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Evaluation of physicochemical water parameters in watersheds of southern Brazil

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ABSTRACT

Water-quality monitoring is one of the main instruments for water-resource management. This work therefore evaluated the water quality of the contribution basin of the Sinnott water treatment plant as well as the relationship between physicochemical water parameters, and analyzed the seasonal variation of water quality parameters as a function of rainfall. The study area encompassed the contribution basin of the Sinnott water treatment plant, formed mainly by the drainage areas of the Pelotas stream and its tributary, the Quilombo Stream, located in the city of Pelotas - Rio Grande do Sul, Brazil. A set of 118,368 data points for each stream was analyzed between 2007 and 2012. The following water quality parameters were evaluated: turbidity, temperature, color, pH, hardness, dissolved oxygen, organic matter, and alkalinity. Results showed that dissolved oxygen and water pH values conformed with Brazilian legislation in the 6 years evaluated. However, water color was the parameter that remained the greatest number of days above the set limits, mainly in the Pelotas Stream. Result indicates the need for conservation actions in the catchment, especially considering the importance of color for the assessment of water quality for public supply, in terms of both treatment costs and of public health. Highest values for water color, turbidity, and organic matter coincided with the occurrence of the highest rainfall values. Agricultural activities may potentiate sedimentation in the contribution basin of the Sinnott water treatment plant.

keywords: color, organic matter, turbidity.

Avaliação de parâmetros físico-químicos da água em bacia hidrográfica do sul do Brasil

RESUMO

O monitoramento da qualidade da água consiste num dos principais instrumentos para gestão de recursos hídricos. O presente trabalho teve como objetivos: (i) avaliar a qualidade da água na bacia de contribuição da estação de tratamento de água de Sinnott bem como a relação entre os parâmetros fisioquímicos da água; e (ii) analisar a variação sazonal dos parâmetros de qualidade da água em função das chuvas. A área de estudo abrangeu a bacia de contribuição da estação de tratamento de água de Sinnott, formada principalmente pelas áreas de drenagem do córrego Pelotas e seu afluente, o córrego Quilombo, localizado na cidade de Pelotas. Um conjunto de 118.368 pontos de dados foi analisado entre 2007 e 2012. Os seguintes parâmetros de qualidade da água foram avaliados foram: turbidez, temperatura, cor, pH, dureza, oxigênio dissolvido, matéria orgânica e alcalinidade. Os resultados mostraram que os valores de oxigênio dissolvido e pH da água estavam de acordo com a legislação brasileira nos 6 anos avaliados. Entretanto, a cor da água foi o parâmetro que permaneceu o maior número de dias acima dos limites estabelecidos, ocorrendo principalmente no córrego Pelotas. Esse resultado indica a necessidade de ações de conservação na bacia hidrográfica, principalmente considerando a importância da cor na avaliação da qualidade da água para abastecimento público, tanto em termos de custos de tratamento quanto de saúde pública. Os maiores valores de cor da água, turbidez e matéria orgânica coincidiram com a ocorrência dos maiores valores de precipitação. As atividades agrícolas podem potencializar a sedimentação na bacia de contribuição da estação de tratamento de água de Sinnott.

Palavras-chave: cor, matéria orgânica, turbidez.

1. INTRODUCTION

Water quality is one of the important issues in water-resource management (Sutadian *et al.*, 2016). Water quality can be classified into three broad categories: physical, chemical and biological, and each category has several parameters (Swamee and Tyagi, 2007). These parameters must be associated with the characteristics of local water uses and relating quality objectives.

Rainfall information is important in the analysis of water quality, as it directly influences the flow and quality of a body of water. Rainfall intensities establish different levels of impacts on the soil and erosive processes of varying degrees that directly influence the rate of runoff (Fraga *et al.*, 2012).

In agricultural systems where there is no adequate soil management, sediment runoff can be substantially altered in comparison to natural biomes (Alvarez *et al.*, 2014; Torres *et al.*, 2017). In Brazil, Taniwaki *et al.* (2017) observed higher concentrations of nitrate and suspended solids in the water quality of streams which drained sugarcane fields, mainly during the wet season. In China, Xiao *et al.* (2019) reported a presence of trace elements such as Cr, Pb, Cd, Cu, and Ag in rivers, mainly due to anthropogenic inputs. In contrast, when evaluating water bodies, Wang *et al.* (2017) described dominant pollutants such as Zn, Cd, and Pb, making the water unsuitable for drinking in that area.

In Southern Brazil, the contribution basin of the Sinnott water treatment plant assists water for human consumption for over 328,275 inhabitants in Pelotas city (IBGE, 2010). Although the Autonomous Service of Pelotas Water Supply (SANEP) evaluates the physicochemical water parameters for later treatment, so far few studies have evaluated these parameters over the years, as well as the relationship between them; and the relation of these parameters with rainfall and use of the areas around the slopes of the basin. From this perspective, the present work evaluated water quality in the contribution basin of the Sinnott water treatment plant and the relationship between physicochemical water parameters, and analyzed the seasonal variation of water quality parameters as a function of rainfall.

2. MATERIAL AND METHODS

2.1. Study area

The study area was the contribution basin of the Sinnott water treatment plant, which is located in the southeast of Rio Grande do Sul State, between the geodetic coordinates 31º30' a 34º35' S e 53º31' a 55º15' O. The basin is formed mainly by the drainage areas of the Pelotas Stream and its tributary, the Quilombo Stream (Figure 1). The main water uses of the contribution basin are irrigation, human consumption, and animal-related.

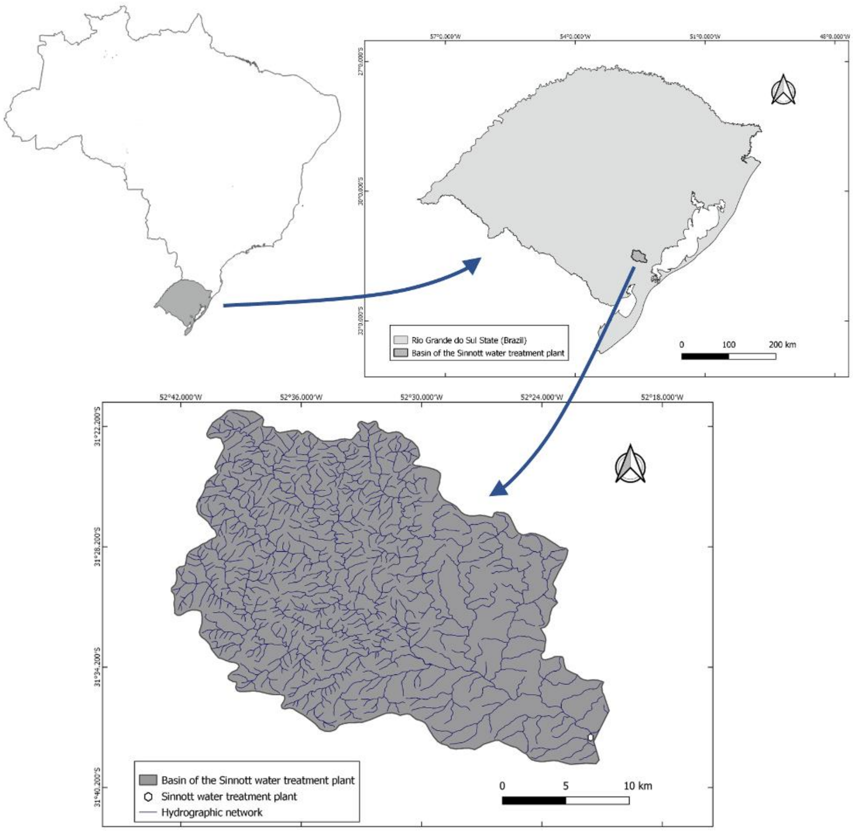

Figure 1. Basin of the Sinnott water treatment plant, located in Pelotas city, Rio Grande do Sul State, Southern Brazil.

According to the Köppen system, the climate of the region was classified as humid subtropical (Cfa), with an average annual temperature of 17°C and an average annual rainfall of 1,400 mm (Alvares *et al*., 2013). The main soil classes around the contribution basin were categorized as Ultisols, Inceptisols, Entisols, Alfisols, and Gleisols (Flores *et al*., 2009).

2.2. Sampling and analysis of water quality parameters

The data used in this study are the results of the water monitoring carried out by SANEP in the Pelotas and Quilombo Streams. SANEP provided data in handwritten spreadsheets with the following water quality parameters: turbidity, temperature, color, pH, hardness, dissolved oxygen, organic matter, and alkalinity. The data set relates the hourly evaluation of each parameter during the period 2007 to 2012.

Water samples were collected at two locations at the Sinnott water treatment plant entrance, between the coordinates of 31°39'31" S and 52°21'53" O. Sample analyses were carried out by SANEP, according to the Standard Methods for the Examination of Water and Wastewater (APHA *et al*., 1998).

The main water uses of the Sinnott contribution basin are animal drinking, irrigation, and, after conventional treatment, human consumption. Thus, the studied parameters must comply with CONAMA Resolution nº 357 of 03/17/2005, in its Article 42, which classifies freshwater bodies as those of the present study as Class 2. Physicochemical water parameters were compared to the Brazilian legislation for freshwaters, specifically to Class 2 (CONAMA, 2005), according to Table 1.

Table 1. Physicochemical water parameters suitable for freshwaters (Class 2) according to the Brazilian legislation (CONAMA Resolution N° 357, March 17, 2005).

Parameter	Unity	Class 2
Color	mg Pt L^{-1}	until 75
Turbidity	UNT	until 100
dissolved oxygen	mg L^{-1} de O_2	not less than 5.0
pH	-	from 6.0 to 9.0

Rainfall data were obtained at Ponte Cordeiro de Farias Pluviometric Station (31º34'26" S and 52º27'47" W), which is inserted into the watershed boundary of the Pelotas Stream, operated by the National Water Agency of Brazil (ANA) and the Brazilian Mineral Resources Research Company (CPRM). Monthly rainfall series were organized based on the historical series available in a database on the Hidroweb- Hydrological Information System homepage.

2.3. Statistical analyses

Descriptive analysis of all data sets was performed by classical statistics, determining the range of values, and calculating their mean. Principal components analysis (PCA) was used to group the water quality indicators, and to therefore explain the relation between them. Pearson correlation analysis was used to verify the relationship between water quality indicators and rainfall.

3. RESULTS AND DISCUSSION

The maximum and minimum values of water temperature followed the seasonal trend, corresponding to the summer and winter seasons, in both the Pelotas and Quilombo Streams between 2007 and 2012 (Table 2). According to Alvarenga *et al.* (2012), temperature varies according to the climatic regime, and superficial water resources show seasonal and diurnal variations, making water temperature the parameter most influenced by flow seasonality.

The highest mean turbidity values were observed in the Pelotas Stream (Table 2), possibly due to the larger area of its contribution basin.

Similar to turbidity, the highest water color values were also observed in the Pelotas Stream, with a mean ranging from 65 to 180 mg Pt L^{-1} between 2007 and 2012. In the Quilombo Stream, the annual average observed was between 53 and 132 mg Pt L^{-1} (Table 2). The higher color values are due possibly to the organic residues of plants deposited in the stream, which promote organic matter degradation by bacteria and by forming humic and fulvic acid. Additionally, the erosive processes of agricultural areas located around the stream promote the transport of sediment, also leading to alterations in the color of the water (Oliveira *et al*., 2010).

Table 2. Minimum (Min), maximum (Max) and mean values of the water quality parameters in Pelotas and Quilombo Streams between 2007 and 2012.

Parâmetros	Min	Max	Mean	Min	Máx	Média	Min	Máx	Média
		2007			**2008**			**2009**	
Water Temperature (°C)	6.7	30.0	18.5	9.0	28.0	18.2	7.5	27.0	18.2
Turbidity (UNT)	3.1	160.8	18.5	2.6	146.1	20.4	4.7	111.5	29.3
Color (mg Pt L^{-1})	14.0	350	70.0	10.0	320.0	65.0	20.0	1037.0	180.0
pH	6.3	7.7	7.0	6.6	7.6	7.1	6.0	7.6	7.0
Hardness ($CaCO_3$ mg L^{-1})	7.5	25.0	17.3	12.0	29.0	18.1	6.0	23.0	15.1
Alkalinity ($CaCO_3$ mg L^{-1})	11.0	38.2	23.8	9.2	37.2	23.0	11.0	28.1	21.1
CO_2 free (mg L^{-1})	2.8	28.8	8.3	2.4	12.0	5.8	3.2	14.4	6.2
Dissolved oxygen (mg L^{-1})	5.4	11.6	8.9	6.5	10.4	8.3	5.4	11.1	8.3
Organic matter (mg L^{-1})	1.4	16.0	5.1	1.5	16.6	4.8	1.0	17.2	5.1
		2010			**2011**			**2012**	
Water Temperature (°C)	9.0	29.0	19.3	8.0	28.0	19.5	9.0	29.0	20.3
Turbidity (UNT)	5.3	151.4	24.3	6.9	181.3	32.2	6.1	274.4	36.0
Color (mg Pt L^{-1})	31.0	1410.0	135.0	29.0	785.0	121.0	21.0	720.0	109.0
pH	5.8	7.5	7.1	6.5	7.8	7.0	6.3	7.3	6.9
Hardness ($CaCO_3$ mg L^{-1})	12.0	28.0	17.2	8.5	22.0	16.5	14.0	29.0	20.5
Alkalinity ($CaCO_3$ mg L^{-1})	13.8	35.0	25.2	12.9	33.7	23.1	10.1	33.0	25.6
CO_2 free (mg L^{-1})	3.2	18.0	5.3	3.2	11.6	5.1	3.2	16.0	6.2
Dissolved oxygen (mg L^{-1})	5.5	11.8	9.1	5.3	10.7	8.4	5.1	17.0	8.5
Organic matter (mg L^{-1})	1.3	27.8	4.7	1.5	19.6	4.6	1.5	18.4	4.7
		2007			**2008**			**2009**	
Water Temperature (°C)	8.0	27.0	18.4	9.0	28.0	19.0	9.7	28.0	19.7
Turbidity (UNT)	0.6	116.6	14.7	1.6	313.1	20.6	1.6	564.3	25.5
Color (mg Pt L^{-1})	8.0	1037.0	80.0	9.0	826.0	73.0	5.0	886.0	65.0
pH	6.1	7.8	7.3	6.4	7.6	7.2	6.5	7.6	7.2
Hardness ($CaCO_3$ mg L^{-1})	13.0	29.0	17.1	8.0	24.0	17.1	14.0	30.0	20.4
Alkalinity ($CaCO_3$ mg L^{-1})	12.8	36.1	24.7	13.5	31.3	23.3	12.8	30.6	24.7
CO_2 free (mg L^{-1})	2.0	12.0	4.9	2.4	8.0	4.5	2.4	12.0	5.1
Dissolved oxygen (mg L^{-1})	6.4	12.9	9.1	6.1	10.6	8.6	5.8	11.3	8.6
Organic matter (mg L^{-1})	0.8	19.8	3.2	0.8	20.0	3.1	0.8	17.8	3.0
		2010			**2011**			**2012**	
Water Temperature (°C)	8.0	29.0	18.1	10.0	28.0	18.4	6.0	26.0	17.6
Turbidity (UNT)	1.7	193.2	14.8	1.4	186.2	16.4	1.4	125.5	21.6
Color (mg Pt L^{-1})	15.0	400.0	56.0	10.0	350.0	53.0	8.0	1808.0	132.0
pH	6.4	7.5	7.1	6.6	7.7	7.3	6.2	7.6	7.2
Hardness ($CaCO_3$ mg L^{-1})	5.0	27.0	17.0	5.7	20.0	9.1	8.0	20.0	15.1
Alkalinity ($CaCO_3$ mg L^{-1})	12.0	37.0	23.5	12.7	35.0	22.8	10.0	28.4	21.3
CO_2 free (mg L^{-1})	2.4	22.0	5.8	2.8	12.0	4.4	2.8	14.0	4.8
Dissolved oxygen (mg L^{-1})	6.3	12.1	9.2	4.0	10.7	8.5	6.2	12.0	8.5
Organic matter (mg L^{-1})	0.9	17.3	3.7	0.0	9.2	1.7	0.4	18.5	3.6

Values for pH ranged between 6.0 and 8.0 in both the Pelotas and Quilombo Streams, considered appropriate according to the Brazilian legislation (Table 2). These results could reflect either the buffering capacity by the ecosystem (Siqueira *et al*., 2012) or could be potentially related to the fact that soil use and occupation around the analyzed points were essentially agricultural, which in general does not tend to affect pH values. Similar results were observed by Piratoba *et al*. (2017). According to Derisio (2016), changes in the pH values of water are caused by industrial wastes.

Mean water hardness values for Pelotas Stream ranged from 15.1 to 20.5 mg $CaCO_3$ L^{-1}, whereas in the Quilombo Stream values ranged from 9.1 to 20.4 mg $CaCO_3$ L^{-1} between 2007 and 2012 (Table 2). Similar results were observed by Estrela *et al*. (2010), when evaluating irrigation water quality in family farms located near the present study, probably due to the presence of the same soil class (Ultisols) in the area around the stream. In both streams, the hardness values were below 50 mg $CaCO_3$ L^{-1} (Table 2) which classifies the water as soft and low-risk to cause damage to the irrigation system.

Water alkalinity varied between 21.1 and 25.6 mg L^{-1} in the Pelotas Stream, and 21.3 and 24.7m L^{-1} in the Quilombo Stream (Table 2). Water hardness and alkalinity can be altered by seasonality and location of sampling points (Piratoba *et al*, 2017). According to Von Sperling (2007), the main constituents of alkalinity are bicarbonates (HCO^-_3) and hydroxides (OH^-), which vary according to pH (pH > 9.4: hydroxides and carbonates; pH between 8.3 and 9.4: carbonates and bicarbonates; pH between 4.4 and 8.3: only bicarbonates). The water pH in the present study remained around 7.0 (Table 2), corresponding to a greater presence of bicarbonates in the Pelotas and Quilombo Streams.

The mean values for CO_2 ranged from 5.1 to 8.3 mg L^{-1} in the Pelotas Stream, whereas in the Quilombo Stream values ranged from 4.4 to 5.8 mg L^{-1} between 2007 and 2012. In general, the Pelotas Stream showed higher free CO_2 values in water, possibly due to higher organic matter values in comparison with the Quilombo Stream (Table 2).

The waters classified as Class 2 must have dissolved oxygen concentrations greater than 5 mg L^{-1} (Table 1); it is observed that in all evaluated years the average values of dissolved oxygen exceeded the minimum stipulated value (Table 2). The highest values of dissolved oxygen were observed in the Quilombo Stream between 2007 and 2012, possibly due to lower values of organic matter (Table 2). According to Siqueira and Aprile (2013), higher organic matter content in water can lead to oxidation-reduction reactions, as oxygen is used as the final acceptor of electrons during the processes associated with organic material degradation.

Between 2007 and 2012, the mean organic matter values ranged from 4.6 to 5.1 mg L^{-1} in the Pelotas Stream, whereas in the Quilombo Stream values ranged from 1.7 to 3.7 mg L^{-1}. It should be emphasized that, in all the evaluated years, the Pelotas Stream presented higher organic matter content in comparison to the Quilombo Stream (Table 2). Bezerra Lopes *et al*. (2008) mention the increase of primary production promoting the generation of a large amount of particulate organic material, resulting in water turbidity with a tendency towards higher values, as observed in the present study. In terms of annual average values, higher organic matter content was found in the Pelotas Stream, leading to higher turbidity and water color values as a consequence (Table 2).

Only in the Quilombo Stream in 0.3% of the days of 2008, the oxygen dissolved values did not meet the values stipulated by legislation (Table 3). This may be related to temperature, since in general the higher the minimum water temperature, the lower the dissolved oxygen.

Turbidity values for both the Pelotas and Quilombo Streams were found to be higher than 100 UNT during the period from 2007 to 2011, in less than 3% of the days of each year. On the other hand, in 2012 turbidity values exceeded the limits of the Brazilian legislation in 4.6 and 5.5% of the days of each year, for the Pelotas and Quilombo Streams, respectively (Table 3). The increased turbidity values may be related to the activity related to sand mining, which generally promotes silting of the Pelotas slopes due to the sediment extraction, as well as due to the use of granite stones and Quarry fines, commonly used as a base for the roads illegally constructed on the stream banks.

Higher color values in the Pelotas Stream were observed in around 30% of the days in 2007 and 2008, above the limit established by the legislation, whereas from 2009 to 2012 the color values exceeded 75 mg Pt L^{-1}in over 50% of the days of each year (Table 3).

Considering all the water quality parameters evaluated, principal components analysis revealed that these factors had an accumulated eigenvalue of 58.95% for the Pelotas Stream and 54.07% for the Quilombo Stream. The first main component resulted from a linear combination of the 9 variables studied, and explained 37.18% and 34.03% of the total variance, whereas the second component explained 21.76% and 20.05% for the Pelotas and Quilombo Streams, respectively.

Table 3. Percentage of days in which the dissolved oxygen, turbidity, color and pH values exceeded the values suitable for freshwaters (Class 2) according to Brazilian legislation (CONAMA Resolution N° 357, March 17, 2005).

Parameters	Days (%)					
	2007	2008	2009	2010	2011	2012
	PELOTAS STREAM					
Dissolved oxygen (mg L^{-1})	0.0	0.0	0.0	0.0	0.0	0.0
Turbidity (UNT)	1.1	0.5	0.8	1.1	2.7	4.6
Color (mgPt L^{-1})	30.1	30.6	76.2	67.4	60.0	54.9
pH	0.0	0.0	0.0	1.1	0.0	0.0
	QUILOMBO STREAM					
Dissolved oxygen (mg L^{-1})	0.0	0.3	0.0	0.0	0.0	0.0
Turbidity (UNT)	1.1	2.2	2.2	0.5	1.4	5.5
Color (mgPt L^{-1})	17.8	19.4	44.1	24.7	22.2	17.8
pH	0.0	0.0	0.0	0.0	0.0	0.0

The first component positively correlated the variables color, organic matter, turbidity, and CO_2, particularly the turbidity parameter, which presented the highest values of correlation with the first component in the Pelotas (Figure 2a) and Quilombo (Figure 2b) Streams. Therefore the physical parameters related to the transport of sediments and their effect on the concentration of CO_2 in the waters. The soil carried to the river directly impacts water color and turbidity, and the soil organic matter increases the CO_2 concentrations, since, in the organic matter oxidation process by aerobic microorganisms, there is the release of carbon dioxide. For both the Pelotas (Figure 2a) and the Quilombo (Figure 2b) Streams, the first component negatively correlated the parameters that are more related to the intrinsic characteristics of the basin, such as climate (water temperature), geomorphology (alkalinity and hardness), soil types, and uses (pH and dissolved oxygen).

The second component was positively correlated with parameters such as water temperature, hardness, alkalinity, pH, organic matter, color, turbidity, and negatively correlated with dissolved oxygen (Figure 2a, b). Water temperature and dissolved oxygen showed the highest correlations, and the relationship between them was inversely proportional. Silva *et al*. (2009) also observed lower water temperatures as directly linked to higher concentrations of dissolved oxygen. According to Post *et al*. (2018), water temperature is the primary regulating metric that determines how much dissolved oxygen water can hold; dissolved oxygen is inversely dependent on water temperature. Increases in water temperature would thus further reduce dissolved oxygen and negatively impact water quality.

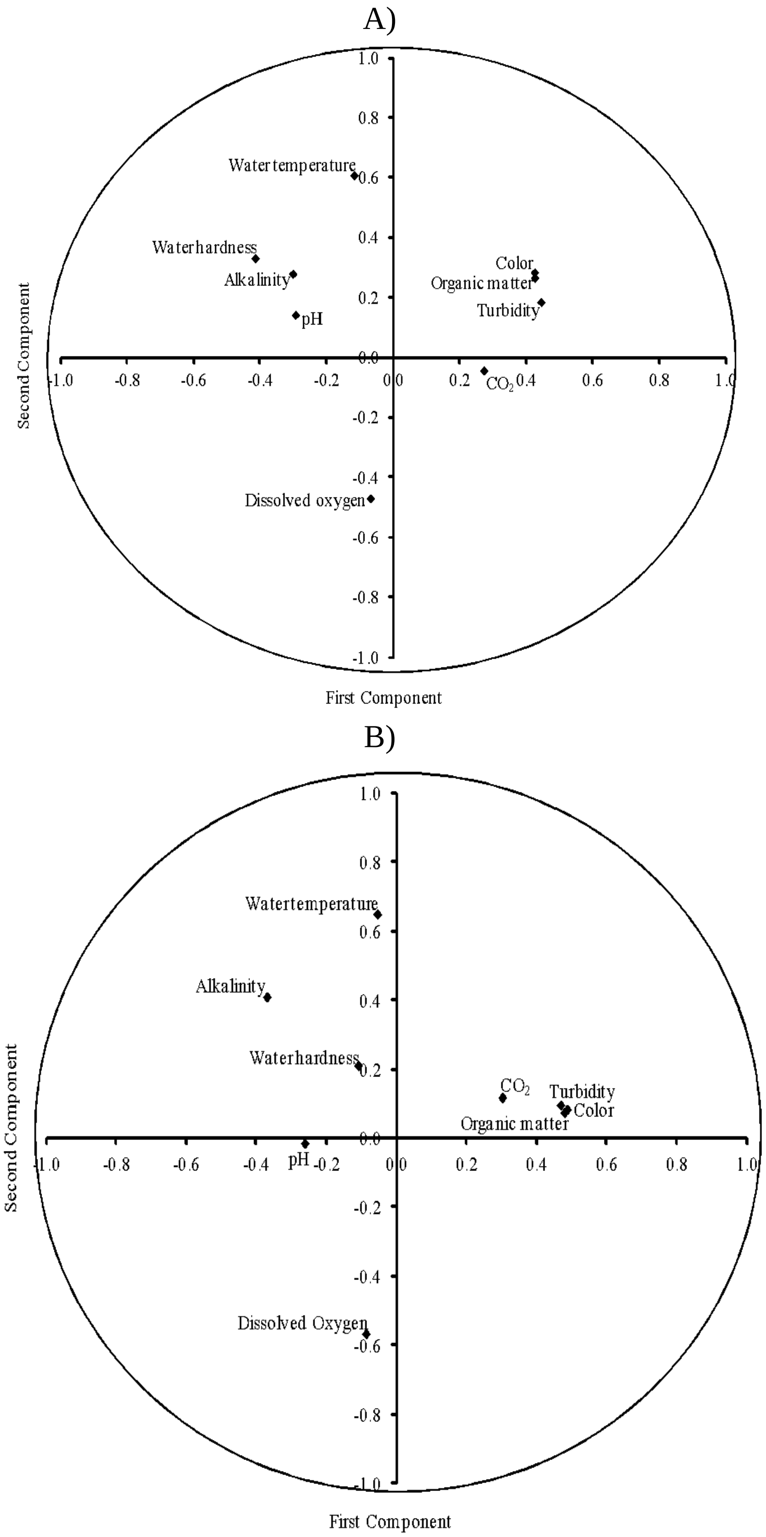

Figure 2. Multivariate analysis between water quality parameters of Pelotas (a) and Quilombo (b) Streams.

Pearson correlation values between the monthly means of the water quality parameters of the Pelotas and Quilombo Streams and the monthly averages of rainfall are found in Table 4. A significant positive correlation between turbidity, color, and organic matter with rainfall was observed in both of the studied streams. Fraga *et al*. (2012) and Silva *et al*. (2009) also observed a positive relation between turbidity values and rainfall accumulated in water sources in different regions of Brazil, indicating the impacts resulting from land use. Similar results were observed by Luíz *et al*. (2012), which found high color values (greater than 75 mg Pt L^{-1}) on days when rainfall was equal to or greater than 25 mm. This can happen because rainfall causes erosion and the runoff of water into the rivers. That increases turbidity, color, and organic matter content in the waters.

Table 4. Pearson correlation between the monthly means of the water quality parameters of the Pelotas and Quilombo Streams and the monthly averages of rainfall.

	Water Temperature	Turbidity	Color	pH	Water Hardness	Alkalinity	Free CO_2	Oxygen dissolved	Organic matter
					PELOTAS STREAM				
Rainfall	0.37^{NS}	0.52*	0.74*	-0.31^{NS}	-0.01^{NS}	0.31^{NS}	0.23^{NS}	-0.43^{NS}	0.54*
					QUILOMBO STREAM				
Rainfall	0.20^{NS}	0.62*	0.92***	-0.52^{NS}	-0.49^{NS}	0.30^{NS}	0.43^{NS}	-0.20^{NS}	0.75**

NS: no significant; * $p < 0.05$; ** $p< 0.01$; *** $p< 0.1\%$.

Fonseca and Salvador (2005) observed a decrease in the values of dissolved oxygen during periods of rainfall, related to an increase of organic matter transported on the soil surface by rain. The positive correlation between organic matter and rainfall was observed in both streams analyzed in the present study (Table 4).

The high values of water turbidity and color, sometimes higher than the limit in Brazilian legislation, in both Pelotas and Quilombo Streams, as well as the positive and significant correlation of these parameters with rainfall, can be associated with agricultural activities carried out in the basin area. During soil preparation for the implantation of summer crops in conventional planting areas, the soil is uncovered and disaggregated due to plowing and harrowing operations; its particles are therefore easily carried by rainwater. The summer crops implanted in the region (corn, soy, and tobacco) are not grown, most of the time, in conservationist soil management systems; consequently, little vegetative cover exists, leaving a large area of uncovered soil. This facilitates the transport of soil particles, fertilizers and pesticides by rainwater.

4. CONCLUSIONS

Values of pH and dissolved oxygen of water conformed with Brazilian legislation for the 6 years evaluated.

Concerning the values put forth by the Brazilian legislation, watercolor was the parameter that remained above the proposed limit for the greatest number of days, occurring mainly in the Pelotas Stream. Such findings indicate the need for soil conservation actions in the area of the contribution basin.

The highest values of color, turbidity, and organic matter occurred when the highest rainfall values were observed, showing a probable sediment transport effect in the basin. Agricultural activities may potentiate sedimentation in the contribution basin of the Sinnott water treatment plant.

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