# Hydrochemistry of Cachoeira River (Bahia State, Brazil)

## Hidroquímica do Rio Cachoeira (Bahia, Brasil)

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**Abstract: Aim:** The aim of this study is to evaluate the spatial-temporal changes of chemical elements in the surface waters of the Cachoeira River in order to evaluate the impacts of anthropogenic activities in water quality; **Methods:** Samples were collected monthly between August 2008 and August 2009 at six collection points along the river. The abiotic parameters dissolved oxygen, pH, electrical conductivity and temperature were performed in the field using portable digital meters; concentration of ions nitrite ($NO_2^-$), nitrate ($NO_3^-$), ammonia ($NH_4^+$), phosphate ($PO_4^-$), sodium ($Na^+$), calcium ($Ca^{+2}$), potassium ($K^+$), chloride ($Cl^-$), magnesium ($Mg^{+2}$), sulfate ($SO_4^{-2}$) were determined by ion chromatography and bicarbonate ($HCO_3^-$) was calculated by a model of ionic associations originated from alkalinity values; **Results:** The spatial variations showed that anthropogenic activities and land use changes (cocoa crops and pasture) appear to be the major factors influencing the distribution of nutrients in the Cachoeira River; however, lithology seems to be the factor influencing the major ions; **Conclusions:** Variations in ion concentrations were directly related to drought and rainy periods, the geological formation, and the various land uses. The lack of treatment of domestic wastes and their incorrect disposal in water bodies has significantly contributed to the aggravation of environmental problems and consequently the health of the population.

**Keywords:** watershed, hydrogeochemical, Cachoeira River.

**Resumo: Objetivo:** O objetivo do presente estudo foi avaliar as variações espaço temporais da química das águas superficiais do Rio Cachoeira a fim de estabelecer os impactos das atividades antropogênicas na qualidade da água; **Métodos:** As coletas foram realizadas mensalmente entre agosto de 2008 e agosto de 2009 em seis pontos de coleta ao longo do rio. Os parâmetros abióticos oxigênio dissolvido, pH, condutividade elétrica e temperatura foram determinados através de medidores portáteis no campo; a concentração dos íons nitrito ($NO_2^-$), nitrato ($NO_3^-$), amônia ($NH_4^+$), fosfato ($PO_4^-$), sódio ($Na^+$), cálcio ($Ca^{+2}$), potássio ($K^+$), cloreto ($Cl^-$), magnésio ($Mg^{+2}$), sulfato ($SO_4^{-2}$) através da cromatografia iônica e o bicarbonato ($HCO_3^-$) através da alcalinidade; **Resultados:** Os resultados referentes a variação espacial no Rio Cachoeira demonstraram que as atividades antropogênicas e os diferentes cultivos ao longo da bacia (cultivo de cacau e pastagem) são os principais fatores que influenciam na distribuição dos nutrientes (N e P). No entanto, a litologia parece ser o principal responsável pelas concentrações dos íons maiores, não havendo diferenças entre os pontos de coleta; **Conclusões:** As variações das concentrações dos íons foram diretamente relacionadas aos períodos mais secos e mais chuvosos, a formação geológica e aos diversos usos da terra. A ausência do tratamento de resíduos domésticos e seu despejo impróprio nos corpos de água têm contribuído para o agravamento dos problemas ambientais e consequentemente à saúde da população.

**Palavras-chave:** bacia hidrográfica, hidrogeoquímica, Rio Cachoeira.

## 1. Introduction

Anthropogenic influences and land use changes in watersheds such as urbanization, agricultural farmland and pasture for livestock promote changes in the water chemistry of rivers (Biggs et al., 2002). These alterations include the input of salts and nutrients that are released in the drainage basins according to land use or directly discharged into rivers (Martinelli et al., 1999a; Daniel et al., 2002).

The composition of river waters presents several variations determined by several factors

such as climate (temperature, humidity, wind, precipitation), rock types, vegetation, groundwater contribution, rainwater, and flow rate variations (Fritzsons et al., 2003).

Rock weatheringin the watershed allows understanding the chemical weathering in the drainage basin because differencesinthe parent rocks increase the cations and anions dissolved inthe solution.

As water can drain different types of soils and chemical compositions resulting from the local geology, there are complex chemical interactions peculiar to each watershed. The changes provoked by human activities also contribute to chemical changes in natural waters: removal of vegetation, different soil treatments, industrial and agricultural dumping (Tundisi and Matsumura-Tundisi, 2008).

Due to deforestation, the bare soil is exposed to surface and deep leaching; such processes result in soil depletion, whereas the soil resources are moved to lower areas, usually concentrated inrivers and lakes, - thus virtually causing an increased use of fertilizers and imbalancingthe content of nutrients in the soil and exposing it to chemical contamination (Chapman et al., 2000).

The use of organic fertilizers and minerals in agricultural systems can result in an excess of important nutrients in the soil, which can reach streams and rivers by means of processes such as leaching, runoff and soil erosion (Corriveau et al., 2009).

Thus, the objective of this study is to evaluate the spatial-temporal changes of chemical elements in the surface waters of the Cachoeira River in order to evaluate the impacts ofanthropogenic activities in water quality. It is expected a decrease in water quality with theincrease of human alterations.

## 2. Material and Methods

### 2.1. Study area

The Cachoeira River Basin is located in the southern portion of the State of Bahia, between coordinates 14° 42'/15° 20' S and 39° 01'/40° 091' W (Bahia, 2001). It comprises a drainage area of about 4600 km² that consist of 13 counties - an estimated population of 600 000 inhabitants.It arises in the headwaters of the Colônia River, at an altitude of 800 m in the Ouricana Mountain Range (Itororó municipality), and reaches its lowest level on the coastal surface of the city of Ilhéus. The Cachoeira River is formed by the confluenceof the Salgado

and Colônia Rivers, and it flows through three municipalities, Itapé, Itabuna and Ilhéus.

From the geotectonic point of view, the basin is included inthe southeast edge of the São Francisco Craton, cratonic land unit formed by the end of the Trans-Amazonian Cycle (2.1 - 1.9 billion years).The territory is composed of– in the west-east direction –the Itabuna Belt (Archaean/Inferior Proterozoic), from the Jequié block (West) to the Atlantic Ocean (East) (CPRM, 1997). All the features found in the study area are located in the Coaraci-Itabuna region. The Itabuna Belt consists of rocks pertaining to: the Paraíso River Intrusive Suite, which consists of granite and monzonite; the Intrusive Suite of Itabuna, which primarily consists of syenite; rocks of São José Complex, where tonalite is predominant; and the Ibicaraí - Buerarema Complex and Japu River Unit , composed of gneissic rocks (Dana and Franco, 1976).Tertiary sediments of Grupo Barreiras are predominant in the extreme southeast region of the basin – close to the coast.Mangrove and coastal sands are present in the mouth of the Cachoeira River (Quaternary) (Barbosa and Dominguez, 1996).

Relief is the main determinant of rainfall variations. The gradual elevation of the ground in an east-west direction constitutes an orographic barrier that,in relation to the unit, stimulates the development of various climate zones (Nacif et al., 2003).

According to the classification of Köeppen, it is possible to distinguish three climatic areas along the basin:a hot and humid tractnear the coast (Af weather), with precipitation exceeding 2000 mm annually and distributed throughout the year, while the average annual temperature is 23.3 °C; a transition range (Am climate), characterized by the occurrence of the dry season in August and September, compensated by high rainfall totals and the average annual temperature of 22.7 °C; finally, a typical range of semi-tropical humid climate (Aw climate), with annual rainfall of 800 mm and average annual temperature of 23.6 °C (Schiavetti et al., 2005). The annual relative humidity of the basin decreases from the Atlantic Ocean towards the interior of the continent. The cities near the coastal strip have humidity above 85%, falling to 84.2% in the age of transition, and reaching 76.3% in the inland (Bahia, 1995).

### 2.2. Field methodology

Samples were collected monthly at 6 sites along the Cachoeira River according to land use and

accessibility (Figure 1 and 2, Table 1 and 2) between August 2008 and August 2009. Due to the high level of the river waters in September and November, no access was allowed to the sampled points, hence preventing the completion of collections.

The samples were collected in the middle of the river upstream to downstream. One sample per sitewas collected directly in the middle of the river in P1, P2, P4, P5 and P6 in high-density polyethylene bottles previously washed with 1:1 HCl and distilled
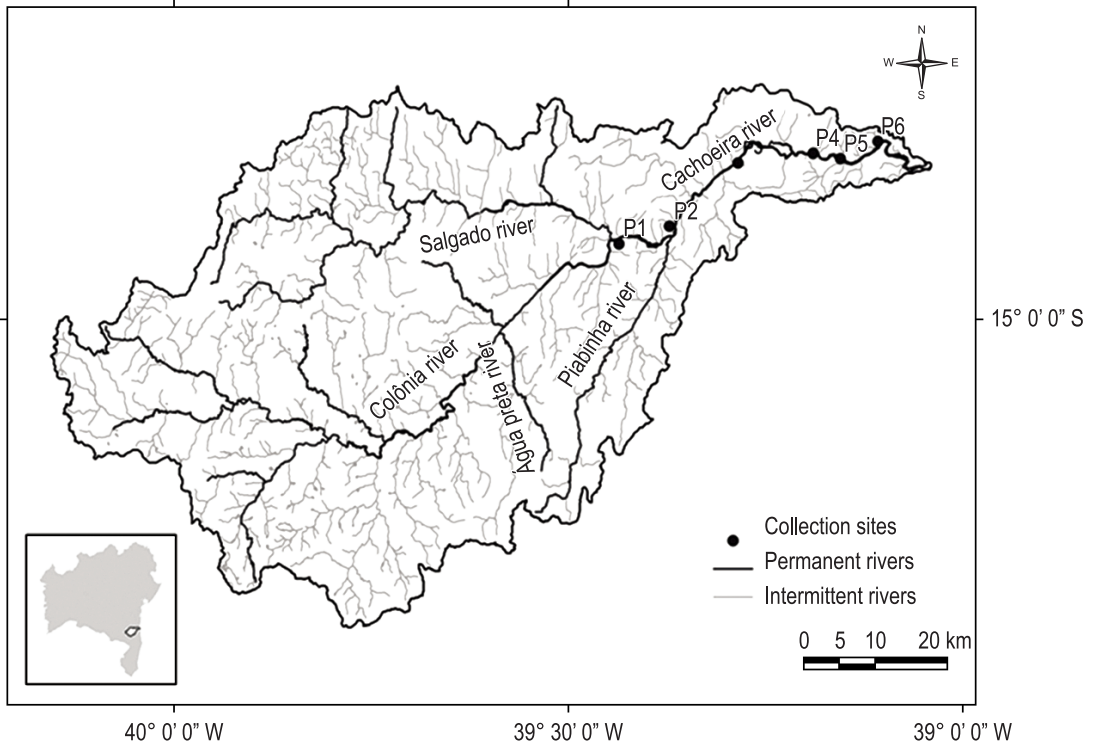


**Figure 1.** Hydrographic map of the Cachoeira River Basin and location of the collection sites.
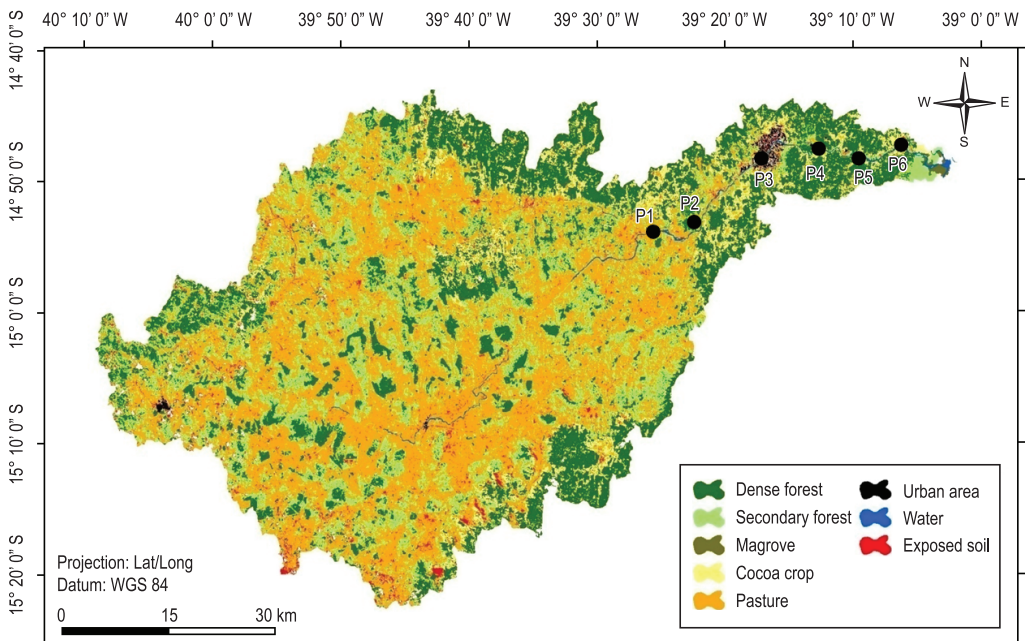


**Figure 2.** Land use map of Cachoeira river basin and location of the collects sites (Source: SOUZA, CM – LAPA/UESC).

**Table 1.** Sampled points along the Cachoeira River, its geographical coordinates and land use.

| | Coordinates | Land use |
|---|---|---|
| P1 | 14° 53' 89.9" S and 39° 25' 67.4" W | Predominance of areas for pastures (grass). |
| P2 | 14° 52' 72.5" S and 39° 21' 77.7" W | Cocoa plantation in the cabruca system (consortium with tree species making the shading), pastures and agriculture areas. |
| P3 | 14° 47' 95.6" S and 39° 16' 65.6" W | Located inside of the urban Center of the city of Itabuna. |
| P4 | 14° 7' 53.1" S and 39° 11' 21.7" W | Presence of spots of Rainforest andpastures areas. |
| P5 | 14° 48' 16.4" S and 39° 09' 17.5" W | Predominance of areas for pastures (grass). |
| P6 | 14° 47' 0.77" S and 39° 06' 25.1" W | The margins are modified by human action. |

**Table 2.** Study area description.

| Sites | Localization (cities) | Land use | Lat/long |
|---|---|---|---|
| P1 | Itapé | Urbanization/Pasture | 14° 53' 89,0" S and 39° 25' 67,4" W |
| P2 | Itabuna | Pasture/Secondary Forest | 14° 52' 72,5" S and 39° 21' 77,7" W |
| P3 | Itabuna | Urbanization | 14° 47' 95,6" S and 39° 16' 65,6" W |
| P4 | Ilhéus | Dense forest/Cocoa crop | 14° 47' 53,1" S and 39° 11' 21,7" W |
| P5 | Ilhéus | Dense forest/Cocoa crop | 14° 48' 16,4" S and 39° 09' 17,5" W |
| P6 | Ilhéus | Dense forest/Cocoa crop | 14° 47' 0,7" S and 39° 06' 25,1" W |

water, and kept in a Styrofoam cooler with ice during transport to the laboratory. In P4 the samples were collected with a cord and a bucket over a high bridge.Samples were filtered using 47 mm glass fiber filters, type GF/F (0.7 µm) previously calcined at 450 °C for subsequent analysis of the filtered sample (dissolved). The temperature, conductivity, pH and dissolved oxygen measurements were performed in the field using portable digital meters (pH/Cond 3401 WTW). The material for analysis of alkalinity was collected separately in syringes previously poisoned with mercury chloride ($HgCl_2$)

### 2.3. Analytical procedures

The concentrations of cations and anions ($Ca^{+2}$, $Mg^{+2}$, $K^+$, $Na^+$, $Cl^-$, $NH_4^+$, $NO_2^-$, $NO_3^-$, $PO_4^-$, $SO_4^{-2}$) were determined by ion chromatography using DIONEX ICS 1000 in filtered samples.

Alkalinity was determined by titration with 0.01N HCl potentiometric tritration using a simplified Gran´s function (Carmouze, 1994). The concentration of bicarbonate ($HCO_3^-$) was calculated by a model of ionic associations using phosphorus, silicate, temperature, alkalinity and pH with the aid of the software CO2SYS.EXE(Lewis and Wallace, 1998)with the dissociation constants K1 and K2 from Merhbach et al. (1973).

Silicate was analyzed using the method described by Carmouze (1994), which consists of a reduction in the Silicomolybdic complex by ascorbic acid.

### 2.4. Statistical analysis

The parametric test *ANOVA* was used for all the variables and a significance level of 5%

(p < 0.05) was employed. The analysis of variance (*Kruskal Wallis*) was used to assess the possible significant differences between the variables and the collection points, and also among the sampling months, followed by the posteriori *Tukey HSD* test. A Principal Component Analysis (PCA) was performed from correlation matrices to ordinate the samples collected along the Cachoeira River in the dry (August and October/2008, February, March and June/2009) and rainy (December/2008, January, April, May, July and August/2009) seasons (software PAST 1.91).

## 3. Results

The results observed in this study showed that Cachoeira river water quality varies according human influence and river flow. The conductivity values did not vary throughout the collection sites, and the higher values were found in P6 with means of 759.0 ± 1246.7 µS.cm$^{-1}$ (Table 3).

The higher temperature, pH and dissolved oxygen values were observed in P1. The lowest pH values were observed at point 5 (6.4 ± 0.5), whosevalues were close to neutral showing significant differences with P1 (KW-H = 13,3; p = 0.02).

Dissolved oxygen concentrations were lower in P3 and P4 compared to P1 and P2 (KW-H = 25,4; p = 0.0001), with values of 4.1 ± 2.3 and 4.8 ± 1.4 mg.L$^{-1}$ and saturation percentages of 51.5 ± 29.7 and 60.2 ± 20.8%, respectively.

Dissolved inorganic nitrogen ($NO_2^-$, $NO_3^-$, $NH_4^+$) and phosphorus ($PO_4^-$) concentrations showed statistical differences for nitrite ($NO_2^-$),

in which different values were found among P2, P3 and P4(KW-H = 21,9; p = 0.0005), for nitrate ($NO_3^-$), in which two groups were observed - the first consisting of P1, P2 and P3 that were not statistically different from each other, and the second consisting of P4, P5 and P6 (KW-H = 39,6; p = 0,00001), in which no differences were found among points; in addition, $PO_4^-$ showed difference between point P1 and points P4 and P5 (KW-H = 19,1; p = 0,002) (Figure 4).

It was not observed spatial variation of major ions (p > 0.05), chloride ($Cl^-$), sulfate ($SO4^{-2}$) and magnesium ($Mg^{+2}$); however, a decrease can be observed throughoutthe river from upstream to downstream. The highest values for these ions were found in P1, near the formation of the Cachoeira River, and the lowest values were found in point 6 (Figure 5).

The ions sodium ($Na^+$) and potassium ($K^+$) presented variations between the sampled points, while an increase was verified in concentrations between P1 and P3. The $Na^+$ values in these points ranged from 1719.3 ± 647.0 to 2029.2 ± 959.6 µM.$L^{-1}$, while the $K^+$ values ranged from 87.7 ± 41.2 to 134.9 ± 39.4 µM.$L^{-1}$ in points 1 and 3, respectively.
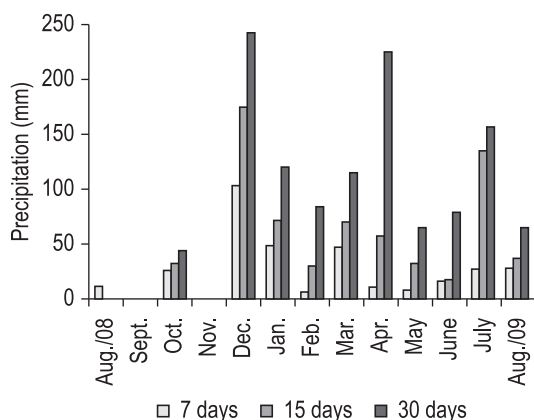


**Figure 3.** Accumulated precipitation during August/2008 to August/2009 in the city of Itabuna. Source: CEPEC / CEPLAC.

Calcium ($Ca^{+2}$) showed no variation between the collection points. The values of this ion ranged from 332.3 ± 114.0 to 398.7 ± 131.0 µM.$L^{-1}$. Bicarbonate ($HCO_3^-$) had an increase in concentrations between the points 1 and 4 with values between 1198.7 ± 375.0 and 1485.2 ± 376.6 µM.$L^{-1}$, respectively. Despite human influence mainly in P3 and P4, no differences were observed in major ion concentrations.

The highest $PO_4^-$ and $NH_4^+$ concentrations occurred in October and August/08, with values of 39.1 and 22.9 µM.$L^{-1}$ for $-PO_4$ and 470.4 and 215.9 µM.$L^{-1}$ for $NH_4^+$, respectively (Figure 6). These values coincide with the months of lowest rainfall - October and August/08 – in which precipitation was 34.4 mm and 74.0 mm, respectively (Figure 3). Same trend was found to nitrate that presents the highest values in driest months (May, August and October/08) and after the last month, there was a striking decrease in the ion concentrations. Nitrite presents a slight increase in concentration between June and August/09; thus, the highest value in all the sampling period was found in June.

In relation to the temporal variation of the other ions, August and October/2008 had the highest concentrations of then all ; some of these ions were $Ca^{+2}$, $Na^+$, $Mg^{+2}$, $Cl^-$ and $HCO_3^-$. These months also had the lowest rainfall: 74.0 mm in August and 34.4 mm in October. A slight increase in the concentration of these ions and $K^+$ in February was also verified, except for $Cl^-$ (Figure 7).

The principal component analysis shows that the first axis was directly correlated with electrical conductivity, $NO_2^-$, $NO_3^-$, $HCO_3^-$ and $Ca^{2+}$ and inversely correlated with pH, OD and $Cl^-$ (36.34% of total variance), whereas the secondary axis was directly correlated with Mg and temperature (24.97% of total variance).

The PCA allowed distinguishing dry and rainy periods of the Cachoeira River. Samples collected in the rainy season were positively correlated with both

**Table 3.** Abiotic parameters in the collection sites in the Cachoeira River - mean ± standard deviation. (Different letters mean significant difference at p < 0.05 level).

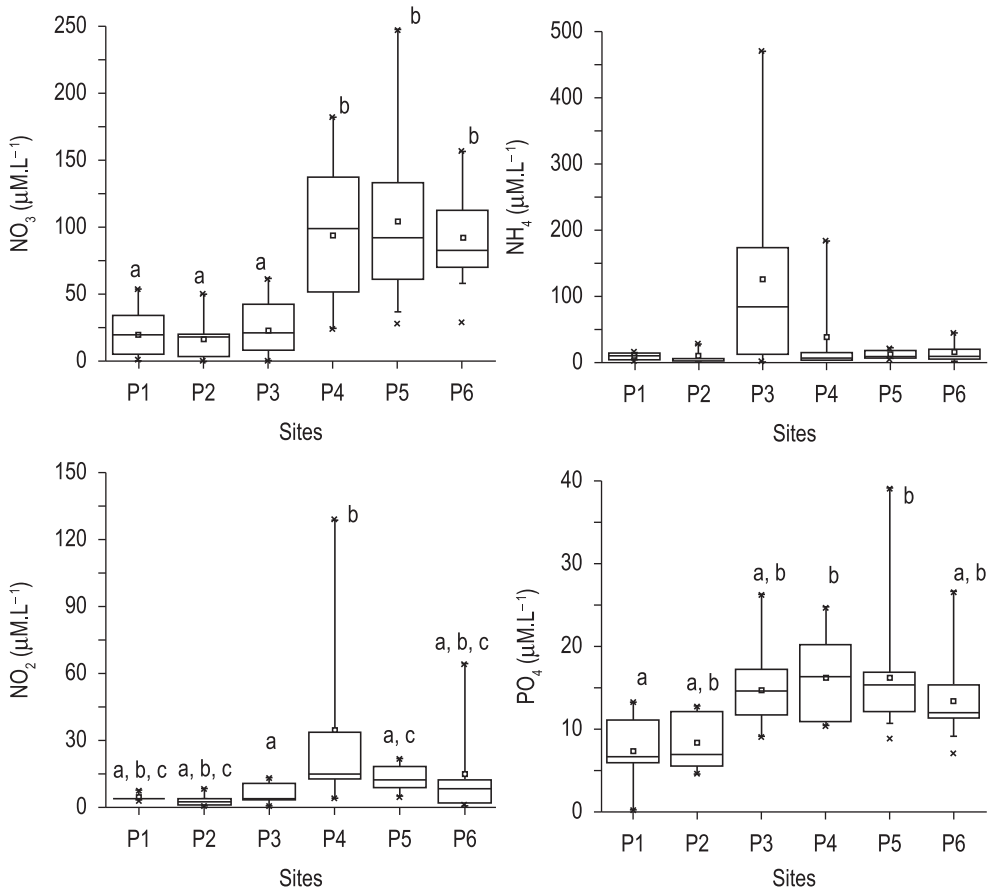| | Conductivity (µS.cm⁻¹) | Temperature (°C) | pH | OD (mg.L⁻¹) | OD (%) |
|---|---|---|---|---|---|
| P1 | 457 ± 103[a] | 28.1 ± 1.9 | 7.22 ± 0.80[a] | 7.7 ± 1.3[a] | 97.8 ± 16.7[a] |
| P2 | 463 ± 101[a] | 27.8 ± 2.0 | 6.98 ± 0.76[a,b] | 6.8 ± 1.5[a] | 86.6 ± 20[a] |
| P3 | 501 ± 148[a] | 27.3 ± 1.9 | 6.66 ± 0.34[a,b] | 4.1 ± 2.3[b] | 51.5 ± 29.7[b] |
| P4 | 483 ± 109[a] | 26.9 ± 1.7 | 6.52 ± 0.38[a,b] | 4.8 ± 1.4[b] | 60.2 ± 20.8[b] |
| P5 | 442 ± 108[a] | 27.4 ± 1.6 | 6.45 ± 0.54[b] | 6.2 ± 1.6[a,b] | 75.0 ± 18.8[a,b] |
| P6 | 759 ± 1247[b] | 27.5 ± 1.3 | 6.79 ± 0.46[a,b] | 6.8 ± 1.3[a,b] | 85.9 ± 17.4[a,b] |

**Figure 4.** Median ± Standard Deviation of the concentration of inorganic nutrients (N and P) over the sites in Cachoeira River. Concentration in μM.L$^{-1}$. (Different letters mean significant differences at p < 0.05 level).

axes whereas samples collected in the dry season were negatively correlated with both axes (Figure 8).

## 4. Discussion

Anthropic activities and land use changes appear to be the major factors influencing the distribution of nutrients in the Cachoeira River; however, lithology seems to be the factor influencing the major ions. The higher $NH_4^+$ and $PO_4^{3-}$ concentrations in points 3 and 4 could be explained by the fact that point 3 is located in an urban center in which domestic sewage directly discharges into the river; in point 4, the contribution of upstream sewage as well as the influx of agricultural tributaries (pasture) should also be noted.

Agricultural practices can provide major changes in the composition of runoff waters: the use of fertilizers increases the amount of nitrates, phosphates and therefore, contributes to the eutrophication of water systems (Todeschini, 2005). In the Cachoeira River, the highest concentrations

of ammonium and phosphate were found in point 3 followed by points 4, 5 and 6.

Higher $PO_4^-$ concentrations have been reported in several studies conducted on the watershed of the Cachoeira River (Pinho, 2001; Klumpp et al., 2002; Lima, 2006). The presence of this ion is associated with organic waste dumping; therefore, it is expected that there is a greater $PO_4^{3-}$ concentrationas a consequence of industrial and domestic effluents.

The same pattern was observed for the nitrogen compounds; $NH_4^+$ was the predominant form in point 3, while $NO_3^-$ was the main form in points 4, 5 and 6. It is possible that the increase of dissolved oxygen from point 4 has facilitated the nitrification processes by increasing the availability of $NO_3$- in the most downstream points of the river.

Compared to other studies, the $NO_2^-$ and $NO_3^-$ found in the Cachoeira River were higher than those found in the Ditinho River- SC (5.4 and 0.1 μM L$^{-1}$) (Dorigon et al., 2008) and the Piracicaba River - SP (Salomão, 2004) with concentrations of 10 and 50 μM L$^{-1}$, respectively.
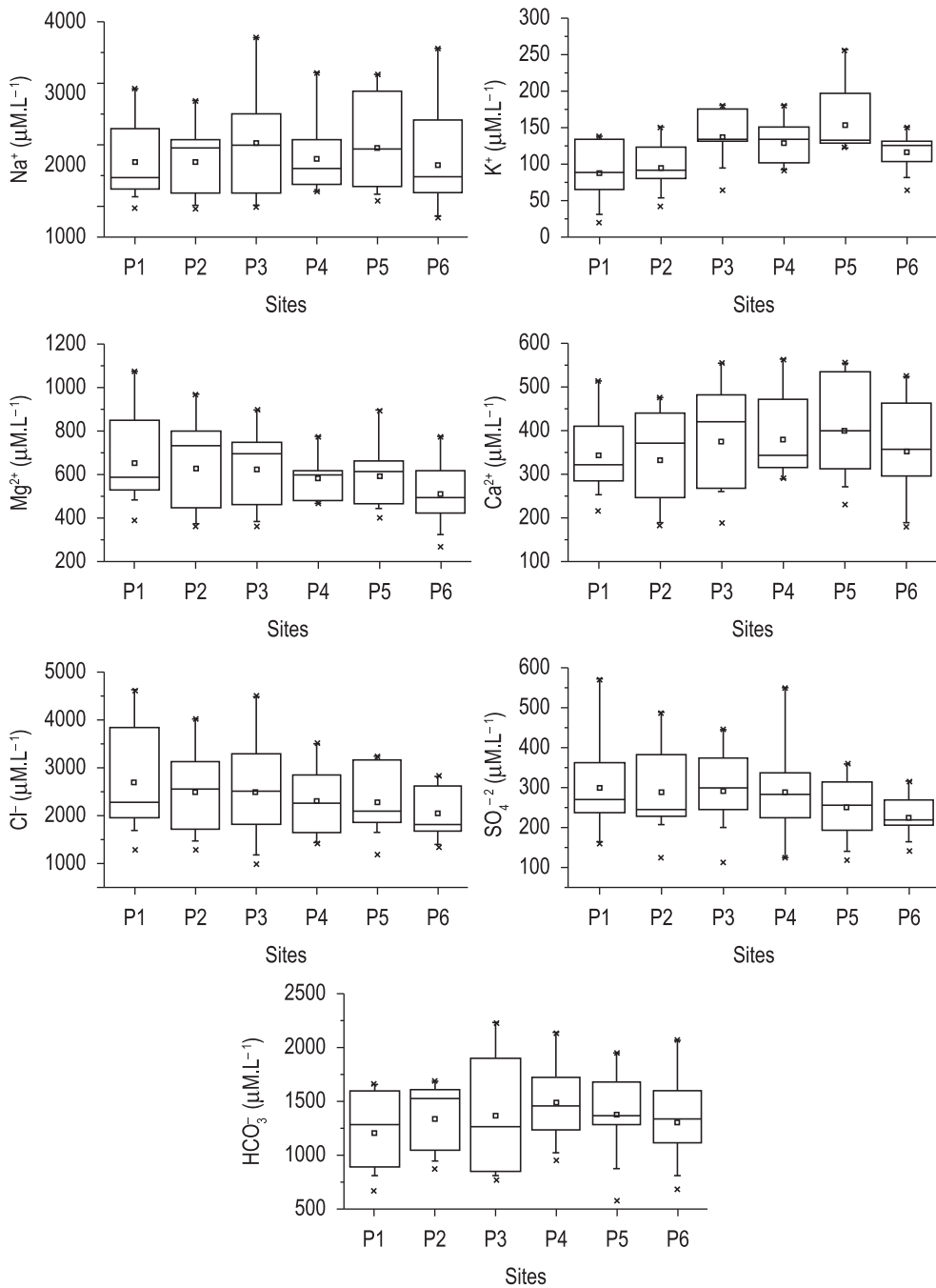
**Figure 5.** Median ± Standard Deviation of the concentration major ions in Cachoeira River. Concentration in $\mu M.L^{-1}$.

However, the $NH_4^+$ concentration showed lower values compared to these studies due to these watersheds present the effects of agricultural activities and the influence of urban centers.

Although the nutrient concentration varies according to land use changes, major ions vary according to the geological formation. A decline in $Cl^-$, $SO_4^{-2}$ and $Mg^{+2}$ concentrations was observed along the river. The main rock chemistry domains provide an overview of the chemical

weathering in the drainage basin, ranging from the parent rock weathering to different combinations of cations and anions dissolved in the solution (Biggs et al., 2002). The highest values were found at point 1, which represents the nearest site of the Cachoeira River formation, in the confluence of Salgado and Colônia Rivers, and the lowest values were found at point 6. This is probably due to the geological formation of the Salgado River, which

has high concentrations of several ions, such as $Cl^-$, $Mg^{+2}$, $Na^+$, $K^+$ and $Ca^{+2}$ (Santos, 2005).

Williams et al. (2001) and Martinelli et al. (2005) have found $Cl^-$, $SO_4^{-2}$, $Mg^{+2}$, $Na^+$ and $Ca^{+2}$ concentrations similar to those found in this work in the Piracicaba River watershed, which is characterized by a highly dense population, large pasture areas, sugar cane farms, and industries. Similar trends were found by Ometto et al. (2000), in a tributary of the Piracicaba River (Pisca River),

which is located in a polluted area; and by Souza and Tundisi (2003), in a river of the Tietê/Jacaré sub-basin (Jaú River), which presents discretesource pollution and small riparian vegetation (Table 4).

Potassium presented the lowest concentration at point 1, showing an increase travelling upstream to downstream with the highest concentration found in point 5. The increase along the river is probably due to growing deforestation for crops and pasture, as this ion is a major constituent of mineral
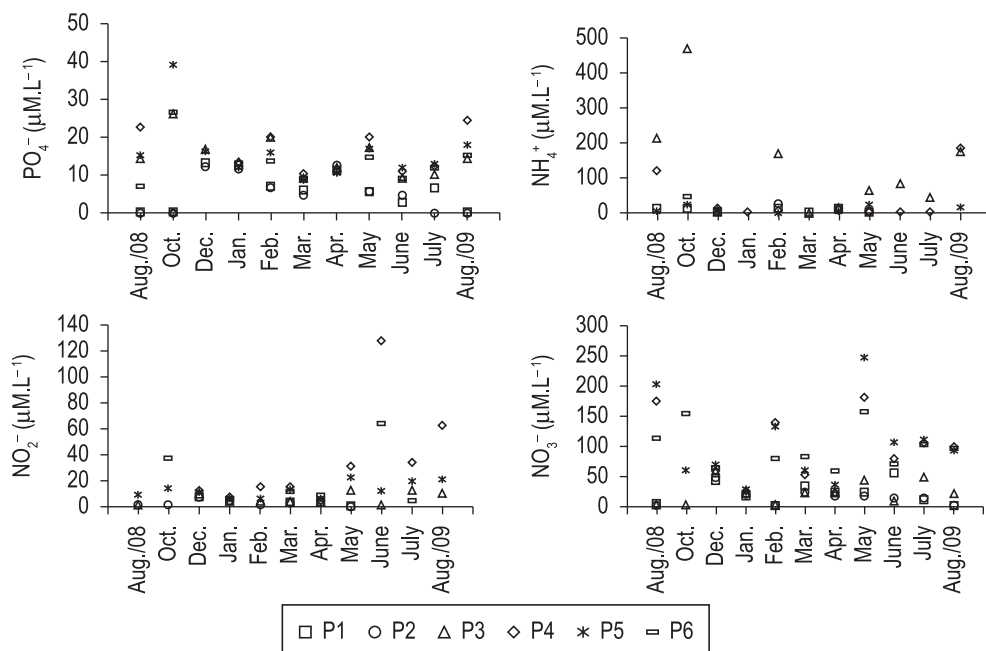


**Figure 6.** Temporal variation of phosphorus ($PO_4^-$), ammonium ($NH_4^+$), nitrite ($NO_2^-$) and nitrate ($NO_3^-$) in Cachoeira River. Concentration in $\mu M.L^{-1}$.

**Table 4.** Comparison of the concentrations of major ions found in this study with other studies conducted in lotic environments. Values in $\mu M.L^{-1}$. Area in $km^2$.

| | Land use | Area of the basin | Population | Cl | SO_4 | Mg^{+2} | Na^+ | Ca^{2+} | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Salgado River (BA) | Pastures | 1020 | 4600 | 9938.0 | 71.5 | 1865.3 | 5136.9 | 2173.3 | Santos (2005) |
| Piracicaba River (SP) | Sugar cane culture and pastures | 12600 | 3400000 | 197.5 | 289.5 | 218.1 | 466.0 | 267.0 | Williams et al. (2001) |
| Piracicaba River (SP) | Sugar cane culture and pastures | 12600 | 3400000 | 627.0 | 349.0 | 85.0 | 1354.0 | 231.0 | Martinelli et al.(2005) |
| Pisca River (SP) | Sugar cane culture and pastures | 130.0 | – | 143.7 | 191.8 | 305.0 | 766.2 | 398.1 | Ometto et al. (2000) |
| Jaú River (SP) | Sugar cane culture, pastures and ciliary vegetation | 745.0 | 173420 | – | – | 169.9 | 346.9 | 200.7 | Souza and Tundisi (2003) |
| Cachoeira River (BA) | Cocoa culture and pastures | 4600 | 4600 | 2361.3 | 268.4 | 588.4 | 1791.4 | 356.8 | This study |

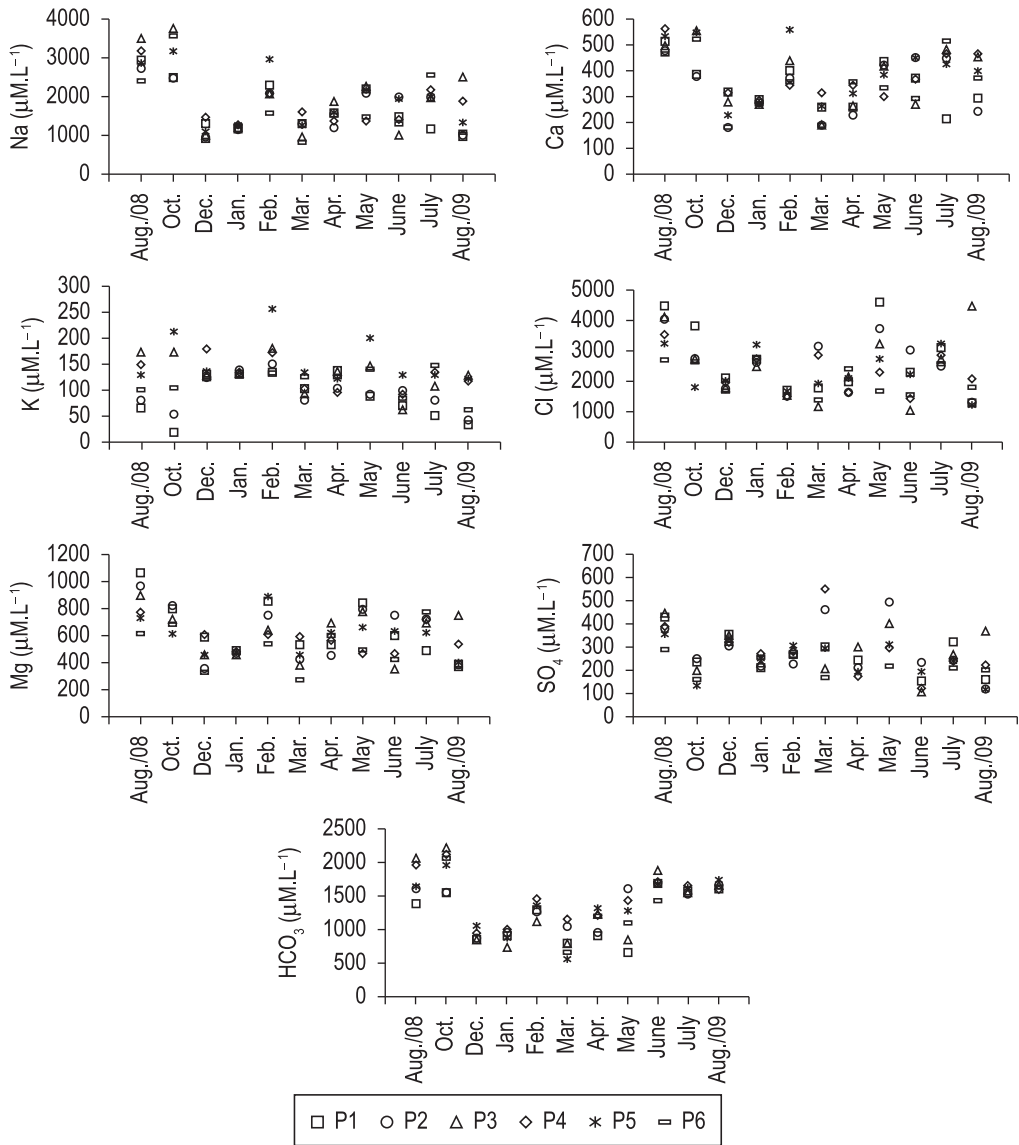**Figure 7.** Temporal variation of cations and anions in the Cachoeira River. Concentration in $\mu M.L^{-1}$.

fertilizers (Biggs et al., 2002). $K^+$ was at its highest concentration in February, at the end of the rainy season, while its lowest concentration was found in October, with the lowest monthly precipitation. Based on this information, it is possible to deduce that $K^+$ originates from the use of mineral fertilizers and its concentration in the water body is influenced by the amount of surface runoff.

The temporal variation showed differences between the dry and rainy season with the higher concentrations found in the driest months. August and October/08 presented the higher $NH_4^+$ and $PO_4^-$ concentrations, which coincides with the months of lower precipitation. The same pattern was observed by Neill et al. (2001) in two watersheds located in Rondônia State, where the highest

concentrations in deforestation areas were observed during the dry season.

Similar to nutrient concentration, the highest values of $Mg^{+2}$, $Ca^{+2}$ e $Na^+$ were also found in the driest periods (August and October/2008). This pattern could be confirmed with PCA where a clear correlation was observed between samples collected in dry season and ions such as $Ca^{+2}$, $Na^+$, $HCO_3^-$ and $Mg^{+2}$ that were positively correlated with axis 2 as soon as P1 and P2 (Figure 8).

In a study of the Salgado River, Santos (2005) also found the highest $Na^+$, $Ca^{+2}$ and $Mg^{+2}$ concentrations at the end of the rainy season. During the lowest rainfall period in the study developed by Martinelli et al. (1999b) on the
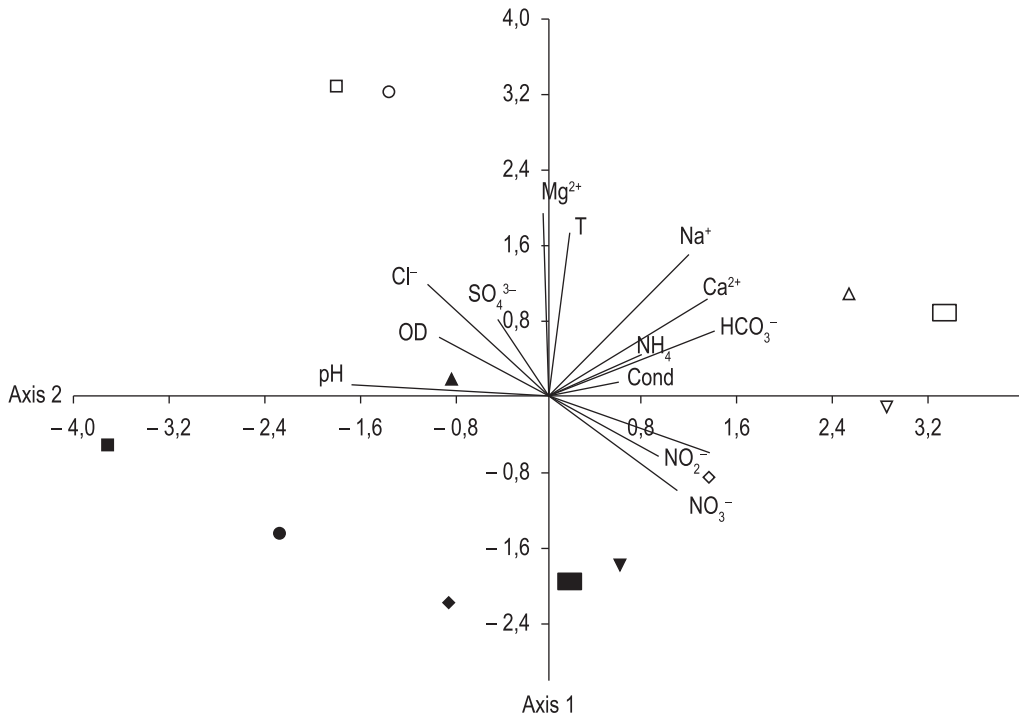
**Figure 8.** Spatio-temporal order by Principal Component Analysis (PCA). Axis 1 (34,36%), Axis 2 (24,97%). Symbols season. P1 (□), P2 (○) P3 (△), P4 (▽), P5 (▭), P6 (◇). Open symbols (dry periods), closed symbols (rainy periods).

Piracicaba River, the highest values of these ions were also found.

Salomão (2004) has observed a correlation between flow and ion concentration; during the lower flow periods, $Na^+$ and $Ca^{+2}$ concentrations were the highest in all the basins studied. The same trend was observed in the Cachoeira River, in which higher concentrations were observed in low flow periods. Likewise Smith (1999) has found the highest $Na^+$ concentrations at the lower portion of the Paraiba do Sul River, in the low-flow period; still, such temporal variation is related to the temporal dilution of base flow and anthropogenic sources. The dilution caused by the increased influence of surface and subsurface runoff during the flood period can dilute the anthropogenic sources (sewage).

The effective contribution of $Ca^{+2}$ in surface waters is explained by the geological predominance and climate. Likewise, $Mg^{+2}$, $Ca^{+2}$ are very sensitive to leaching; drainage water is, therefore, the main contributor to the influxof such elements to waterways in rainy periods (Boyer et al., 2002).

Besides the contribution of lithology and soil, aquatic environments also receive contributions from vegetation, climate, living organisms and human activities. Among the latter contributions, we highlight: domestic, industrial and agricultural

sewage (Todeschini, 2005). This fact can be observed in this study, since the Cachoeira River directly undergoes the effects of the release of untreated sewage and water originating from surface runoff increasing the nitrogen and phosphorus concentration.

## 5. Conclusion

The environmental degradation resulting from the replacement of native vegetation by agricultural crops - mainly cocoa monoculture - and thereafter transformed into livestock areas has provoked deterioration of the water resources of the Cachoeira River. This damage caused to the drainage basin was worsenedby deforestation (lack of riparian vegetation) and the inadequate use of soil, which causes increased runoff, the contribution of untreated effluents from cities, and agricultural and industrial activities. This condition is enhanced by the low river discharge in the dry months. Variations in ion concentrations were directly related to drought and rainy periods, the geological formation, and the various land uses.The lack of treatment of such residues and their incorrect disposal has significantly contributed to the aggravation of environmental problems and the health of the population.The proper handling of surface waters

in this area requires that effluents be collected and treated before being discharged into water bodies.

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