ANALYSIS OF CHEMICAL FLOW HYDROLOGY OF WATER BODIES IN URBAN AND RURAL AREAS: A CASE STUDY

Keliani Bordin[1]; Diego Alex Mayer[2]; Weber da Silva Robazza[3]; Gilmar de Almeida Gomes[4]

RESUMO

The human activity has changed the water quality of rivers and their branches. This study investigated the effects of human activity on the deterioration of water resources in the city of Pinhalzinho- SC. Physical and chemical quality was evaluated of three water springs and two of its streams. It was observed that the Spring 3, presented high total solids content with an average of 0,071%. The Springs 1 and 3 located in the urban area, had a higher content of chloride, $CaCO_3$ (hardness) and EC (electrical conductivity). The second point of Stream 1 showed different properties due to its location is with high population density. At this point, the COD (chemical oxygen demand) was 50 mg/l, while the average was 26,11mg/l. With the increasing volume of the water flow, there was a decrease in some parameters, such as EC, Cl^-, $CaCO_3$ and pH probably due to interferences and reactions throughout the process.

Keywords: Chemical hydrological flow; Urban area; Rural area; Pollution

ANÁLISE QUÍMICA DO FLUXO HIDROLÓGICO DE CORPOS D'ÁGUA EM ÁREAS URBANAS E RURAIS: UM ESTUDO DE CASO

RESUMO

A atividade humana vem alterando a qualidade dos rios e seus afluentes. Esse trabalho investigou os efeitos da atividade humana na deterioração de nascentes e córregos no município de Pinhalzinho-Santa Catarina. A qualidade físico-química foi avaliada em três diferentes nascentes e dois córregos. A Nascente 3 apresentou elevado conteúdo de sólidos totais com uma média de 0,071%. As nascentes 1 e 3 localizadas na zona urbana apresentaram elevado conteúdo de cloreto, $CaCO_3$ (dureza) e EC (condutividade elétrica). O segundo ponto do córrego 1 mostrou propriedades diferentes provavelmente devido a localização com elevada densidade populacional. Nesse ponto, a demanda química de oxigênio (COD) foi de 50 mg/l, enquanto a média do córrego foi de 26,11mg/l. Com o aumento no fluxo de água do córrego, houve uma diminuição de alguns parâmetros, como EC, Cl^-, $CaCO_3$ e pH provavelmente devido a interferentes e reações geradas ao longo do processo.

Palavras-chave: Fluxo Químico Hidrológico; Zona urbana; Zona rural; Poluição.

Trabalho recebido em 20/07/2012 e aceito para publicação em 01/04/2013.

[1]Doutoranda em Ciências da Engenharia de Alimentos- Departamento de Engenharia de Alimentos-USP. e-mail: keliani.bordin@yahoo.com.br. Autor para correpondência: Rua Dona Leopoldina, 156, Bairro Jardim Elite, CEP: 13635-014, Pirassununga- SP.
[2]Graduando em Engenharia de Alimentos- Departamento de Engenharia de Alimentos- UDESC. E-mail: diegoalexmayer@yahoo.com.br.
[3]Professor- Departamento de Engenharia de Alimentos. E-mail: wrobazzi@yahoo.com.br.
[4]Professor- Departamento de Engenharia de Alimentos. E-mail: gilmargomess@yahoo.com.br.

1. INTRODUCTION

Freshwater ecosystems play unique roles for society through provision (products and food), supporting (waste processing and supply of clean water) and enriching or cultural (aesthetic and recreational) services. However, with the development of industry and agriculture, the number and magnitude of anthropogenic stressors arose from the myriad of human activities including pollution, engineering and overexploitation of water resource that threaten these services was growing rapidly (HONG-JUN *et al*., 2007).

Rivers are dynamic systems and may change in nature several times during their course because of changes in physical conditions such as slope and bedrock geology. They carry horizontal and continuous one-way flow of a significant load of matter in dissolved and particulate phases from both natural and anthropogenic sources. This matter moves downstream and is subject to intensive chemical and biological transformations (BELLOS; SAWIDIS, 2005).

Many research studies have shown a close relationship between water quality and urban development. LeBlanc *et al*. (1997) found that land-use intensification increased water temperature. Fisher *et al*. (2000) also discovered that land use had impacts on the quality of surface water. Wang *et al*. (2008) observed which results indicated that the spatial pattern of surface water quality was determined by the level of urbanization. Identification and quantification of these influences should form an important part of managing land and water resources within a particular river catchment (BELLOS; SAWIDIS, 2005).

Water pollution is a relatively new problem and increases the stress arising as a result of unprecedented population growth, urbanization, and industrialization since the 1990s (CHEN, 2002). The increasing use of water resources has resulted in problems not only of water lack, but also the degradation of its quality. In Brazil, 92 % of the sewers are launched in the rivers and 87% of the wastes are deposited under rain influence (WENDLAND *et al*., 2006).

The rural water can also be contaminated by human waste and animals that are thrown open by the lack of sanitation and become constant sources of pollution. The lack of sanitation in rural areas, independently of the occupation, is a worrying factor for the case of constant release of pollutants into the environment (GODOI, 2008). Moreover the agricultural production generates toxic waste and excess substances, serving as a pollution vehicle in many water sources (SOMURA *et al*., 2009).

The growth in the monitoring of surface water is an important element in preserving, restoring and protecting water quality (OUYANG, 2005). Large natural variations in water quality may be observed even where only a single watercourse is involved. Its water quality varies with time, requiring for their control to test at different times of the year, and only repetition can give reliable results (RICHTER; NETO, 2003).

The quality of surface water is affected by the type and amount of pollution. Contaminants and interferences are changed with time and distance (EJAZ; PERALTA, 1995). The flow of elements in rivers and small streams is calculated to estimate the variation of physic and chemical component of transportation by water (CERNY *et al*., 1994).

Its temperature variations are part of normal climate regime and natural bodies of water show seasonal and diurnal variations. The temperature has an influence on biological processes, chemical and biochemical reactions that occur in water and other processes, such as the solubility of dissolved gases and minerals (MACEDO, 2004).

The pH is a measure of the relative acidity or alkalinity of water. The pH of water is a composite reading of the balance between water, free carbon dioxide, carbonate, bicarbonate and hydroxide. A shift in any one of these species will produce a shift in the pH. The pH can be affected by chemicals in the water, it is an important indicator of water that is changing chemically (HUI, 2006).

The electrical conductivity of water is determined by presence of dissolved substances that dissociate into anions and cations (RICHTER; NETTO, 2003).

Hardness in water is caused by dissolved minerals, primarily those producing divalent, or double charged, cations including calcium (Ca^{2+}), magnesium (Mg^{2+}), iron (Fe^{2+}), strontium (Sr^{2+}), zinc (Zn^{2+}) and manganese (Mn^{2+}). Calcium and magnesium ions are usually the only ones present in significant concentrations in most waters (HUI, 2006). The elements calcium, magnesium and silicium are typical of soils, and are present in high concentrations in surface waters due to the presence of urban domestic sewage, carrying detergents and soaps that have these elements in their composition (GODOI, 2008).

The chloride ion is present in all waters and is used as a track chemical, since he is a conservative ion in the analysis of flow these resources and their rise may be related to the contact of water with mineral deposits and/or drain pollution (domestic and industrial) or by water used in agriculture irrigation. When compared with other ions, increasing the chloride content in water shows the contribution of a source of Cl^-, for example, domestic drain as each person expels the urine about 6 g chloride in day, or by industrial waste speeding the process of corrosion in tube of steel and aluminum, and change the taste of water (PHILIPPI *et al*., 2004).

According with works (as VYRIDES; STUCKEY, 2009), the chemical oxygen demand (COD) is an important parameter used to estimate the content of organic material in surface water compared with the other topics studied.

The objective of this study was to investigate the effect of human activity in pollution of rivers and springs in the region of Pinhalzinho and the difference in the flow of chemicals, comparing the pollution generated in urban and rural. Was evaluate three sources and two streams, through the following experimental parameters: pH, electrical conductivity (EC), temperature of the sample (T sample), temperature (T), chloride, total solids, hardness, and COD.

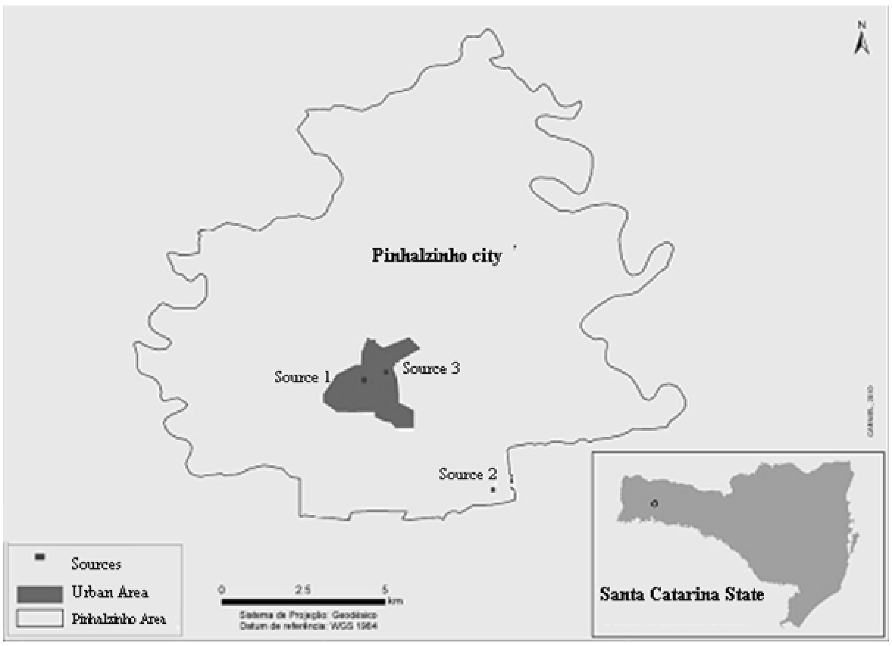

Figure 1. Location of the studied sources

The Streams 1 (Lajeado Bonito River) and 2 (Ramos River), has its springs located in the urban area, passing through the countryside and then disembogues in the following rivers, Saudades and Chapecó. Strategic sampling points were chosen close to most populated areas, industrial activities and agricultural production.

Figure 2 shows the sampling points of the two examined streams. In the Lajeado Bonito River (a) 3 of the 6 sampling point, were distributed in the urban area (A, B and C) and the other three in the rural area (D, E and F), at Ramos River (b), 2 were within the urban area (G, H) and 4 in the rural limits (I, J, K and L).

Figure 2 (a) is an overview from 555m above the surface with coordinates 26º54’47,89” S and 52°46'13,43" O. Figure (b) is an overview from 444m above the surface with coordinates 26°51'09,34"S and 52°57'54.87"O. The straight distance among the points was calculated to estimate this flow.

(a) (b)

Figure 2- Collection points at Ramos River (a) and at Lajeado Bonito River (b) both located in Pinhalzinho city in a transition from urban to rural area.

2. MATERIAL AND METHODS

2.1 Description of the Case Study

The city of Pinhalzinho is located in the western portion of Santa Catarina, southern Brazil (Figure 1). As part of the Uruguay River basin this territory is rich in fresh water, and covers one of the largest groundwater reservoirs in the world, the Guarani Aquifer System (GAS) integrated with water storage of about 37.000 km^3 and a natural recharge of 166 km^3 per year (OFFICE FOR SUSTAINABLE

DEVELOPMENT & ENVIRONMENT, 2005).

The GAS has a high water potential, and is highly relevant to the region, but at the same time establishes a strong complexity in the flow system and the contamination forms. In this sense, solutes from industrial, agricultural and household activities generated in surface can reach the local reservoir (WENDLAND *et al*., 2006).

The city of Pinhalzinho, located in the coordinates 26º50'53"S 52º59'31"O, at 515m of altitude, has many fresh water springs spread throughout its extent. Three of them were selected because they are important sources in the region water supply.

The studied sources are shown in Figure 1 and sources number 1 and 3, correspond respectively to Streams 1 and 2. For the second source there is no comparison because the water harvesting occurs in the spring.

2.2. Samples and analises

Five samples of water in two streams and five points in the three compared sources were collected from March to July in 2009 and evaluated periodically according to weather conditions, in all collected points (3 springs and 2 streams).

The samples were stored in 500 ml PET bottles and kept cool until the arrival at the laboratory. The physical and chemical analyses were carried in the chemistry laboratory of the Santa Catarina State University, Food Engineering Department. Due to the lack of systematic weather data collection and quantification of rainfall in this work was not possible.

The pH was determined *in loco* using a pH meter (AZ model 8686), while electrical conductivity was determined by a conductivity meter (Quimis Q-795A2) according with Instituto Adolfo Lutz (1976).

The sample temperature and the environment temperature were measured with a thermometer at the same time of the sampling.

The chloride content was determined by titration with standard silver nitrate used as the chromate potassium indicator. The determination of hardness was performed with the addition of a buffer and direct titration with standard EDTA and indicator Eriochrome black T, and Total solids content was determined by checking the weight of the sample residue after evaporation and drying to constant weight, at 103-105 ° C, all of the previous methods were performed according to the recommendations of the Instituto Adolfo Lutz (1976)

The Chemical Oxygen Demand analyses was performed by chemical oxidation of organic matter with a strong oxidant (potassium dichromate $K_2Cr_2O_7$) in acid medium (Equation 10), at temperatures near to 250°C in a reflux system. After two hours of material oxidation, the sample was quantified by means of titration with ammonium ferrous sulfate, as reported by Rocha *et al*. (2004) in Equations 10 to 14.

$$\text{Organic matter} + Cr_2O_7^{2-} + H^+ \rightarrow 2\ Cr_3^+ + CO_2 + H \quad (10)$$

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O \quad (11)$$

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 4Fe^{3+} + 2Cr^{3+} + 7H_2O \quad (12)$$

$$Fe^{+2} \rightarrow Fe^{+3} + 1e \quad (13)$$

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \quad (14)$$

The parameters were compared significant differences between urban and rural areas by ANOVA established in the General Linear Model of SAS ® (SAS INSTITUTE, 1992) to evaluate statistically the correlation among the parameters studied between the streams.

3. RESULTS AND DISCUSSION

3.1 Evaluation of quality parameters in water sources

The pH value diverged from 5,87 to 7,38, with average of 6,8 (Table 1). These values are within the water quality standard in Brazil established by National Environment Council (CONAMA, 2005), however, are lower than the criterion for tap water in USA and German (BIRKE *et al*., 2010).

The pH levels, sample temperature and temperature variation on the other hand, are lower in the Spring 2, compared with 1 and 3, probably due to the underground course of the source.

In Springs 1 and 2 the total solids content shown no significant difference, however, the values found in Spring 3 were significantly higher, almost three times higher than the other values. Chloride results varied from 7,59 to 5,39 mg Cl-/L, with average 6,65 mg Cl-/L, lower than Haruna *et al*. (2005) found in their studies with stream in the urban area, where the chloride content in the studied springs differed from 12 to 64 mg Cl-/L. Possibly this variation is due to the different environmental conditions of studied regions.

Table 1- Results of temperature, sample temperature, pH, EC, hardness and chloride obtained in the analysis of water collected in the 3 sources.

Source	CaCO3 (mg/L)	Cl^- (mg/L)	Total solids (%)	EC (mS/cm)	pH	T sample (ºC)	T environment (ºC)
1	13,18	7,59	0,027	93,20	7,38	19,80	17,66
2	8,63	5,39	0,029	54,22	5,87	17,84	15,76
3	16,36	6,99	0,071	117,30	7,15	19,00	10,75

In Figure 3 show that the Springs 1 and 3 located in the urban area, the chloride, hardness and EC levels were higher. This behavior is possibly associated with a higher concentration of ions, due to anthropogenic action (sewage disposal nearby).

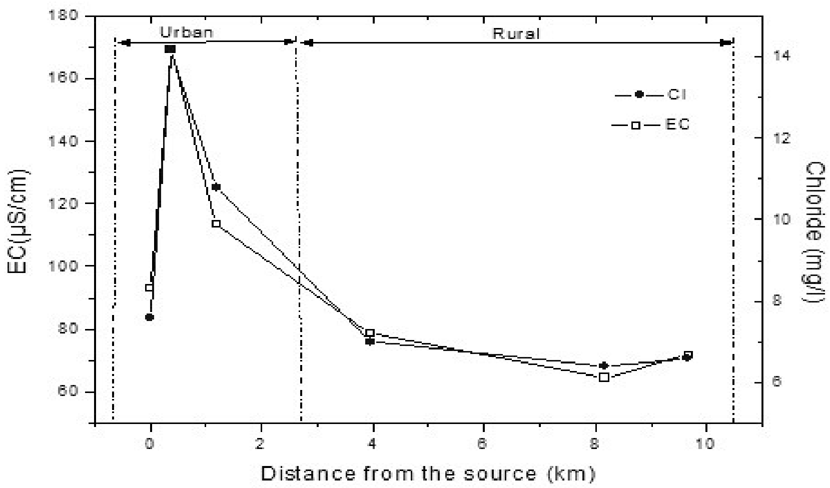

Figure 3- Chloride content and electrical conductivity in urban and rural areas.

3.2 Analysis of chemical flow in streams located in urban and rural

The Point 2 in Stream 1, presented different properties from the others due to the high population density in its location (Table 2). Furthermore, the irregular terrain near the site may interfere. It is characterized by having a high concentration of organic matter which can be noticed by its turbidity, color, and smell and experimentally confirmed.

The sample temperature presented considerable changes due to weather variation, not resulting in a good fit. The increase in temperature increases the speed of reactions, decreasing the solubility of gases dissolved in water - mainly the oxygen, basis for the aerobic decomposition.

Table 2- Results for electrical conductivity, pH, T of sample, T environment, changes in temperature, hardness and in two analyzed streams.

Stream 1								
Locality	**Points**	**Dist. source (km)**	**$CaCO_3$ (mg/L)**	**Cl (mg/l)**	**EC (µS/cm)**	**pH**	**T sample (ºC)**	**T environment (ºC)**
	1	0	13,18	7,59	93,2	7,38	19,8	17,66
	2	0,37	14,14	14,17	169,5	6,92	20,26	16,86
Urban	3	1,19	13,11	10,79	113,42	7,2	17,94	16,78
	4	3,96	10,99	6,99	78,78	7,26	16,86	17,8
	5	8,17	10,13	6,39	64,4	7,24	16,52	18,18
Rural	6	9,67	10,88	6,59	71,72	7,42	17,1	18,38
Average			12,07	8,76	98,5	7,24	18,08	17,61
Stream 2								
Locality	**Points**	**Dist. Source (km)**	**$CaCO_3$ (mg/L)**	**Cl^- (mg/l)**	**EC (µS/cm)**	**pH**	**T sample (°C)**	**T enviroment (°C)**
	1	0	16,36	6,99	117,3	7,15	19	10,75
Urban	2	0,98	9,2	11,49	97,25	7,4	16,7	14,9
	3	1,29	9,93	7,99	66,57	7,4	15,97	14,43
	4	1,64	8,61	7,66	62,6	6,7	15,7	14,83
	5	3,2	8,39	4,66	55	6,8	15,63	14,77
Rural	6	3,82	8,75	4,66	63,4	6,9	15,43	14,4
Average			10,21	7,24	77,02	7,06	16,41	14,01

In Stream 1, the pH value declined in point 2, with further growth. In Stream 2, the pH increased in Points 2 and 3. The presence of ions or acid salts can decrease the pH, which may be related to the sanitary quality (RICHTER; NETTO, 2003).

The highest value of hardness in Stream 2 (16,36 mg CaCO3/L) is located in the urban area (Point 1) occurring a subsequent decrease, possibly due either to its precipitation and deposition in rivers or to its conversion in CO2 and emission into the atmosphere (RAYMOND; COLE, 2003).

Compared with Ouyang (2005), where the average alkalinity of water was 78,70 mg CaCO3/L, was this study found a significantly higher value. Similarly, the pH value found by Ouyang (2005) was higher, 8,02 with a average of 7,14 (directly related to the alkalinity).

There is a significant difference in Stream 1, between the electrical conductivity in Points 1 and 2 (76,3 µS/cm) with a decrease along the course. The maximum value in Stream 2 was in the spring exhibiting a gradual decrease after this point. Silva and Sacomani (2001), examined the variations in physical and chemical parameters of the lower reaches of Pardo River (the only economically feasible source of fresh water in the region- Botucatu/Brazil) and obtained variations in conductivity from 17,77 to 687,91 µS/cm in different seasons. The highest values of EC and chloride are observed in Point 2 and are probably related to sewage pollution, which flows along the stream.

The high content of Cl- obtained in this work indicates the presence of many domestic residues, what is consistent with others works as Azzolini (2002) which attributes its high levels to illegal sewage contamination presenting an increase of more than 50% in the chloride concentration comparing to the river where it was dumped. Corroborating the study of Chen and Driscoll (2009), the content of Cl- is greater in areas with higher population density, probably because to human interference.

It is observed that the levels of Cl-, CaCO3, pH, EC suffered a relative reduction along the path. These compounds may vary with rainfall, topography and react with other substances may be lost or undergo change in its composition.

Table 3- Results of both streams comparing urban and rural.

Locality	$CaCO_3$ (mg/L)		Cl^- (mg/l)		EC (µS/cm)		pH		T sample(ºC)		T env. (ºC)	
	Aver.	Σ	Aver.	σ	Aver.	Σ	Aver.	σ	Aver.	Σ	Aver.	σ
Urban	12,65	2,67	9,84	1,24	109,54	34,5	7,24	0,19	18,28	1,71	15,23	2,52
Rural	9,62	1,18	6,16	2,79	65,98	8,22	7,05	0,29	16,21	0,71	16,39	1,91

When comparing the rural and urban area it was observed that $CaCO_3$ content, Chloride levels and EC values were always higher in the urban area (Table 3). The pH and the environment temperature did not vary significantly among the surveyed locations. The temperature uniformity was probably because the samples were collected during the same period of the day. The difference between sample average temperatures and environment average temperatures was statistically distinct between urban and rural areas, possibly due to the large temperature variation in these areas (Table 3).

The regression of the $CaCO_3$ (mg/L) concentration values according to the distance from the source, generated the following 3rd degree polynomial, $y = 16,243 - 9,256\ x + 3,422\ x^2 - 0,397\ x^3$. The correlation coefficient obtained was $R = 0,968$, indicating a good fit. The pH did not show a good linear fit (Figure 4).

It is observed that the pH declines along the route (Figure 5). This effect may be related to the fact that most of the hardness results also showed a decrease over the points analyzed, and those factors are directly related.

The hardness is a water quality parameter that results mainly from the presence of dissolved calcium and magnesium ions which are impurities. However, high hardness levels can partially mitigate the toxicity of many dissolved metals to aquatic life. Hence, it is important to measure water hardness in order to evaluate the hazards of dissolved metals (WEINER, 2000).

It is observed that the pH declines along the route (Figure 5). This effect may be related to the fact that most of the hardness results also showed a decrease over the points analyzed, and those factors are directly related.

Although the monitoring of oxygen concentration in rivers is not a new subject, the biological, chemical, and physical processes involved in the increase of oxygen in rivers are so numerous and complex that there is no model that can be used without a careful analysis of local characteristics (SILVA; SACOMANI, 2001). The highest value of COD was recorded at Point 2 (Figure 5), probably due waste concentration such as sewage, industrial waste and biological.

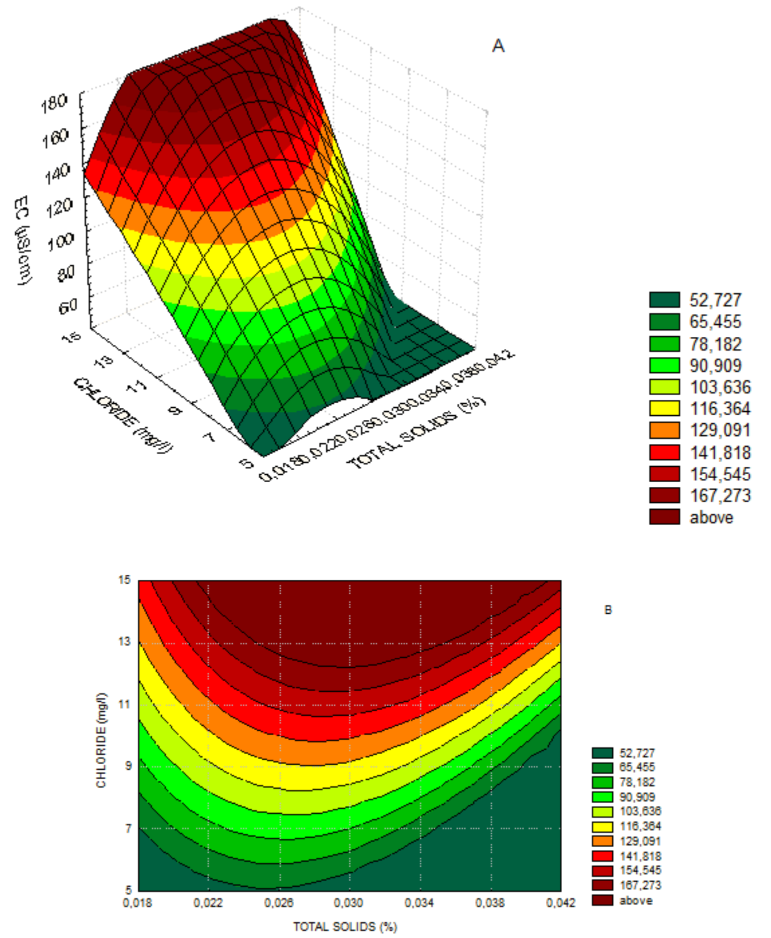

Figure 4- Response surface and contour plot of the conductivity as a function of chloride and total solids.

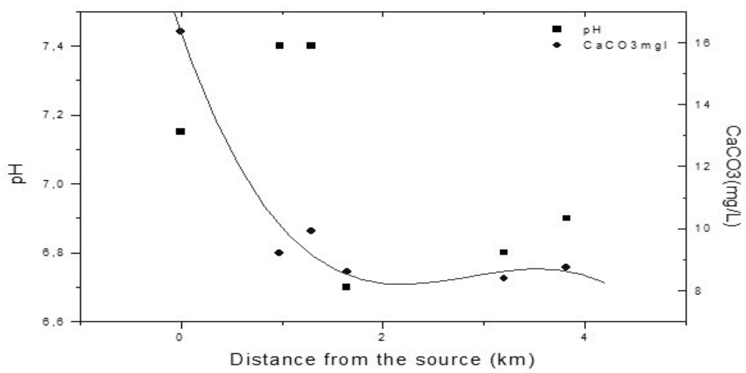

Figure 5- The pH and hardness results at Stream 2 sampling points.

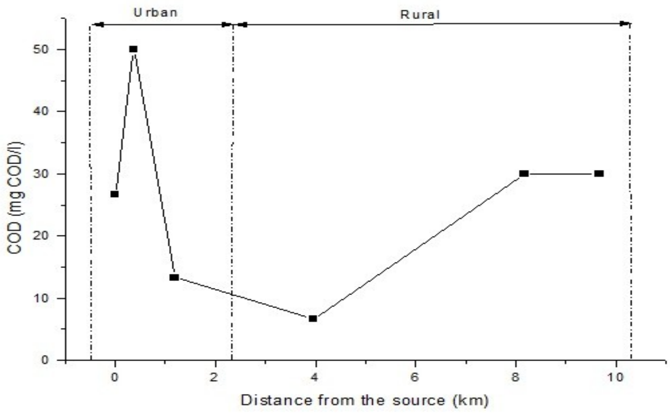

Figure 6- Chemical oxygen demand for different sampling points of the first stream.

Similarly as the other results, there was a high value in Point 2 and a low value in Point 4. The chemical oxygen demand is used as an estimate of the organic material content in water, the results in this study were more pronounced in urban areas.

4. CONCLUSION

The Sources 1 and 3, located in urban areas showed higher levels of chloride, hardness and EC, possibly due to anthropogenic intervention in this area. The analyzed streams were similar, with higher content of chloride, EC, $CaCO_3$ at points located in urban areas. The Point 2 and Stream 1 showed different properties from the others, due to its location, with higher population density. With the increase in the path of water flow, there is a decrease in the EC, Cl^-, $CaCO_3$ and pH, probably due to reactions during the process, indicating less contamination in more distant places.

5. ACKNOWLEDGEMENTS

This work was supported by the Pinhalzinho city council from the State University of Santa Catarina.

6. REFERENCES

AZZOLINI, J. C. Contribuição da poluição física, química, e bioquímica nas águas do Rio do Peixe pelo afluente Rio do Tigre. **Dissertação** (Mestrado), Universidade Federal de Santa Catarina, Florianópolis, 2002.

BELLOS, D.; SAWIDIS, T. Chemical pollution monitoring of the River Pinios (Thessalia—Greece). **Journal of Environmental Management**, Greece, vol. 76, p. 282–292, 2005.

BIRKE, M.; RAUCH, U.; HARAZIM, B.; LORENZ, H.; GLATTE, W. Major and trace elements in German bottled water, their regional distribution, and accordance with national and international Standards. **Journal of Geochemical Exploration**, Holanda, vol. 107, p. 245–271, 2010.

CERNY, J.; BILLET, M.F.; CRESSER, M.S. **Biogeochemistry of small catchments, a tool for Environmental research**. Chichester: Wiley, 1994.

CHEN, J. Analysis of water environment in the Xinjiang arid region. **Arid Environmental Monitoring**, China, vol. 16, p. 223–227, 2002.

CHEN, X.; DRISCOLL, C.T. Land Use Controls on Chemical Inputs to Lake Ontario Embayments. **Journal of Environmental Quality**, Estados Unidos, vol. 38, p. 2084-2085, 2009.

CONAMA. Resolution nº 357, de 2005. **Estabelecimento da classificação das águas doces, salobras e salinas no Brasil.** Official Gazette of Brasilia, 2005.

EJAZ, M.S.; PERALTA, R.C. Maximizimg conjunctive use of surface and ground water under surface water quality constraints. **Advances in Water Resources**, Inglaterra, vol. 18: p. 61-75, 1995.

FISHER, D.S.; STEINER, J.L.; ENDALE, D.M.; STUEDEMANN, J.A.; SCHOMBERG, H.H.; FRANZLUEBBERS, A.J; WILKINSON, S.R. The relationship of land use practices to surface water quality in the Upper Oconee Watershed of Georgia. **Forest Ecology and Management**, Holanda, vol. 128, p. 39-48, 2000.

GODOI, E.T. Monitoramento de águas de superfície densamente poluídas: o córrego Purajussara localizado na Região Metropolitana de São Paulo, Brazil. **Dissertação** (Mestrado), Instituto de Pesquisas Energéticas e Nucleares, São Paulo, 2008.

HARUNA, R.; EJOBI, F.; KABAGAMBEZ, K. The quality of water from protected springs in Katwe and Kisenyi parishes, Kampala city, Uganda, **African Health Sciences**, Nigeria, vol. 5, p. 14-20, 2005.

HONG-JUN, Y.; ZHE-MIN, S.; JIN-PING, Z.; WEN-HUA, W. Water quality characteristics along the course of the Huangpu River (China). **Journal of Environmental Sciences**, Estados Unidos, vol. 19, p. 1193–1198, 2007.

HUI, Y.H. **Handbook of Food Science, Technology, and Engineering**. Boca Raton: CRC Press, 2006.

INSTITUTO ADOLFO LUTZ. Métodos físico-químicos de análise de alimentos. São Paulo, 1976.

LEBLANC, R.T.; BROWN, R.D.; FITZGIBBON, J.E. Modeling the effects of land use change on the water temperature in unregulated urban streams. **Journal of Environmental Management,** Inglaterra, vol. 49, p. 445-469, 1997.

MACEDO, J.A.B. Waters & Waters. Belo Horizonte: CRQ, 2004.

OFFICE FOR SUSTAINABLE DEVELOPMENT & ENVIRONMENT. Water Project Series, Number 7. Guarani Aquifer System, p. 1-4, 2005.

OUYANG, Y. Evaluation of river water quality monitoringstations by principal component analysis, **Water Research**, Estados Unidos, vol. 39, p. 2621-2635, 2005.

PHILIPPI, A.J.; ROMERO, M.A.; BRUNA, G.C**. Course on Environmental management**. Manole. Barueri, 2004.

RAYMOND, P.A., COLE, J.J. Increase in the export of alkalinity from North America's largest river. **Science**, Estados Unidos, vol. 301, p. 88-91, 2003.

RICHTER, C., NETO, J.M.A. Water treatment. São Paulo: Edgard Blucher, 2003.

ROCHA, J.C.; ROSA, A.H.; CARDOSO, A.A. **Introdução a química ambiental**. Porto Alegre: Bookman, 2004.

RYDING, S.O.; FORSBERG, A. Mercury-free accelerated method for determining the chemical oxygen demand of large numbers of water samples by autoclaving them under pressure with acid-dichromate,

Water Research, Estados Unidos, vol. 11, p. 801- 805, 1977.

SAS Institute. SAS user's guide: statistics. SAS Institute. Cary. NC. 1992.

SILVA, A.M.M., SACOMANI L,B. Using chemical and physical parameters to define the quality of pardo river water (Botucatu-SP-Brazil). **Water Research**, Estados Unidos, vol. 35, p. 1609–1616, 2001.

SOMURA, H.; TAKEDA, I.; MORI, Y. Influence of puddling procedures on the quality of rice paddy drainage water. **Agricultural Water Management**, Holanda, vol. 96, p. 1052-1058, 2009.

VYRIDES, I.; STUCKEY, D.C. A modified method for the determination of chemical oxygen demand (COD) for samples with high salinity and low organics. **Bioresource Technology**, Inglaterra, vol. 100, p. 979-982, 2009.

WANG, J.; DA, J.; SONG, K.; LI, B.L. Temporal variations of surface water quality in urban, suburban and rural areas during rapid urbanization in Shanghai, China. **Environmental Pollution,** Estados Unidos, vol. 152, p. 387-393, 2008.