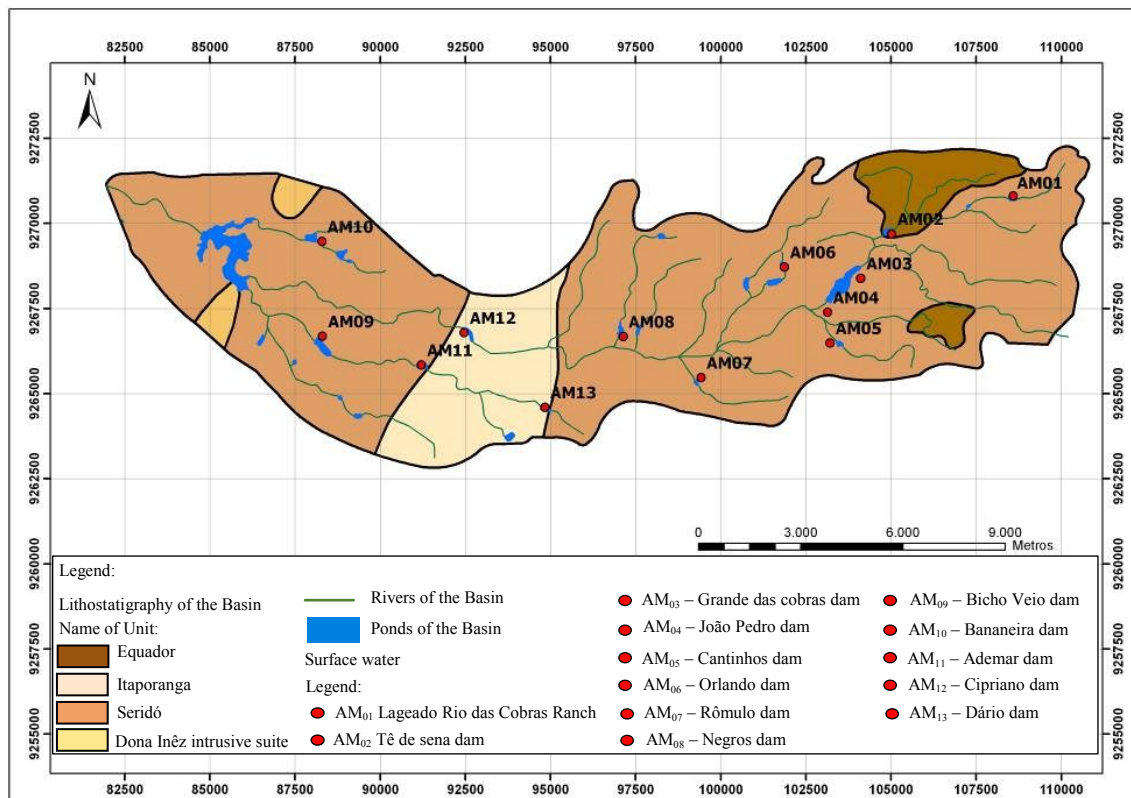


Figure 2. Location of water collection and service area of the existing lithology along the Cobras River sub-basin, RN State, northeastern Brazil.

**Evaluation of quality and control mechanisms of water**

The water quality was accessed with a Piper diagram using the software Qualigraf Water. The

quality is classified within the triangular diagram by comparing the different water groups according to the dominant cations and anions (BARROSO et al., 2011; RAVIKUMAR et al., 2011).

The Gibbs diagram (GIBBS, 1970) was used for understanding the control mechanisms of major ion entry to the water system. The relationship between the ionic composition of the water (hydrochemistry) and the characteristics of the predominant lithology in the region was established, taking into consideration the precipitation and evaporation.

The molar ratio between of the dissolved ions was used to identify the source of the leachate material. Therefore, distinction of aquifers was made

according to their chemical composition, major cations and anions analysis and comparisons of relationships between these factors. The molar ratio was calculated from sampled period averages, totaling four average values throughout the two-year study period.

The software Qualigraf was used to perform the classification of samples using the Piper diagram to compare and classify water variability in relation to the dominations.

**Table 1.** Location and water collection period sampling points along the Cobras River sub-basin, RN State, northeastern Brazil.

Sampling time: year 2009			
End of the wet season		End of dry season	
Sample	Location (Dam's name)	Sample	Location (Dam's name)
1	Lajedo	14	Lajedo
2	Tê de Sena	15	Tê de Sena
3	Cobras	16	Cobras
4	João de Pedro	17	João de Pedro
5	Cantinhos	18	Cantinhos
6	Orlando	19	Orlando
7	Rômulo	20	Rômulo
8	Negros	21	Negros
9	Dario	22	Dario
10	Cipriano	23	Cipriano
11	Ademar	24	Ademar
12	Bicho veio	25	Bicho veio
13	Bananeiras	26	Bananeiras

Sampling time: year 2010			
End of the wet season		End of dry season	
Sample	Location (Dam's name)	Sample	Location (Dam's name)
27	Lajedo	40	Lajedo
28	Tê de Sena	41	Tê de Sena
29	Cobras	42	Cobras
30	João de Pedro	43	João de Pedro
31	Cantinhos	44	Cantinhos
32	Orlando	45	Orlando
33	Rômulo	46	Rômulo
34	Negros	47	Negros
35	Dario	48	Dario
36	Cipriano	49	Cipriano
37	Ademar	50	Ademar
38	Bicho veio	51	Bicho veio
39	Bananeiras	52	Bananeiras

## RESULTS AND DISCUSSION

### Hydrochemistry assessment

Increasing values of hardness, TDS and EC were observed between the first 2009 sampling, at the end of the rainy season, and the fourth collection at the end of the 2010 dry season (Table 2). This is probably due to a reduction of rain in the dry season when evaporation increases the salt concentrations in the water. Despite the low levels of salinity at some sampling points, for example, the first collection in 2009 ( $EC = 0.1 \text{ dS m}^{-1}$ ), this water presents some salinization potential for irrigated areas if management practices for keeping the EC in the root zone close to the threshold EC of crops are not adopted (PORTO FILHO et al., 2011). The EC

results of collected water samples indicated that the sources had a low risk of salinity and sodicity for use in irrigation (Table 2).

The levels of bicarbonate in the water directly influenced the water pH in both years (Table 2). Minimum, maximum and average values of water pH were 7.5, 8.8 and 7.0, respectively, which are within the range of normality for irrigation purposes; thus, waters can be used for irrigation without restriction with regard to nutritional imbalance risks to crops (AYERS; WESTCOT, 1999).

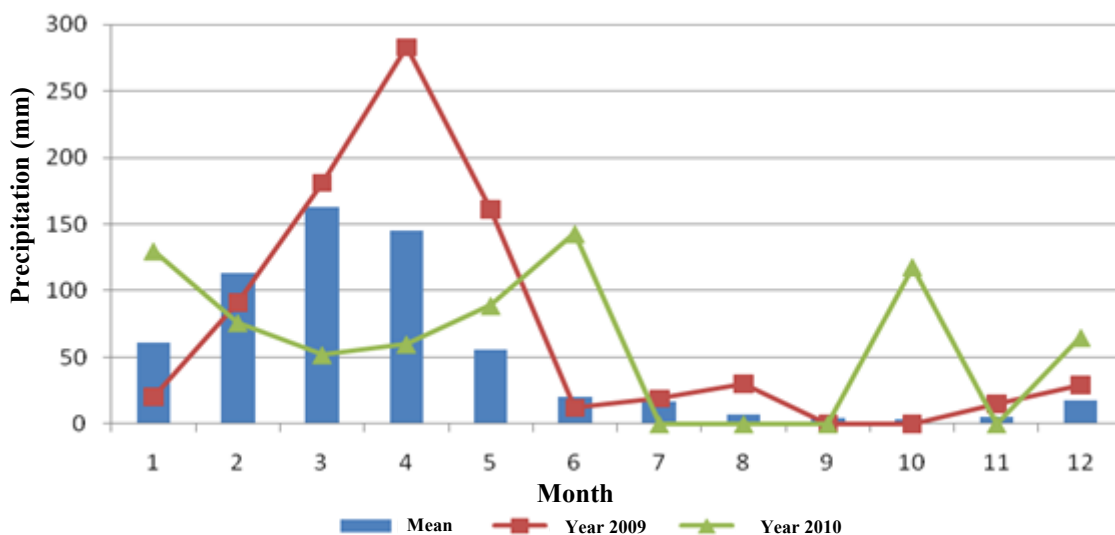
Maximum nitrate ( $4.54 \text{ mg L}^{-1}$ ) and nitrite ( $1.0 \text{ mg L}^{-1}$ ) concentrations were within the acceptable value ranges. Nitrate is a major contaminant of groundwater and surface water, thus there was no evidence of anthropogenic contamination.

**Table 2.** Maximum, medium and minimum values of quality in collected water samples in the years of 2009 and 2010 hydrological in Cobras River sub-basin, RN State, northeastern Brazil.

Parameters	1 collection (final rain-2009)			2 collection (dry end-2009)			3 collection (final rain-2010)			4 collection (dry end-2010)		
	Max.	Min.	Average	Max.	Min.	Average	Max.	Min.	Average	Max.	Min.	Average
pH	8.20	7.00	7.60	8.50	7.40	8.06	8.80	7.00	7.69	8.50	4.70	7.28
EC (dS m <sup>-1</sup> )	0.55	0.10	0.23	1.00	0.15	0.42	1.88	0.16	0.65	2.42	0.22	0.76
TDS (mg L <sup>-1</sup> )	364.00	38.80	138.23	557.20	85.20	238.49	1,180.00	92.00	405.32	1,694.00	126.80	491.58
Hardness (mg L <sup>-1</sup> )	119.98	30.24	63.27	213.3	42.66	98.44	295.49	34.32	130.45	448.35	32.30	147.41
Nitrite (mg L <sup>-1</sup> )	0.46	0	0.084	1.00	0	0.134	0.52	0	0.097	0.45	0	0.13
Nitrate (mg L <sup>-1</sup> )	0	0	0	4.54	0	1.20	1.55	0	0.532	1.04	0	0.36
Ca <sup>++</sup> (mg L <sup>-1</sup> )	19.73	0	10.34	66.06	10.42	23.05	40.07	3.63	19.12	33.78	3.09	18.54
Mg <sup>++</sup> (mg L <sup>-1</sup> )	17.18	4.26	8.63	17.51	3.33	10.79	47.45	5.09	20.04	93.17	5.39	24.67
Na <sup>+</sup> (mg L <sup>-1</sup> )	70.00	6.11	24.04	126.08	16.76	47.28	346.15	17.22	94.44	442.1	14.7	102.54
K <sup>+</sup> (mg L <sup>-1</sup> )	26.96	3.12	9.498	20.53	5.75	11.59	44.12	8.93	18.80	32.63	7.50	15.27
Fe (mg L <sup>-1</sup> )	3.75	0.09	0.86	6.07	0.11	1.58	21.19	0.95	4.79	10.86	0.30	3.58
CO <sub>3</sub> (mg L <sup>-1</sup> )	0.39	0	0.052	7.72	0	1.45	30.52	0	4.36	10.85	0	2.24
HCO <sub>2</sub> (mg L <sup>-1</sup> )	145.76	46.94	88.03	314.03	68.04	155.18	486.61	64.77	193.21	541.00	9.80	182.50
SO <sub>4</sub> (mg L <sup>-1</sup> )	5.91	0	2.73	6.86	0	3.10	24.02	0.78	6.50	11.95	0.66	4.74
Cl <sup>-</sup> (mg L <sup>-1</sup> )	101.06	9.94	35.56	178.06	14.54	63.00	468.08	15.17	133.38	656.27	20.86	155.87

As previously mentioned in Table 2, a study of chloride concentrations in the Cobras River sub-basin indicated that chloride concentrations exceeding 650 mg L<sup>-1</sup> contributed to increased EC (2.42 dS m<sup>-1</sup>) in the sub-basin during end of the 2010 dry season (four samples). Many of the resultant concentrations of chloride in the sub-basin studied were 100 to 650 mg L<sup>-1</sup>, which is above the standard for chloride (100 mg L<sup>-1</sup>) for class one streams.

Precipitation reached 841 mm (27% above average) in 2009 and 733 mm (16.4% above average) in 2010 (Figure 3), which probably influenced the EC. The TDS and EC in streams are usually higher during low flow periods than during high flow periods. The semiarid zone is characterized as a region of high temperatures and high temporal and spatial rainfall variability; therefore, water shortage is the major limiting factor in agricultural production (BARROSO et al., 2010).

**Figure 3.** Precipitation observed in the area of the Sub-basin of the Cobras river in 2009 and 2010.

#### Evaluation of water hydrochemistry and molar ratios

A predominance of sodic waters in an 82 and 18% mix was observed (Figure 4). For anions, bicarbonate was predominant at 76%, chloride at

14% and mixed anions at 10% in the samples. The joint analysis of cations and anions indicated the predominance of sodium-bicarbonate in waters at 58%, followed by sulphated or sodium-chloride water at 24% and bicarbonated-calcium or magnesium at 12%.

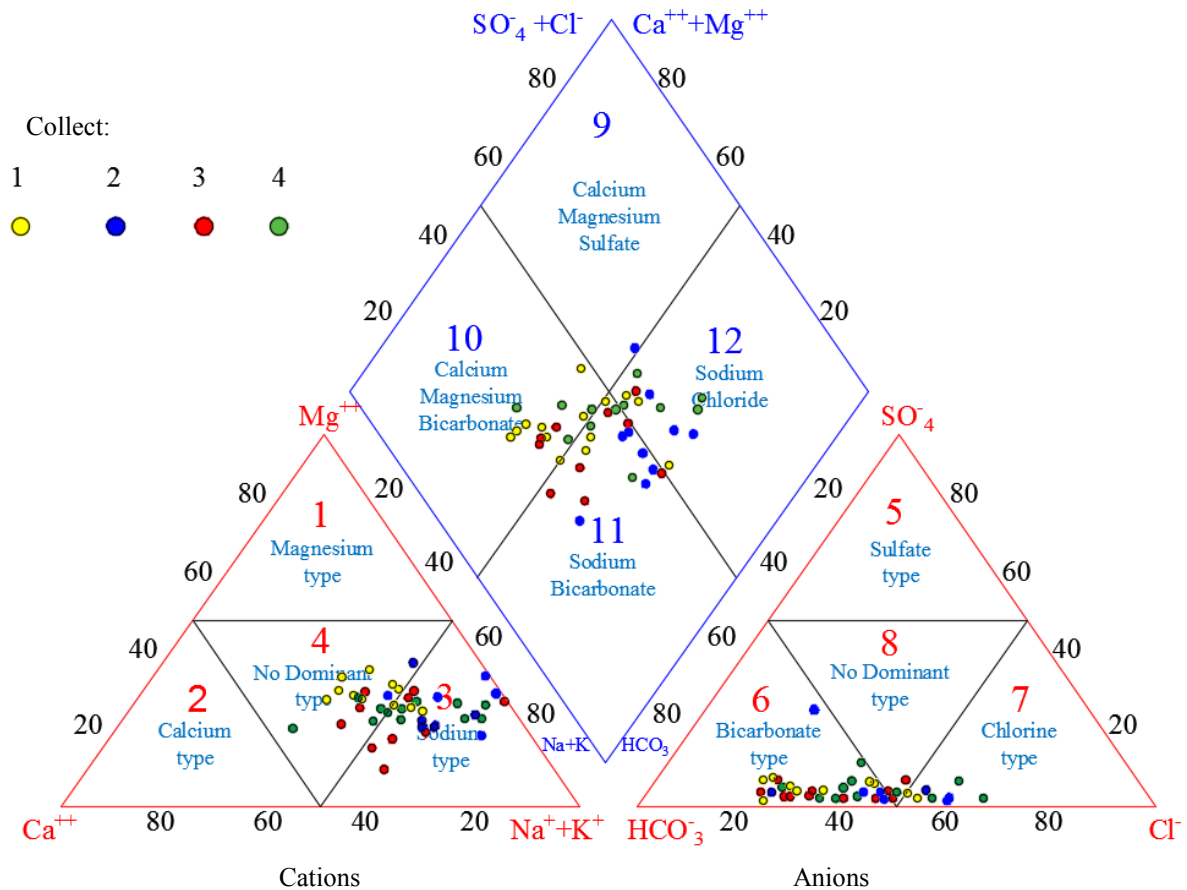
This behavior shows that the water hydrochemistry responses are related to the precipitates, since in 2010 the rains were smaller and irregularly distributed throughout the year, when compared to the year 2009 (Figure 3).

**Larger cations**

Na<sup>+</sup> was dominant cation in the four samplings. The predominance of cations in samples

were: 1st) Na<sup>+</sup> > K<sup>+</sup> > Mg<sup>++</sup> > Ca<sup>++</sup>; 2nd) Na<sup>+</sup> > Ca<sup>++</sup> > K<sup>+</sup> > Mg<sup>++</sup>; 3rd) Na<sup>+</sup> > Mg<sup>++</sup> > Ca<sup>++</sup> > K<sup>+</sup> and 4th) Na<sup>+</sup> > Mg<sup>++</sup> > Ca<sup>++</sup> > K<sup>+</sup>.

Molar ratio rNa/rCl was always < 1 (Figure 5A) and there was an increase in this relationship between the end of the rain in 2009 and the end of the dry period of the same year. At the end of the rainy season of 2010 there was a sharp decrease rNa/rCl because of the increased quantities of Cl<sup>-</sup> dissolved in the water.



**Figure 4.** Piper diagram for surface water samples along the Cobras River sub-basin, RN.

Calcium occupies intermediate positions, even with significant losses of this cation in relation to original rock (also observed for Na<sup>+</sup>) due to its adsorption by colloidal particles (clays and organic matter) and becoming part of a complex, thus reducing its presence as a dissolved cation in the water (PEREIRA et al., 2006).

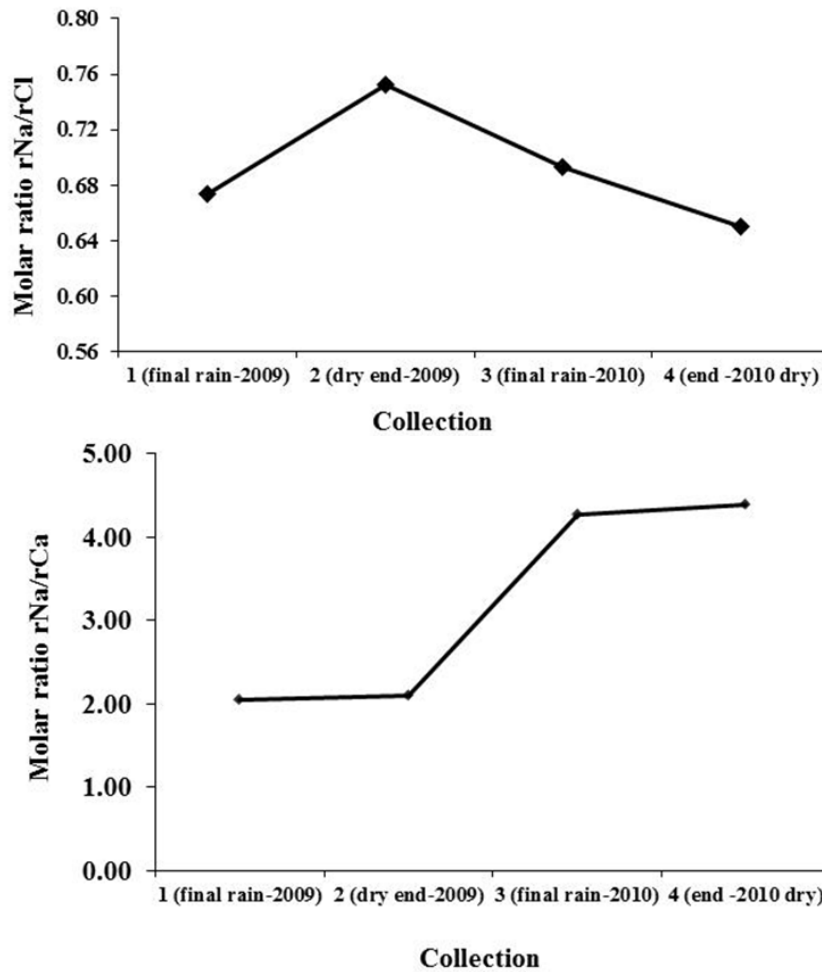
This trend can be observed in the relationship between rNa/rCa molar (Figure 5B), where it is clear that between the first sampling in 2009 and the last in 2010, a gradual growth occurred in the relationship, with a consequent increase in the EC.

The K<sup>+</sup> had a prominent position in the first sampling at the end of the 2009 rainy season when rainfall and runoff were higher. After that, there was a progressive decrease in K<sup>+</sup> dissolved in water.

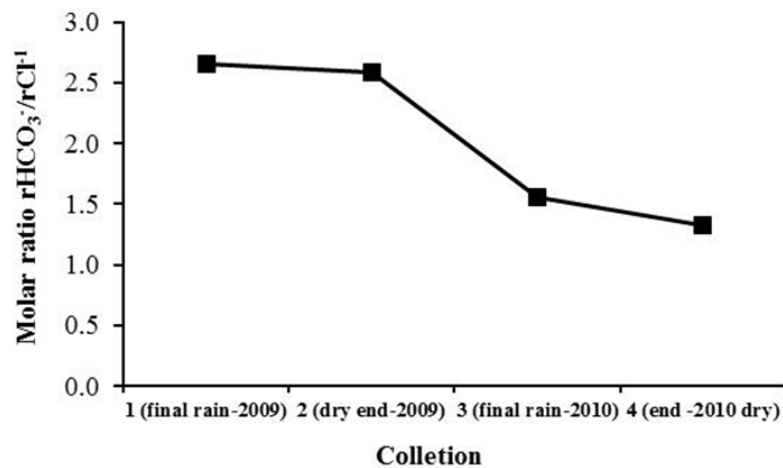
**Larger Anions**

Bicarbonate was the larger anion (Table 2), showing HCO<sub>3</sub><sup>-</sup> > Cl<sup>-</sup> > SO<sub>4</sub><sup>-2</sup> > CO<sub>3</sub><sup>-2</sup> in the four samplings. There was a gradual decrease of the relationship rHCO/rCl over the hydrological years of 2009 and 2010 due to the increase of Cl<sup>-</sup> concentration in water (Figure 6).

This growth can be related to lower precipitation (Figure 3) that lead to lower water levels in the reservoirs and resulted in increasing concentrations of organic matter and increasing EC between 2009 and 2010 (Table 2).



**Figure 5.** Variation of the molar ratios  $rNa/rCl$  (A) and  $rNa/rCa$  (B) into the dry and rainy seasons of 2009 and 2010 in Cobras River Sub-basin, RN.



**Figure 6.** Variation of the molar ratio  $rHCO_3^-/rCl^{-1}$  in the dry and rainy seasons of the years of 2009 and 2010 hydrological in Cobras River Sub-basin, RN.

There are three main mechanisms of inclusion of  $Cl^-$  ions in water: atmospheric contribution through rain, rock weathering of silicate minerals and rocks, and anthropogenic pollution (SINGH et al., 2004; JALALI, 2007; AL-SHAIBANI, 2008).

The owners of these reservoirs routinely plant grass for supplying cattle fodder and this contributes to the large accumulation of organic matter, which

enhances these locations as  $Cl^-$  sources to the system. This fact was corroborated by Helena et al. (2000) who also found no geological explanation for the presence of  $Cl^-$  in the water of the River Pisuerga, Spain; instead, they justified the results by contamination by sewage and waste deposits (organic matter).

As mentioned earlier, in the case of the



Cobras River Sub-basin/RN, it is possible to suggest that the two possible mechanisms for the inclusion of  $\text{Cl}^-$  must be related to rock weathering of biotite and via the release of  $\text{Cl}^-$  via vegetable decomposition (primary source). As this sub-basin is 170 km from the sea (which is a main source of chlorine via precipitation), the inclusion mechanism via precipitation should contribute to a lesser degree since there is an exponential decrease in precipitation  $\text{Cl}^-$  content with distance from the coast.

The origin of  $\text{HCO}_3^-$  is related to the presence of  $\text{CO}_2$  dissolved in rainwater:  $\text{CO}_2 + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+$ . Depending on the closeness and contact with the atmosphere there is a tendency for the superficial reservoirs to have a large  $\text{HCO}_3^-$  content, when compared to confined aquifers.

Other sources of this anion are organic degradation and rock weathering of silicates. Thus, the prevalence of  $\text{HCO}_3^-$  in surface water points to the aforementioned sources (organic degradation and interaction with the atmosphere).

### Control mechanisms of water quality

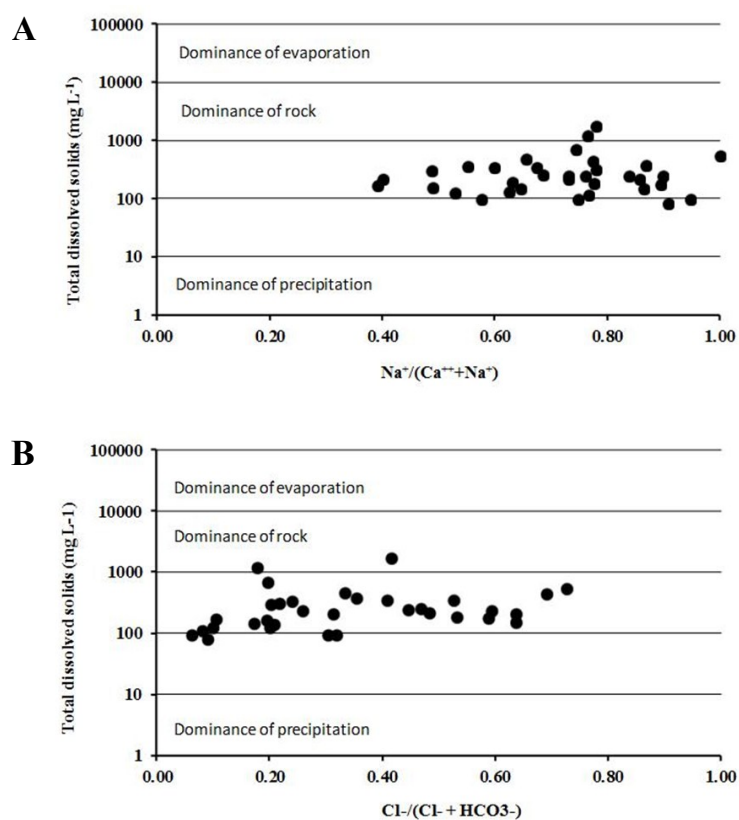
From the information above,  $\text{Na}^+$ ,  $\text{HCO}_3^-$  and  $\text{Cl}^-$  ions dominate in water samples collected in the Cobras River sub-basin, RN, regardless of season

(rain or dry). Furthermore, the  $\text{Na}^+$  and the  $\text{Cl}^-$  have a strong influence on the EC of the sub-basin water. Due to this dominance, it is appropriate to assess the origin of these ions within the study area, in addition to the processes related to their entry into the system.

A diagram that is widely used to understand the sources of hydro chemical controllers and the chemical composition of the water, is the model proposed by Gibbs (1970). According to the results obtained from the use of this diagram (Figure 7), it is observed that the origin of the ions is most strongly related with the local geology.

However, as the contact-time of dam surface water with the geology is short when compared with the confined aquifers groundwater (YADANA, 2009), we can say that the influence of lithology settles through the colloidal particles of mineral origin arriving to dams through runoff, with cation exchange capacity prevailing as a mechanism of control (solid-water interface).

Also by using the Gibbs diagram to understand the source of ions in the Gameleira River basin in Ceará, Pereira et al. (2006) reached the same conclusion when assigning rock-water integration as the dominant control on the ions present in the abovementioned area waters.



**Figure 7.** Gibbs diagram for control factor of water quality related to surface cations (A) and anions (B).



## CONCLUSIONS

There was no evidence of anthropogenic contamination within the Cobras River sub-basin, RN.

Na<sup>+</sup> was the dominant cation in all four samplings. For anions, HCO<sub>3</sub><sup>-</sup> was dominant and there is a trend of decreasing of HCO<sub>3</sub><sup>-</sup> with the increase of Cl<sup>-</sup> and EC during the last sampling.

The main salinity control mechanism is related to rock-water interactions, through the interaction of colloidal particles with the ions dissolved in water (cation exchange).

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