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Hydrogeochemical Research of Surface Water of the Córrego Sujo Watershed, Teresópolis, RJ, Brazil

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Abstract

The surface water quality was investigated in the Córrego Sujo watershed, located in the municipality of Teresópolis, a mountainous region in the state of Rio de Janeiro, Brazil. The emphasis focused on inorganic parameters of water, since there are applications of pesticides in agricultural cultivations. The natural and anthropogenic contributions of the study area were monitored monthly in eight sites in the river channels of the drainage basin. The results were analyzed using an ICP-OES spectrophotometer and subsequently compared to Conama Resolution 357/05. In order to support the interpretation of the results of water quality, flow and precipitation data were measured in the watershed, along with the land use and vegetation cover map produced from a GeoEye satellite image. The study revealed that the surface waters were in high concentrations and above those recommended by Conama Resolution. It was noted also that the lithological and pedological variables influenced the results of water quality. Regarding seasonality, it has not been possible to establish a common standard to all elements in the rainy season or dry season, however, in the analysis of each parameter separately, there was evidence of a concentration distribution in temporal variation. Therefore, the results of this study indicate that it is also necessary to highlight these issues in the territorial planning of the municipality and in the management of the Committee of Rio Piabanha watershed, to avoid the increasing of uncontrolled expansion of irrigated crops and intensive use of agrochemical inputs.

Keywords

Hydrogeochemistry, Natural and Anthropogenic Influences, Land Use, Surface Waters Rivers

1. Introduction

The environmental issue is taking a new direction, due to the impacts that exist on a planetary level, this issue being progressively highlighted in socioeconomic discussions. Water, in turn, being am important substantial natural resource is increasingly incorporated in these discussions, making it a focus for new environmental movements and international environmental policies.

As a result of water quality changes and its scarcity, the degradation of this resource has a significant impact and already is preventing the development of some regions and productive activities. Hence, it is fundamental that periodic investigations of water are established. An effective program of monitoring would assess water quality and analyse the actual status of water bodies [1].

A monitoring plan forms part of a management system. The implementation of this plan and associated data collection is essential to complement other water management information, particularly to make new investments possible in water resource projects [2].

Corroborating with Rebouças [1] the planning and management of water resources is essential to obtaining basic and reliable information. Included in this study is data related to vegetation cover, soil, hydraulic works, amongst others.

It is known that the quality of the water is also subject to the chemical and chemical-physical variations, in addition to other factors such as local geology, climatic fluctuations and flow. Fritzsons *et al.* [3] points out that the research of changes in flow is also an essential factor for study, since this parameter allows for understanding the behaviour of a given water body through seasonal variations and their influences on patterns of concentration of pollutants.

Another important factor for the change in water quality is land use. In agricultural areas, the use of pesticides is common. Runoff from these areas into water courses generates significant sources of pollution and by nature of the varying landforms and runoff patterns, are complex to identify, measure and control.

These contaminants are transported and adsorbed to clay particles, resulting from erosion, increasing the sediment concentration. Thus, arriving at the water flows, these contaminants can cause many implications for human health and ecosystem dysfunction.

The issue of classification of freshwaters should also be observed. Because it is a feature that lends itself to multiple uses, the water will provide differentiated levels of quality. For this reason, the Federal Resolution 357/2005 [4] (which provides for the classification of water bodies and environmental guidelines for its framework, as well as establishes the conditions and standards for effluent discharge) established by the National Environment Council (CONAMA), outlines the different classes for this resource, grouping it into sweet, salt and brackish. Moreover, this resolution established for each class, the standards with maximum permissible values for each parameter, which can be found in the water.

The State of Rio de Janeiro still does not have a specific legislation that classifies the bodies of water, therefore, uses the CONAMA Resolution 20/86 [5], which states that the frameworks of certain water flows have not yet been made, it is necessary to consider them as fresh waters of class II.

Thus, the objective of this research is to determine the concentrations of the following chemical parameters: Al, Ca, Mg, Mn, Fe, and K in the surface water channels of Córrego Sujo (Teresópolis, RJ) watershed, subsequently comparing the results obtained with the maximum values established by CONAMA Resolution 357/2005 for surface fresh water class II. The ionic charges of the parameters are not shown, because the determinations of ICP-OES do not allow definition of the valence of the original element.

This study was carried out in the Córrego Sujo catchment, located in the district of Venda Nova—Teresópolis—RJ, where agriculture is the main economic activity and encompasses an area of 53.5 square miles on (according to **Figure 1**); with coordinates 22˚15' - 22˚10'S latitude and 42˚55' - 42˚45'W longitude (UTM: 0720000/7534000 and 0720000/7546000).

The Córrego Sujo is a direct tributary of the Rio Preto channel, this in turn drains into the river Piabanha, and later into the Paraíba do Sul river.

As shown in the 1961-1990 Climatological Normal from Brazil developed by the National Institute of Meteorology (INMET) [6], the climate of the city of Teresopolis has an annual average temperature of 17.7˚C, presenting well-defined characteristics, with a warmer and rainy period and another period followed by drought and lower temperatures (**Figure 2**).

Geologically, the basin sits in Sierra Unit of the Organs, the following composition: hornblende-biotite granitoid coarse-grained and composition from tonalite to granite expanded calcium-alkaline.

According to Barreto [7], classes of predominant soils in the drainage basin

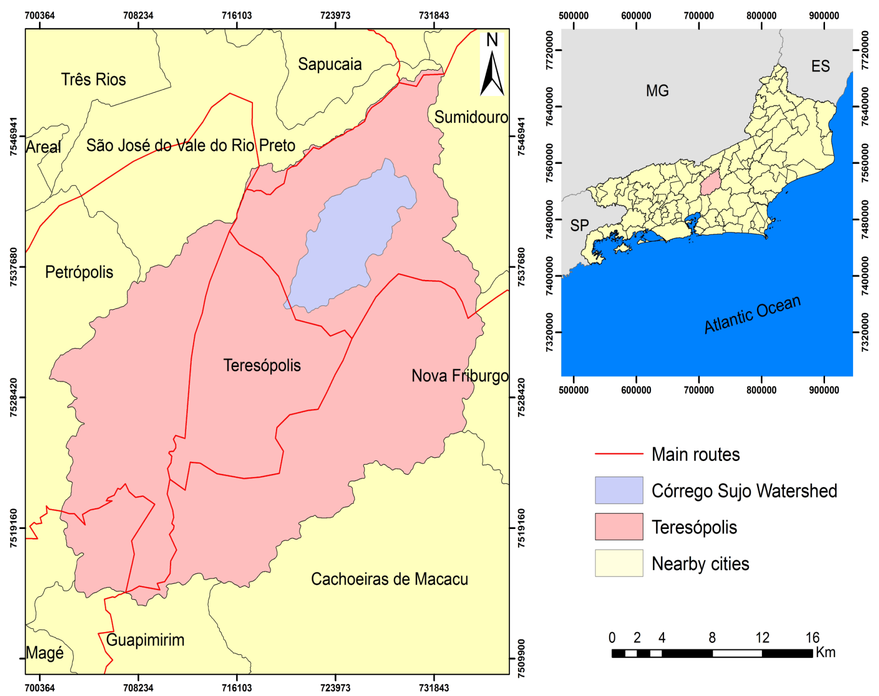

Figure 1. Location map of Teresópolis city.

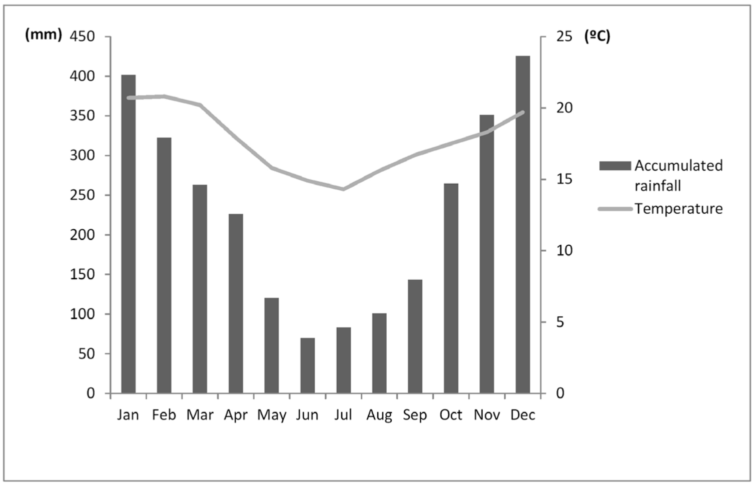

Figure 2. Accumulated rainfalls and average temperature-compensated of Teresopolis (RJ), between the years 1961-1990 (Source: INMET 2009).

are Dystrophic Latosol (Oxisol), Dystrophic Cambisol Tb, Dystrophic Fluvic Neoso Tb, Argilluvic Orthic Chernosol and Dystrophic Ultisol. Vegetation is represented by Atlantic Forest remnants; secondary vegetation in different successional stages may also be found.

2. Materials and Methods

2.1. Monitoring of Water Quality

With the purpose to define the sampling stations of water, subsidy printed topographic maps were used at scales of 1:50,000. Along with these, we used the Ikonos digital image collected in 2001/2002, with 1m spatial resolution, and the map called "Land Use and Land Cover" prepared by Araujo [8]. In addition to cartographic data, other research sources also contributed to the definition of the seasons, as the studies by Oliveira [9] and Nunes [10], which used the same approach and were produced in the same watershed.

Based on the information obtained, it was possible to establish a sample network (**Figure 3**). The sample considers the stations that suffer direct influence of agricultural activities and other uses of land (P1—Estação Sorvete; P2—Ponte CPRM; P3—Ponte Selig; P5—Ponte Gilberto; P7—Tento; P8 ancho B), as well as collection points in the forest environment and spring; these aim to establish the indicator of natural water composition (P4—Floresta Selig e P6—Nascente Tento).

For defining the geographic coordinates and selected points, we used Garmin 60 CSx GPSMAP.

Analysis of water was performed at the Laboratory of Analytical Development (LADA)-Chemistry Institute/UFRJ, with Inductively coupled plasma optical emission spectrometry (ICP-OES), brand Thermo Scientific iCAP 6300 model.

The survey was conducted in a total of eight field visits covering the months of February, March, May, June, August, September, October and November 2012.

The sampling procedure initially started in the field with the collection of three 350 ml polyethylene water bottles. Subsequently, the collected water was

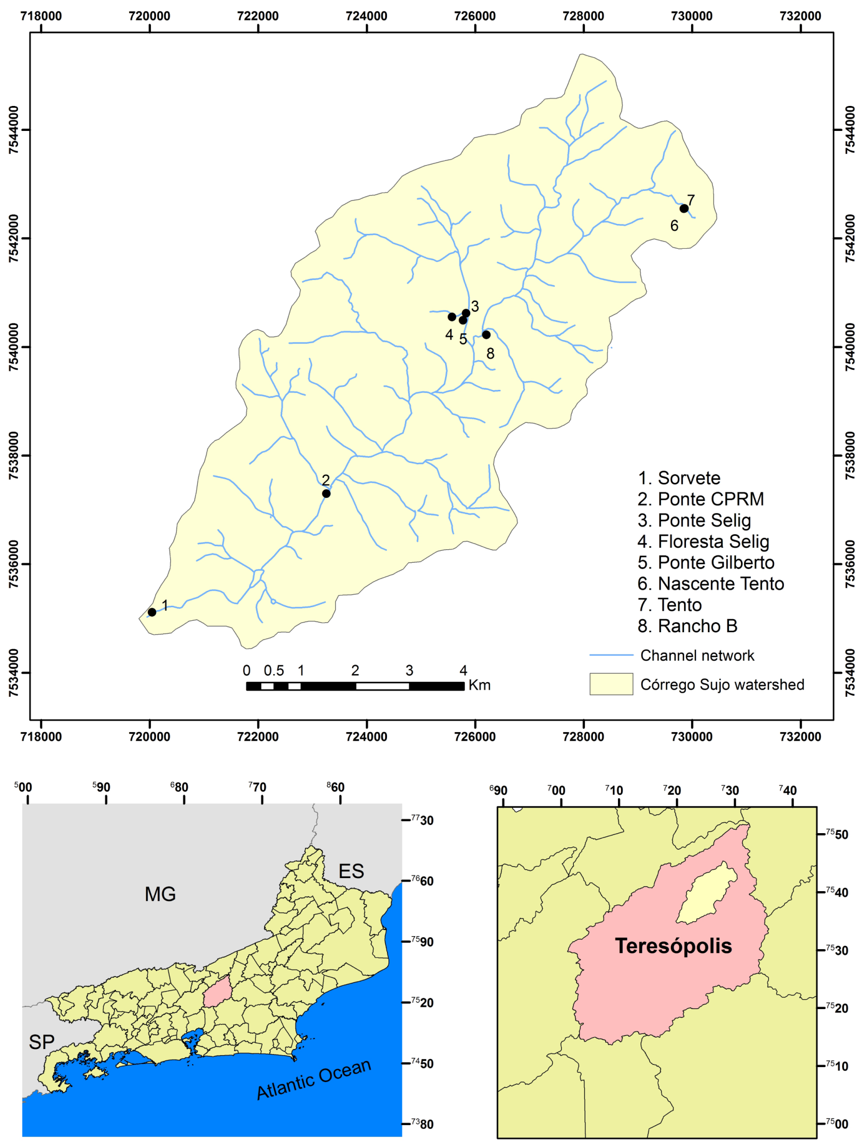

Figure 3. Map of the sampling points of water collects in the Córrego Sujo watershed. (Araujo, 2008)

acidified with concentrated nitric acid (HNO_3) until it reached the pH ≤ 2, in order to preserve the characteristics of the water. After this acidification, the samples were identified and wrapped in a thermal box with ice and transported to the laboratory, with aim of avoiding possible chemical reactions. In the laboratory, the samples were placed in the fridge and kept under refrigeration.

2.2. Mapping of Land Use and Vegetation Cover

The land use and vegetation cover map of the watershed was developed from satellite image Geoeye-coloured composition and panchromatic, obtained in March 2012, containing high spatial resolution: 0.41 m in Panchromatic (P & B) and 1.64 m in Multispectral (colour). The first stage consisted of fieldwork, in order to recognize the primordial features in the landscape, selecting 15 control points that favoured features for easy recognition in images, such as intersection of roads, bridges, swimming pools, amongst others. The collection of points was performed in Differential Global Positioning System—DGPS, a system that gives greater accuracy in the data collected from GPS receivers. These receivers have a differential correction from a base station and through these corrections in real time, can have errors eliminated within detail of 1 to 3 m [11].

Georeferencing of images was performed in the laboratory and subsequently the vectoring of different classes of land use and vegetation cover, through the visual classification in a scale of 1:20,000. For this work the following classes were catalogued: agriculture, bodies of water (dams), exposed soil, forest, forestry (eucalyptus), grass, rocky outcrop and underbrush. The network class of channels was extracted from the level curves (scale of 1:10,000) provided by the company Ampla and a reinterpretation of channel networks was carried out.

Due to the high amount of information to be analyzed, it is important to incorporate statistical tools with the ability to view the phenomenon globally, from a simplified analysis, to enable the interpretation of the complex and multi-dimentional results.

Multivariate Data Analysis works with a group of several variables of which interpretation of their results considers the correlation between them (if by chance there are any), to the detriment of individual characteristics of each one. As Reis [12], the Multivariate Analysis is based on a set of statistical methods contributing to the simultaneous examination of multiple measurements for each individual or object. According to Kendall [13], multivariate analysis includes different approaches, among them the simplified representation of the data structure, as well as the grouping of variables according to their similarities.

Among the methods of Multivariate Data Analysis is the Principal Component Analysis (PCA), which is widely used in studies in geosciences. Andriotti [14] points out that the PCA is a technique used to understand the relationship between elements of a database and to simplify interpretation when working with many interacting variables simultaneously in a phenomenon. Also according to this author, the PCA determines the major axes of a multidimensional setting, sorting the elements of a set as their similar classes-also known as clouds of elements, thus establishing the correlation between the variables in the study.

The method of principal components was therefore used to identify the correlation between variables, from the elaboration of a graph in the software Statistical Package for the Social Sciences (SPSS). Correlation between the sampling stations was made according to the average annual chemical parameters of the research, with selected variables including: potassium, magnesium, calcium, iron, aluminum and manganese.

3. Results and Discussion

3.1. Land Use and Vegetation Cover

The spatialisation of the land use and vegetation cover of the Córrego Sujo watershed showed that there is a predominance of agriculture, with their crops in the valley bottom, distributed along the fluvial channel (**Figure 4**). Due to the intense dynamics in land use, it is believed that this farming activity is directly interfering with the quality of surface waters, particularly due to the conventional land management practises causing soil erosion. These practises are accelerating the pollution of waters by contributing to contaminated particles being transported into waterways. **Figure 5** shows the distribution by percentage of land use in the basin and the vegetation cover.

Of note, Brum [15] also measured the areas of soil and vegetation from the map produced in the Ikonos satellite image (2001/2002) and he found a predominant grass cover of 40%, whilst this research found only 24% coverage (**Figure 5**). Although the areas are based on images and different resolutions, Brum [15] believed that the value found in their studies were incongruous when compared with the predominant activities in the region.

Also of note is the significant growth in forestry (eucalyptus) in the basin of 16.40%, in contrast to only 1.02% in 2001 [15]. Interestingly, the growth in eucalyptus coincided with a decline in agricultural development from 5.88% to 5.54% and a reduction in remaining forests by 4.62%. Therefore it is determined that this increase in eucalyptus forestry is specifically as a result of increased economic profitability of eucalyptus products.

Further to this, the few areas of exposed soil indicate that the soil is being

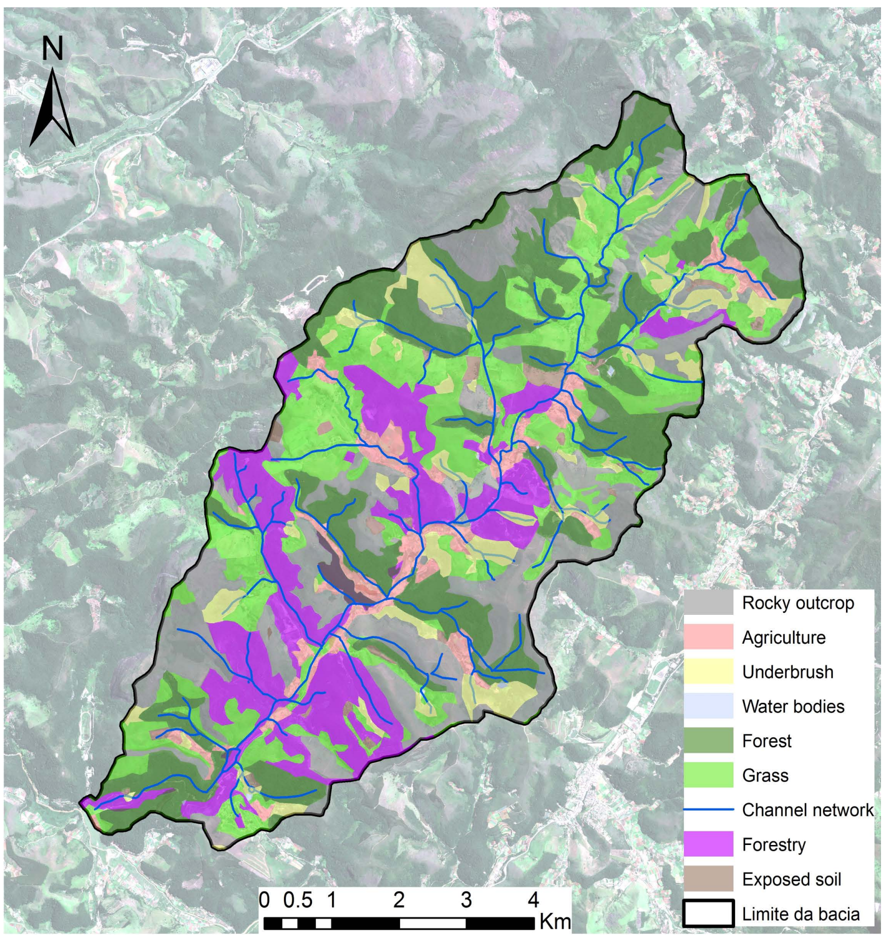

Figure 4. Land use and vegetation cover map of the Córrego Sujo watershed.

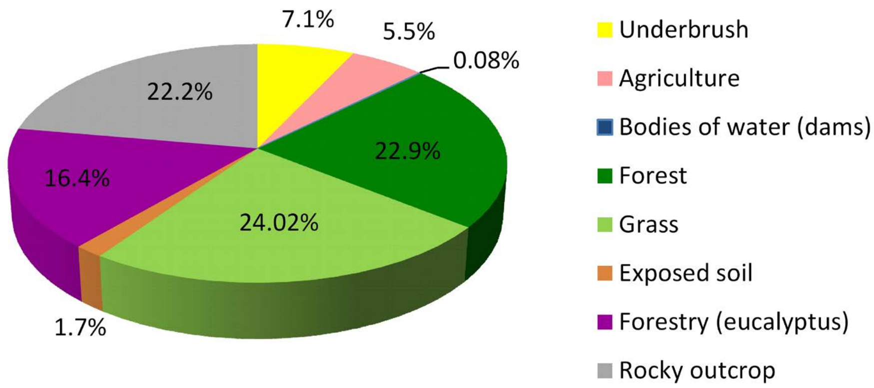

Figure 5. Percentage of land use and vegetation cover (2012).

prepared for planting a certain culture or cyclical associated with eucalyptus plantations.

3.2. Geochemical Analysis

Aluminium is one of the most abundant metals in the Earth's crust. In natural waters, small concentrations of Al ions occur due to contact with rocks, minerals and clays (Baird 2002) or through the soil, sediment and water compartments having been deposited or made available in watercourses. It should be noted that Al may also be released to the environment through chemical weathering and, together with the hydrological flows, there will be the mobility of ions and their subsequent transport [16].

In addition to the natural factors for the occurrence of Al, concentrations of the element also occur due to anthropogenic factors. To meet the high market requirements, conventional agricultural production demands excessive application of this element. Application enables improved soil fertility, its character of acid pH and thus productivity.

Throughout the sample period were found high concentrations of Al in the basin. Data showed a progressive increase from upstream to downstream, with the exception of the sample point that is embedded within a forest area (Floresta Selig), according to the specifications of CONAMA. It is important to emphasize that the quality of spring water for three months was in non-compliance with the legislation and showing high values. A pattern of exceedance can also be observed in two other points (Estação Sorvete e CPRM) further downstream in the drainage basin, as shown in **Figure 6**.

In natural waters, the aluminum concentration can vary greatly depending on physicalchemical and mineralogical properties. Al concentrations dissolved in water, with an approximately neutral pH, vary in the range of 0.001 to 0.005 mg/L. In already acidic water or water rich organic matter, these values can reach as high as 0.5 - 1 mg/L (Fawell 2010). The basin of Córrego Sujo is an example of the second case; that is, it shows an acid character and in some sampling stations showed a concentration greater than the limit established by Fawell [16] and significantly higher than the CONAMA 357/2005 (0.1 mg/L). Levels included: Estação CPRM (1.7 mg/L) and Ponte Gilberto (1.86 mg/L).

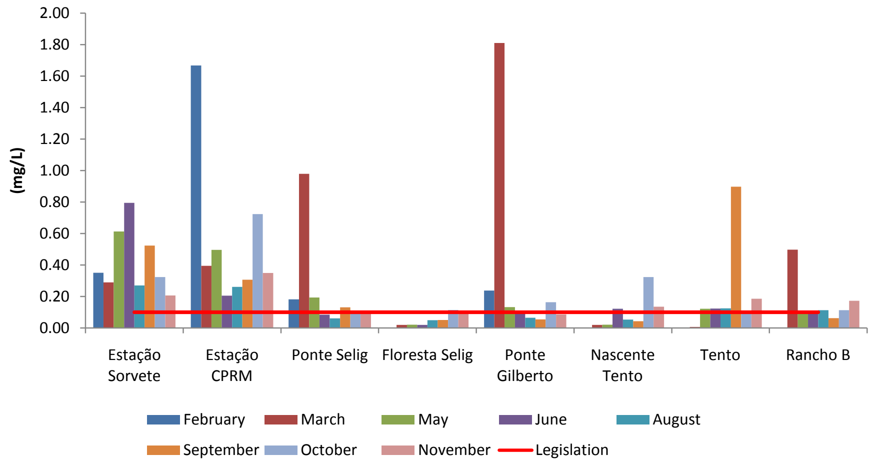

Figure 6. Aluminum results in the Córrego Sujo Watershed.

In the case of the study, we may assign the high concentration of aluminum in the water to both the natural conditions and the associated anthropogenic factors. The Oxisols soil naturally contains high levels of aluminium. Additionally, the traditional agricultural management made in this already weathered soil, enhances the process of disintegration of the particles.

Along with this factor, the predominant mineral composition in the drainage basin is hornblende-biotite (which contains high concentrations of Al). This rock is prone to physical and chemical weathering and the subsequent release of particles via surface water runoff.

In this research, it was found that with increasing precipitation and therefore the river flow, there was an increase in aluminum content in the water of verified sampling points (Estação Sorvete, Estação CPRM and Ponte Gilberto) due to soil leaching [17].

With respect to Calcium (Ca) and Magnesium (Mg), Brandão *et al.* [18] emphasize that the acidity of the soil decreases the provision of nutrients such Ca^{+2}, Mg^{+2} and K^{+}, in turn increasing the solubility of toxic cations such as Al^{+3}. For plant growth, the deficiency of Ca and the toxicity of Al are the main chemical limitations. Therefore, to ensure increased productivity in crop development, farmers make use of agrochemicals in excess to counter the acidic, nutrient deficient basin soil, rich in Al and low Ca and Mg content.

Considering that the CONAMA resolution does not set limits for Ca and Mg, for comparison purposes we only took the studies conducted by Pires [19]; these investigated the quality of Penitentes channel of water located in the Parque dos Três Picos (Rio de Janeiro State). The author found the following averages: Ca: 0.42 mg/L in summer and 0.29 mg/L in winter, and Mg: 0.65 mg/L in summer and 0.76 mg/L in winter.

In relation to the responses of Córrego Sujo, it is noted that the average of Ca (Table 1) are higher than those of Pires [19], however, showed Mg behavior closer than the author's values (Table 1).

In areas where agriculture is developed, soil components such as clay and organic matter are affected by the environmental contaminants [20]. In other words, the clays perform the cation exchange capacity between various hydrated silicates, and the oxides make them adsorb cations that are in contact, including the metal ions. Thus, from the soil-water interaction, the clay particles will reach the water surface with high levels of these compounds. This is reflected in the results of water quality and justifies the excessive presence of Ca in the water.

In this research, calcium and magnesium demonstrated the same behavior in the concentration of ions, with respect to spatial and temporal variation. Both parameters exhibited higher concentrations in the dry season, while the channel remained at base level. The result of these parameters is contrary to that observed with Al, with a decrease of calcium and magnesium ions seen as flow rate increased.

The other element key to the investigation of environmental quality of bays of water, sediments and soils is iron (Fe). In a previous study carried out in the same basin by Oliveira [9], Fe values were found with greater levels than in this review, leading the author to classify the waters of the dirty stream as Class III.

As with the results obtained for Al, Fe proved to register in high concentrations at all stations, except for the forest and Nascente Tento (with only a single sampling over the limit). Results showed exceedances above the maximum legal limit (0.3 mg/L).

The occurrence of the parameter Fe in water is due to the same reasons as the Al-soil and mineralogical composition that are transported to surface waters via clay particles. Additionally, in sampling locations where agricultural fertilizers were in use in surrounding areas, an excessive concentration of Fe was also identified in the water.

For Manganese (Mn), the occurrence of this metal in forest areas is generally associated with certain rock types that contain this element in their composition. From previous studies, it is accepted that the level of ion concentrations in surface waters is generally below 100 μg/l or 1.0 mg/L [21], [22]. In this study, minimum values of <0.01 mg/L (**Figure 6**) were detected, particularly at the

Table 1. Descriptive statistics results for calcium and magnesium.

Ca (mg/L)	P1 (E. Sorvete)	P2 (E.CPRM)	P3 (Ponte Selig)	P4 (Floresta Selig)	P5 (Ponte Gilberto)	P6 (N. Tento)	P7 (C. Tento)	P8 (Rancho B)
Maximum	3.01	3.05	2.94	0.82	2.48	2.66	3.62	2.45
Minimum	1.42	1.34	0.99	0.14	0.99	1.12	1.42	1.10
Average	2.51	2.53	2.13	0.33	2.09	2.24	2.88	2.04
Standard deviation	0.53	0.60	0.55	0.23	0.49	0.54	0.74	0.47
Mg (mg/L)	**P1 (E. Sorvete)**	**P2 (E.CPRM)**	**P3 (Ponte Selig)**	**P4 (Floresta Selig)**	**P5 (Ponte Gilberto)**	**P6 (N. Tento)**	**P7 (C. Tento)**	**P8 (Rancho B)**
Maximum	0.63	0.65	0.66	0.10	0.65	0.50	0.70	0.52
Minimum	0.35	0.34	0.31	0.04	0.32	0.26	0.30	0.27
Average	0.56	0.56	0.54	0.06	0.54	0.43	0.53	0.44
Standard deviation	0.35	0.11	0.10	0.02	0.10	0.08	0.13	0.08

Floresta Selig sampling point, whilst a maximum value of 0.64 mg/L was seen at the Tento station.

In investigations carried out in the soil of this season (where broccoli cultivation had occurred) by Barros [23] showed that the concentrations of Mn and Zn were higher in comparison to others in the region due to the use of fungicide Manzate. Thus, the higher values seen at Tento station could be attributed to the use of such fungicides.

It was also observed that the ions of this parameter were greater in concentration in the period of less precipitation; including even the month of October, despite this month being part of the traditional "rainy season". This observation can be seen more clearly in Ponte Gilberto and the Stations CPRM and Sorvete (**Figure 7**).

Main minerals that are composed of the element potassium (K) are potash feldspar, biotite and muscovite mica; each of these having low resistance to physical and chemical weathering [24]. As previously outlined, the watershed lithological composition is dominanted by biotite, thus contributing to the presence of K in surface waters. The limit value set by CONAMA this parameter is 0.1 mg/L, however, being available in abundance by the surrounding lithology, the results obtained in the evaluation of the water showed that K exceeds the law, even the background station (Floresta Selig).

Nitrogen plays a relevant role in the nutrient absorption of crops [25]. However, in the Córrego Sujo drainage basin agricultural practises include heavy use of additives, especially NPK (nitrogen, phosphorus and potassium), which is in exceedance of what is required for normal nutrient absorption. The areas of greatest agricultural concentration were at Estação CPRM, Estação Sorvete and Rancho B. These were found to have high incidence of K, with an average of 1.69 mg/L, 1.69 mg/L and 1.80 mg/L respectively; this confirms the dispersion of contaminants in soil and water as indicated by Oliveira [9] and the irrigation water as Nunes [10].

With regards to the behavior exhibited in the flow of the channels, from a space-time perspective, a higher concentration of K was found during the dry season (and less water volume in the river channel) in the three observed stations (**Figure 8**).

3.3. Statistical Results

Graphical representations of the sampling stations aimed to obtain the correlation between stations and ratify statistically those that are the most are related. Parameters considered are the influence of land use in the watershed and physical arrangements that influence the degradation of water channels.

To obtain the results, the first step consisted of performing the test of Kaiser-Meyer-Olkin (KMO) to check the fit of the data to the methodology adopted. The KMO has values between 0 and 1. Values close to 1 indicate that the method is suitable for the study. Negative values indicate that the correlation is not suitable. The result obtained was 0.686, which demonstrates the suitability for the study.

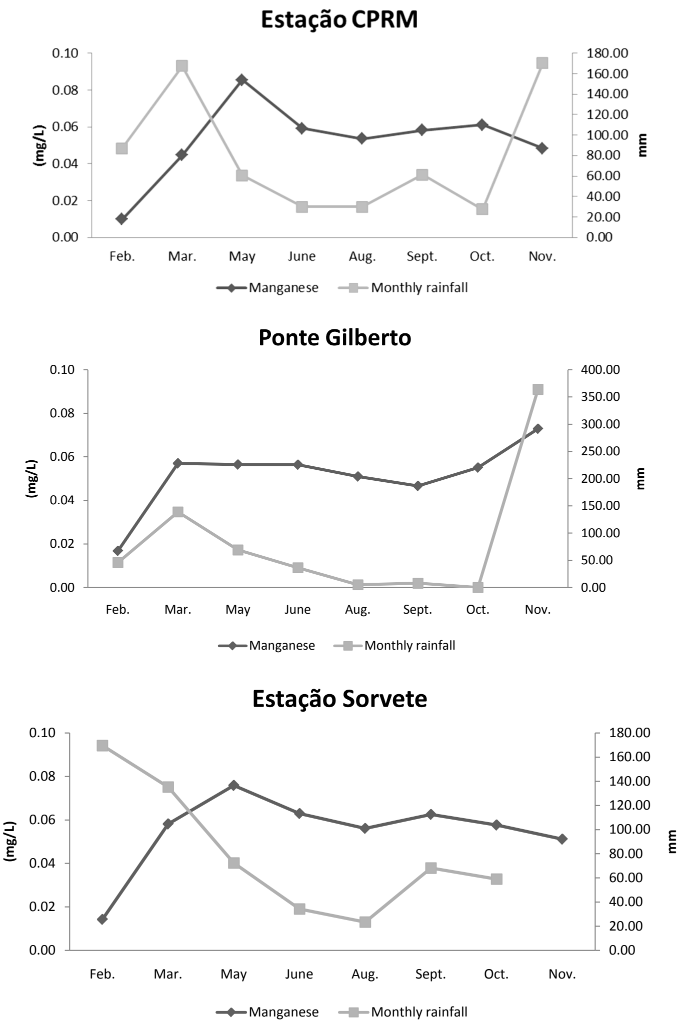

Figure 7. Variation of manganese concentration according to rainfall.

The correlation of results from the Estação Sorvete and Estação CPRM stations demonstrates alignment to some of the characteristics observed in the field and proven throughout the research; this includes land use (presence of olericulturas and silviculturas in both stations) and the large volume of domestic wastewater released in these water bodies (with higher concentrations of pollutants in the water).

Already the stations Rancho B, Ponte Selig, Ponte Gilberto and Canal do Tento are related due to the direct influence of agriculture. With regards to Floresta Selig and Canal do Tento, the correlation between them is significant in Figure 9, however what was observed in the results, especially the chemical composition, is that in fact the Floresta Selig may be a reference (background values), since the spring (Nascente Tento) did not demonstrate this behavior.

4. Conclusions

The seasonal monitoring and geochemical conditions of surface water contributed to the observation that the surface waters of the Córrego Sujo catchment

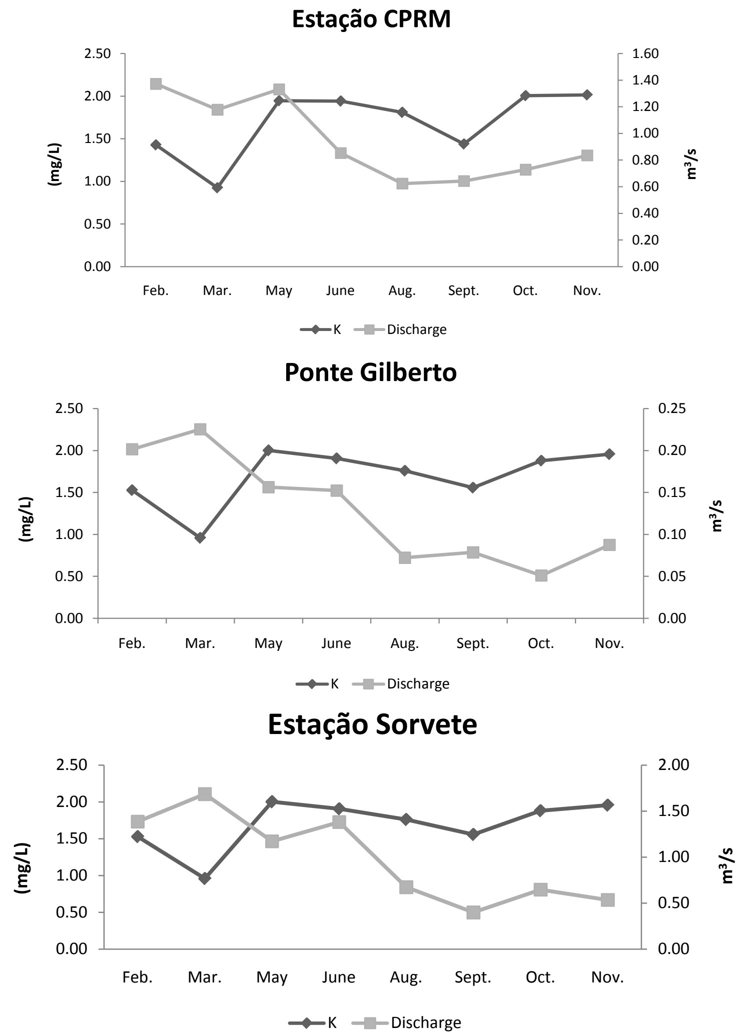

Figure 8. Variation of potassium concentration according to discharge.

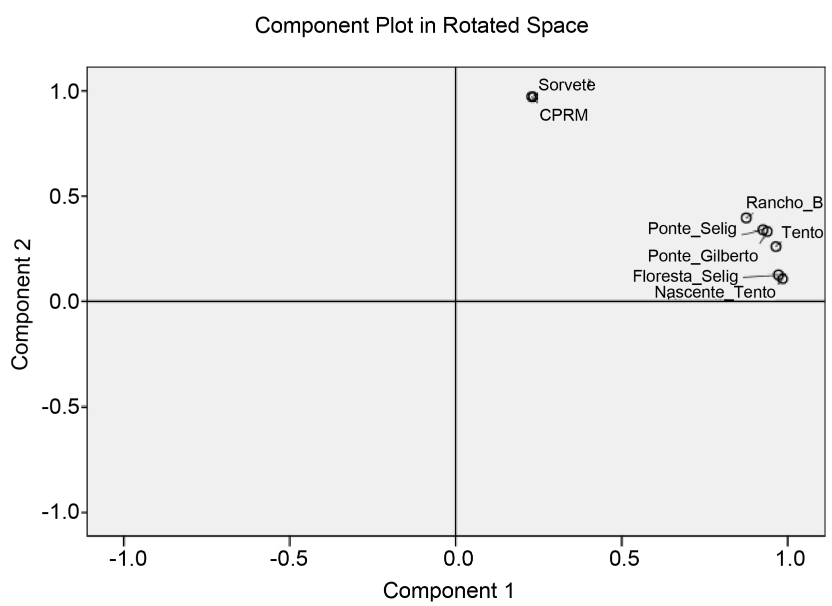

Figure 9. Correlation between the sampling stations for water quality (Source: SPSS).

have high concentrations for the analyzed parameters-Al, Ca, Mg, Fe and K. To find only one parameter in violation of the law, is enough to determine the water classification in the sample observed point.

Regarding seasonality (rainy vs dry season), a common pattern was not found between all the elements, however in the review of each parameter in isolation, a distribution of concentration on the temporal variation was evident. It was also noted that the water quality results are closely related to lithologic and soil variables, the hydrodynamics of the basin and the particular land use of the soil.

Another point was raised by the results at the Estação Sorvete and Estação CPRM stations, the farthest downstream points of the basin. These stations returned the lowest levels of quality, showing that the self-purification process in water is not efficient enough for dilution of pollutants. This fact is attributed to the longitudinal profile of the relief of the basin, which suffers no significant change.

The survey also shows that the spring, being an area of environmental fragility and a water producer, is exposed to the impacts of agriculture and is susceptible to degradation and may compromise the multiple uses of water. In that sense, it is identified that further research is needed in these drain bedside environments, including the diagnosis of biological parameters.

Following results of the numerous studies performed in the basin, it is clear that the concentrations of the pollutants have increased and that the physico-chemical and chemical elements are higher in concentration in relation to the assessments carried out in adjacent areas. The conclusion is that the anthropogenic activities are contributing to the main sources of water pollution and the deterioration in the quality of the water; namely agricultural activities, the suppression of forest vegetation and soil erosion.

Therefore, it is possible to frame the waters as Class III, according to CONAMA Resolution 357/2005, with the exception of first-order channel located in the "Selig Forest" location. Results show that in this basin, in general, the use of chemicals in agriculture has grown rapidly without control and without supervision of public bodies, generating incidence of diseases in the population by direct contact with these products. There are reports in the basin studied health problems related to pesticide use and direct human consumption of water from the canals and springs.

Therefore, the results of this study indicate the need for continuity of monitoring, research and effective environmental management in the Córrego Sujo watershed. Additionally, research into the quality of parameters and inorganic trace elements in soils and sediments is critical to understanding potential impacts on the watershed and the generation of potential management practises. It is also necessary enter these issues in territorial planning of the municipality.

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