

Influence of urban area on the water quality of the Campo River basin, Paraná State, Brazil

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Abstract

The Campo River basin is located on the third plateau of the Paraná State or *trap* plateau of Paraná, at the middle portion between the rivers Ivaí and Piquiri, southern Brazil, between the coordinates 23° 53' and 24° 10' South Latitude and 52° 15' and 52° 31' West Longitude. The basin has 384 Km² area, being 247 km² in the municipality of Campo Mourão and 137 km² in the municipality of Peabiru, in Paraná State. The Campo River is a left bank tributary of the Mourão River, which flows into the Ivaí River. The objective of this study was to monitor water quality in the Km 119 River and the Campo River, tributaries of the Mourão River, with monthly collection of water samples to determine pH, temperature, turbidity, biochemical oxygen demand, dissolved oxygen, fecal coliforms, total solids, total nitrogen, ammoniacal nitrogen, nitrite, nitrate and total phosphorus. The results obtained were compared with the indices established by the environmental legislation and applied in the determination of the Water Quality Index (WQI) used by the Water Institute of Paraná State, regulating environmental agency. Poor water quality in these rivers presents a worrying scenario for the region, since this river is the main source of water supply for the public system. Results of organic matter, fecal coliforms and total phosphorus were higher than the limits established by Resolution CONAMA 357/2005 to river class 2, specially at downstream of the Km 119 River and the Campo River, due to the significant influence of the urban anthropic activity by the lack of tertiary treatment and also rural by the lack of basic sanitation in this area. Results of WQI of Km 119 River and do Campo River indicated that water quality can be classified as average in 71% and good in 29% of the sites evaluated.

Keywords: water quality, water resources, Anova, Tukey.

Influência da área urbana na qualidade das águas na Bacia do Rio do Campo River, estado do Paraná, Brasil

Resumo

A Bacia Hidrográfica Rio do Campo está situada no terceiro planalto paranaense, na porção média entre os rios Ivaí e Piquiri, Sul do Brasil, entre as coordenadas 23° 53' e 24° 10' de Latitude Sul e 52° 15' e 52° 31' de Longitude Oeste. A bacia ocupa área de 384 Km², sendo 247 km² no município de Campo Mourão e 137 km² no município de Peabiru, no estado do Paraná. O Rio do Campo é um afluente da margem esquerda do Rio Mourão, que deságua no Rio Ivaí. O objetivo deste trabalho foi monitorar a qualidade da água do rio Km 119 e rio do Campo, afluentes do Rio Mourão, com coletas mensais de amostras de água para determinação do pH, temperatura, turbidez, demanda bioquímica de oxigênio, oxigênio dissolvido, coliformes fecais, sólidos totais, nitrogênio total, nitrogênio amoniacal, nitrito, nitrato e fósforo total. Os resultados obtidos foram comparados aos limites estabelecidos na legislação ambiental vigente para poluentes na água e aplicados na determinação do Índice de Qualidade das Águas (IQA) usado pelo Instituto das Águas do Paraná, órgão ambiental fiscalizador. A má qualidade observada nestes rios é preocupante para a região que usufruiu destas águas como principal fonte de abastecimento público. Resultados de matéria orgânica, coliformes totais e fósforo total extrapolaram os padrões estabelecidos na Resolução CONAMA 357/2005 para rio classe 2,

especialmente à jusante do rio Km 119 e do Rio do Campo, devido à influência significativa da atividade antrópica urbana pela falta de tratamento terciário e rural pela falta de saneamento básico nesta área. Os resultados do IQA do Rio Km 119 e Rio do Campo indicam que as águas podem ser classificadas com qualidade média em 71% e boa em 29% nos pontos avaliados.

Palavras-chave: qualidade das águas, recursos hídricos, Anova, Tukey.

1. Introduction

The quality of life is directly related to availability and quality of water consumed. Population growth, industrial development and disordered land occupation has contributed to the worsening of the contamination and consequently the lack of preservation of surface and groundwater sources (Demirak et al., 2006).

The relationship between land use and changes in water courses may be influenced by organic, physical, chemical and bacteriological pollution caused by urban and industrial supply, discharge of sewage and industrial effluents, and runoff in urban areas. In rural areas, these changes can result from the consumptive use of water for crop irrigation, use of pesticides and fertilizers, animal waste, deforestation, fires, and inappropriate use of techniques and procedures for management that cause soil erosion, and drainage water from rural roads (Goldstein et al., 2007).

Beyond pollution of water bodies, these factors can cause damage to biota and humans (Margalef, 1991; Villela et al., 2007).

In recent decades, the disordered occupation of the Campo River basin has contributed to contamination of water and soil, degradation of fauna and flora, due to agricultural, urban and industrial uses, poorly maintained rural roads, power generation (Mourão Hydroelectric Power Plant) and water supply (Water Treatment Plants of Km 119 and Campo).

Water quality study in this basin is relevant for the population of the region, since about 80% of Campo Mourão municipality water supplying comes from the Campo River. The Km 119 and Campo rivers are tributaries of the Mourão River that flows into the Ivaí River, main river of the Ivaí River basin, with total length of approximately 671 km and drainage area of 36,587 km².

The monitoring of water quality through physical, chemical and microbiological parameters of the main river and its tributaries in a watershed enables to obtain important information for watershed management, with current diagnosis and prediction of the future (Huntsaker and Levine, 1995; Moreno and Callisto, 2004; Ioris et al., 2008).

The Brazilian classification of surface waters according to the quality required for main purposes is based on the Conama Resolution 357 from 2005 (Brasil, 2005). Water courses belonging to the Ivaí River basin were classified as class 2 in the SUREHMA Ordinance 19, from May 12nd, 1992 (Paraná, 1992). According to Conama 357/05 (Brasil, 2005), the class 2 refers to waters for

human supply after conventional treatment, irrigation of vegetables and fruit plants, among other uses of direct contact with the public.

In Brazil, the Water Quality Index (WQI) was firstly used from 1975 (ANA, 2009). The WQI was created by the National Sanitation Foundation in 1970 in the United States, and represents a tool for analysis of quality of water bodies, gathering diverse information into a single numerical result (Almeida and Schwarzbald, 2003).

The present study sought to perform a diagnosis of water quality in river Km 119 and Campo to compare the results obtained with the indexes established by the environmental legislation and also determine the Water Quality Index (WQI).

2. Material and Methods

2.1. Study area

The Campo River basin is on the third plateau of the Paraná State or *trap* plateau of Paraná, at the middle portion between the rivers Ivaí and Piquiri, southern Brazil (Maack, 2002), between the coordinates 23°53' and 24°10' South Latitude and 52°15' and 52°31' West Longitude (Figure 1). The basin has 384 Km² area, being 247 km² in the municipality of Campo Mourão and 137 km² in the municipality of Peabiru. The Campo River is a left bank tributary of the Mourão River, which flows into the Ivaí River (Crispim et al., 2012).

The Campo River basin has a great importance for the population of the municipality of Campo Mourão (87,194 inhabitants), with population density of approximately 144.12 inhab/km², once about 80% of public water supply comes from the Campo River (IBGE, 2010). The catchment area is used for urban and rural purposes, mainly soybean production, which has intensified in recent years, according to Colavite (2008), Crispim et al. (2012) and Villwock et al. (2013).

Soils of the basin have volcanic origin, with a portion on the outcropping area of sandstone of the Caiuá Formation. Red latosol and red argisol are the soil types in the area occupied by the basin. The climate of the region is Cfa: mesothermal humid subtropical, with hot summer and infrequent frosts, rainfall concentrated in summer months, without well-defined dry season (Köppen, 1948). The temperature of the coldest month ranges from +18 °C to -3 °C and the mean of the warmest month is 22 °C. On average, rainfall indices are 1,400 mm to 1,500 mm per year (Maack, 2002).

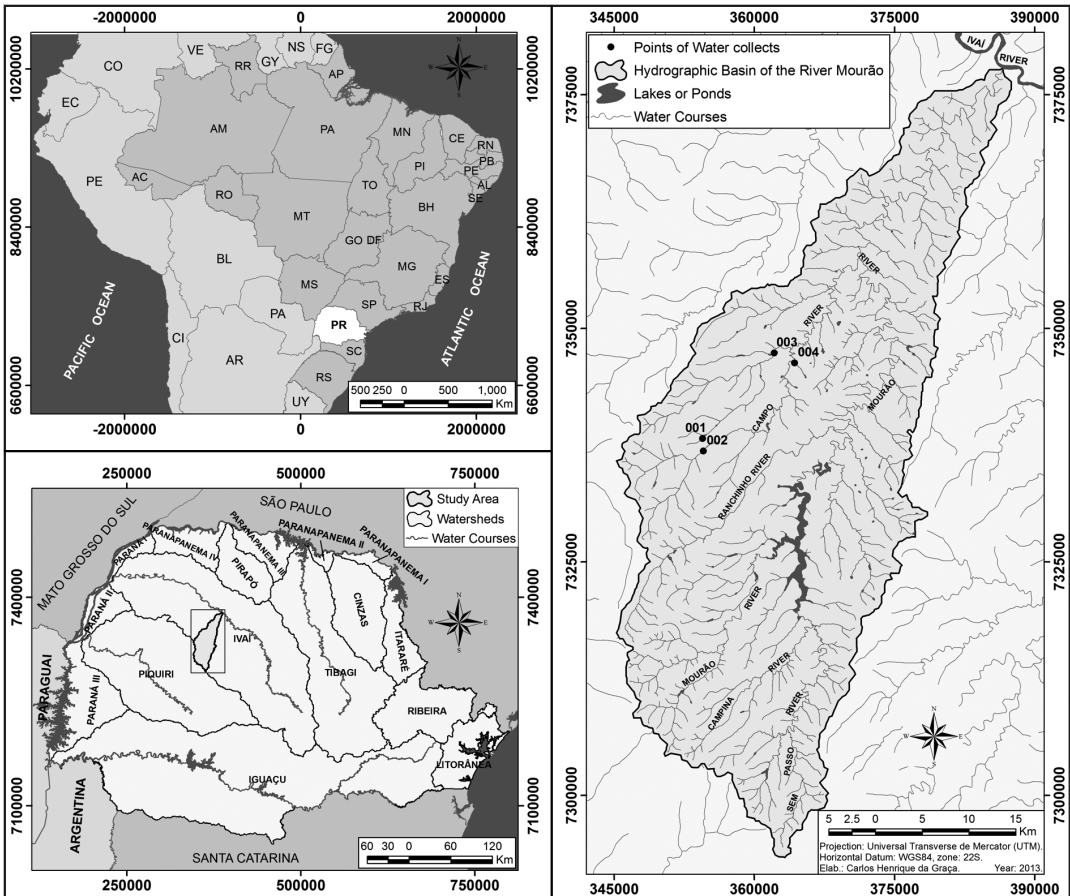


Figure 1. Location of Mourão River basin, in Paraná State, Brazil and sampling sites (P1, P2, P3 and P4) in the area of study.

2.2. Sampling sites

Four sites were chosen for water sampling in the Mourão River basin - P1 and P3 – Km 119 River; P2 and P4 – Campo River, based on mapping and field researches, near urban and rural areas, covering the rivers Km 119 and Campo (Figure 1). Sites for sample collection, their respective geographical coordinates and locations on the Campo River basin are shown in Table 1.

Monthly samplings were performed from November 2012 to November 2013, totaling 12 collections. Water samples were collected about 10 cm below the surface, by the morning, and kept on ice until laboratory analysis at the Environmental Engineering Research Center, the Federal Technological University of Paraná, according to procedures in ABNT (1987). The following parameters were determined: pH (4500-H⁺), water temperature (2550), dissolved oxygen (DO, 4500-O), biochemical oxygen demand (BOD_{5,20}, 5210), total nitrogen (TN, 4500-N), ammoniacal nitrogen (4500-NH₃), nitrite (4500-NO₂⁻), nitrate (4500-NO₃⁻), total phosphorus (4500-P), turbidity (T, 2310), total solids (TS, 2540B) and fecal coliforms (FC, 9221) according to Eaton et al. (2005), in triplicate.

The Water Quality Index (WQI) was calculated considering the parameters pH, temperature, T, DO, BOD_{5,20}, TN, P,

TS and TC, since it is used for monitoring water quality of watersheds in the Paraná State by the Water Institute. This index is expressed as a value ranging from zero (0) to one hundred (100), classifying water samples into excellent (91-100); good (71-90), average (51-70), poor (26-50) and very poor (0-25) (Sperling, 2007; Mophin-Kania and Murugesan, 2011) (Equation 1).

$$WQI = \prod_{i=1}^n q_i^{w_i} \tag{1}$$

Where:

WQI = Water Quality Index (value between 0 and 100);
 q_i = sub index score of ith parameter, a value between 0 and 100 obtained from its average curve of quality change according to its concentration or measurement;
 w_i = relative weight (weight factor) of the ith parameter, a value between 0 and 100, assigned according to its importance to the overall quality;
 i = number of the parameter, ranging from 1 to 9 (n = 9, i.e., the number of parameters that compose the WQI is 9).

The results of monitoring the water quality parameters in the rivers Km 119 and Campo were compared to limits

Table 1. Geographical positions of the sampling sites of Mourão River basin, Paraná, Brazil.

Site ID	Locations	Latitude	Longitude	Height (m)
P1	Km 119 river, upstream, urban perimeter of Campo Mourão municipality	24°03'23"	52°25'31,6"	563
P2	Campo river, upstream, close to Campo Mourão municipality	24°04'24"	52°25'49"	562
P3	Km 119 river, downstream, between the municipalities of Campo Mourão and Peabiru	23°28'47,9"	52°21'19,6"	490
P4	Campo river, downstream, close to the ring road of Campo Mourão municipality	23°59'23,8"	52°20'02,2"	480

set by the Conama Resolution 357/2005 (Brasil, 2005) for Class 2 in which the Ivai River basin is classified, according to the Ordinance 19 of SUREHMA (Paraná, 1992).

2.3. Data analysis

Data collected were analyzed with descriptive statistics, comparing measures of central tendency and dispersion, using statistical inference and a significance level of 5%. Statistical inference was carried out by parametric ANOVA. Tukey's post hoc test was used to compare the means. Data of monitoring are presented in line charts and WQI results with box plots, which allow observing the central tendency and variability of the sample data. In this, it was included the median (50% percentile), the lower (25% percentile) and upper (75% percentile) quartiles and the measurement of the dispersion of the data, as the minimum and maximum values.

3. Results and Discussion

In general, values of physical-chemical parameters increased from upstream (P1 and P2) towards downstream (P3 and P4) sites of the rivers Km 119 and Campo, respectively. ANOVA revealed no difference for the mean results of pH (p-value 0.8393) and temperature (p-value 0.8393) between collected samples. The smallest variation was 0.3 (7.2-6.9) in the mean pH value between P4 and P2 and 0.1 (22-21 °C) in the mean temperature between P1 and P3 and P2 and P4. Maximum values were 9.0 at P2 and 8.4 at P4 (var. 0.6), and 26 °C at P2 (var. 2 °C) and 24 °C at P4. However, maximum pH values at sites of the Campo River are within the range (6.0-9.0) set forth by the Conama Resolution 357/2005 (Brasil, 2005) for Class 2.

The minimum pH was 5.4 at P3, which may indicate insufficient buffering capacity to maintain the environment in balance due to disposal of industrial effluents and sewage downstream of Campo Mourão municipality into the Km 119 River. The trend to acidity was associated with organic matter decay by Blume et al. (2010) (6.8-7.3) in the Sinos River basin (Rio Grande do Sul State); Siqueira et al. (2012) in the Parauapebas River basin (Tocantins State); Tarossi et al. (2006) (6.9-7.1) and Lima et al. (2005) (5.5-7.0) in the Jaguari Mirim River basin (São Paulo State). Figure 2 shows the turbidity values of water samples from the sites P1, P2, P3 and P4.

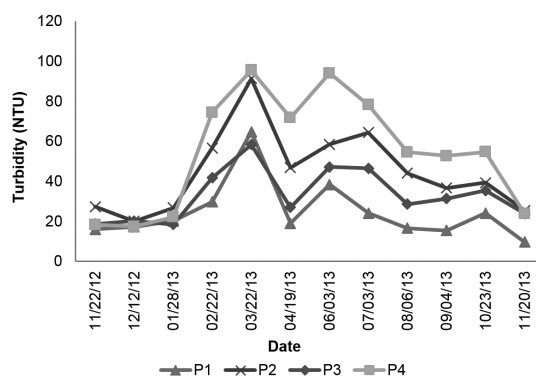


Figure 2. Variation in turbidity (NTU) of water samples from the Km 119 River (P1 and P3) and Campo River (P2 and P4).

Higher values of turbidity at P2 (91.4 NTU) and P4 (95.5 NTU) on March 22nd, 2013 correspond to rainy days, with consequent higher river discharges. In accordance with Crispim et al. (2012), another factor that has contributed to increased turbidity in the Campo River, averaging 30 - 40 NTU, is the transport of sediments from the overflow of retention boxes filled with eroded soil, from compaction and preparation for sowing, towards the slope, and from rill erosion on roadsides by the poor maintenance of rural roads. With the overflow of retention boxes, sediment is no longer retained during rainy periods, leading to increased turbidity in the river water. High turbidity in rivers may raise the cost for water treatment, whether for public supply or other purposes, and affects the aesthetics of rivers (Aprile and Siqueira, 2011).

In the other sites, turbidity values were below the limit of 100 NTU, recommended by the Conama Resolution 357/2005 (Brasil, 2005) for Class 2. ANOVA indicated significant differences for mean turbidity (p-value 0.00394), and the post-hoc test identified the difference between P1 and P4, with higher variation, 30.2 NTU (54.8-24.7 NTU). Maximum values exhibited a slightly greater variation of 30.8 NTU, from P4 (95.5 NTU) to P1 (64.7 NTU) (Table 2).

There was an increase in average BOD_{5,20} from upstream towards downstream, P2 to P4 (3.2 to 3.7 mg/L) in the Campo River, and more pronounced from the P1

Table 2. Results of the statistical tests applied to the data obtained in the monitoring of physical-chemical parameters and WQI.

Parameter	P1			P2			P3			P4						
	Aver.	Max	SD	Aver.	Max	SD	Aver.	Max	SD	Aver.	Max	SD				
T	24.7	64.7	14.68	44.8	91.4	20.1	33.1	58.4	18.5	12.9	ns	54.8	95.5	17.5	28.86	> 1
BOD _{5,20}	6.0	8.0	2.0	4.0	7.0	1.0	3.0	8.0	1.0	2.0	ns	3.0	7.0	1.0	2.0	ns
FC	1,348	5,022	1,718	2,413	9,955	451	9,920	29,409	402	9,998	ns	7,326	29,409	199	7,943	ns
TN	1.7	4.3	0.7	1.5	3.8	0.9	5.7	10.6	2.4	2.9	<3	2.5	6.0	1.6	1.2	<3
AN	1.3	3.4	0.6	1.1	3.4	0.6	3.5	9.0	1.1	2.1	<3	1.6	5.0	0.6	0.9	<3
N-NO ₃	0.2	0.4	0.1	0.3	0.5	0.1	2.0	5.3	0.6	1.6	<3	0.7	1.2	0.4	0.2	<3
TP	0.18	0.37	0.09	0.10	0.19	0.03	0.05	0.23	0.01	0.06	ns	0.09	0.19	0.03	0.05	ns
TS	68	97	24	70	136	21	40	64	16	15	ns	69	117	42	22	ns
WQI	60	67	51	60	73	51	74	88	62	9	>4	68	80	57	7	<1; <2

T – turbidity (NTU); DBO_{5,20} – biochemical oxygen demand (mg/L); FC – fecal coliforms (MPN/100 mL); TN – total nitrogen (mg/L); AN – ammoniacal nitrogen (mg/L); N-NO₃ – nitrite (mg/L); P – total phosphorus (mg/L); TS – total solids (mg/L); WQI – water quality index; Ave – average value; Max- maximum value; Min – minimum value; SD – standard deviation; ns – significant differences for greater (>) or lesser (<) in the mean results at the site analyzed; ns – no significance.

to P3 (3.2 to 5.6 mg/L) in the Km 119 River (Figure 3). This increase may be related to contamination of water bodies by the disposal of effluents from sewage treatment plants - Km 119 and Campo, which serve more than 69,000 inhabitants in the urban area of the municipality of Campo Mourão. Higher BOD_{5,20} values were observed at P3 (downstream) in the Km 119 River, 66% of these results were above the limit of 5.0 mg/L of the Conama Resolution 357/2005 (Brasil, 2005), indicating a contamination point due to sewage discharge. The other sites remained in compliance with the legislation in 83% of samples.

ANOVA detected significant differences for mean values of BOD_{5,20} between analyzed samples (p-value 0.011) and the post-hoc identified the difference between P1 and P3, i.e., upstream and downstream of the Km 119 River, respectively. The variation in the mean BOD_{5,20} between P1 and P3 was 2.5 (5.6-3.2 mg/L) (Table 2).

Fecal coliforms in water indicate contamination by warm-blooded animals or sewage. The presence of fecal coliforms was observed in all samples (Figure 4).

It is important to emphasize the high count of fecal coliforms in samples of P3 (9,920 MPN/100 mL) and P4 (7,326 MPN/100 mL), reflecting the contamination of water of the rivers Km 119 and Campo, respectively, which can be related to the growing urbanization and lack of infrastructure in the region. At these sites, sewage is treated to secondary level, by biological processes, without including disinfection.

Higher values of fecal coliforms were verified on July 3rd, 2013 at P3 (23,000 MPN/100 mL upstream of Km 119 River) and P4 (29,000 MPN/100 mL, upstream of Campo River), which can be directly related to the discharge of sewage and runoff containing fecal material deposited in the drainage area. It is important to highlight a daily rainfall of about 43 mm recorded in the period from February 29th to March 2nd, 2013. At the site P3, turbid visual aspect and unpleasant odor were noticed in the water during the collection of samples.

Regarding the mean values of fecal coliforms, significant differences were evidenced between P1 and P3, according to ANOVA (p-value 0.0086) and post-hoc test, with higher values at P3 (Table 2).

The results of fecal coliforms indicate the poor quality of water in the Km 119 and Campo rivers at the sites evaluated, from 1,348 to 9,920 MPN/100 mL and from 2,413 to 7,326 MPN/100 mL (upstream to downstream). These values were superior in 16.7%, 41.7%, 83.3% and 91.7% at P1, P2, P3 and P4, respectively, relative to the limit of 1,000 MPN/100 mL set by the Conama Resolution 357/2005 (Brasil, 2005). Likewise, Rocha et al. (2006) found values 63% higher than the standard in a rural area; Siqueira et al. (2012) recorded values from 200 to 1,300 MPN/100 mL in an urban area.

Figure 5 illustrates the temporal variation of dissolved oxygen (DO), from 5.86 to 9.3 mg/L, 7.6 to 9.3 mg/L, 5.8 to 9.4 mg/L and 7.0 to 9.2 mg/L at P1, P2, P3 and P4 sites, respectively, that is, above the limit of 5.0 mg/L of the Conama Resolution 357/2005 for Class 2 (Brasil, 2005).

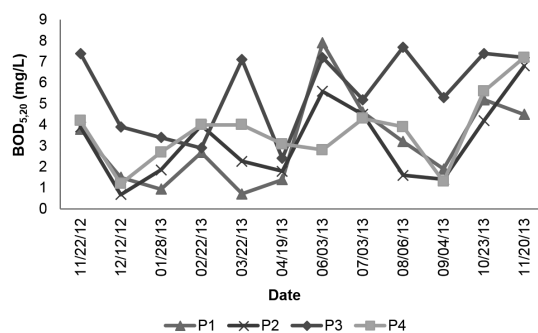


Figure 3. Profile of biochemical oxygen demand (BOD_{5,20}) concentration at the sampling sites investigated in the Km 119 River (P1 and P3) and Campo River (P2 and P4).

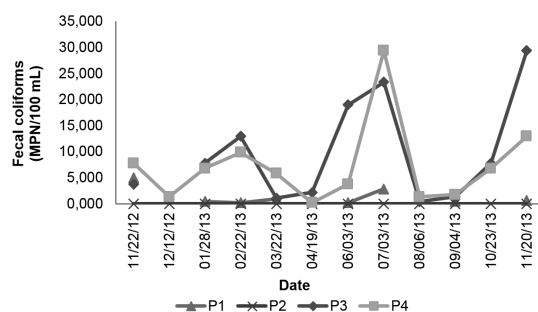


Figure 4. Profile of fecal coliforms (MPN/100 mL) at the sampling sites investigated in the Km 119 River (P1 and P3) and Campo River (P2 and P4).

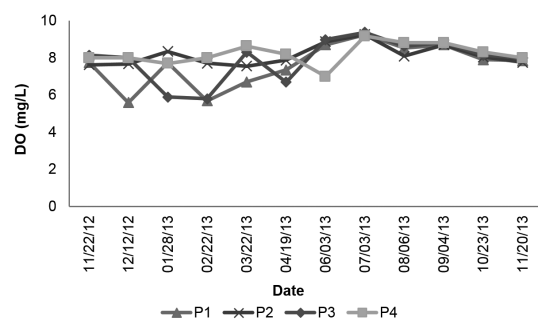


Figure 5. Temporal variation of dissolved oxygen (mg/L) of water samples from the Km 119 River (P1 and P3) and Campo River (P2 and P4).

The high concentration of DO is explained by the rocky bottom of the rivers, which causes greater turbulence and consequent increased transfer of oxygen at the air-water interface. Villwock et al. (2013) ascribed the high values to the lentic period (low water flow) of the water body in the Campo River basin, and to the mean temperature of 22°C. The results are similar to those registered by Silveira et al. (2003) of 5.54 mg/L, Brites and Gastaldini (2007) and Lima and Medeiros (2008) of 5.0 to 8.2 mg/L in urban and rural micro basins.

The mean variation between P1 and P3 was 3.1% in the Km 119 River and 1.11% between P2 and P4 in the Campo River, with upstream values lower than those in downstream.

Maximum values of nitrite were below 1.0 mg/L recommended in the Conama Resolution 357/2005 for Class 2 (Brasil, 2005) at the sites P1 and P2 (upstream) in the rivers Km 119 (0.4 mg/L) and Campo (0.5 mg/L), respectively (Figure 6). Blume et al. (2010) observed similar concentrations in an urban basin. The value of 1.0 mg/L is also recommended as maximum allowed by the Ordinance 2914/2011 of the Ministry of Health (Brasil, 2011).

There was an increase in nitrite concentrations at P3 and P4, downstream of the rivers, to maximum values of 1.2 mg/L and 5.3 mg/L, respectively, suggestive of partial decomposition of organic matter, excessive discharge from water treatment plant or industrial pollution. Nitrite in polluted waters may indicate the presence of nitrate reducing bacteria, under anaerobic conditions (Galdino and Trombini, 1985).

The highest value of nitrate was 0.7 mg/L at P3 (downstream) in the Km 119 River, followed by 0.6 mg/L, 0.6 mg/L and 0.5 mg/L at P1, P2 and P4, respectively (Figure 7), that is, inferior to 10.0 mg/L, standard of the Conama Resolution 357/2005 for Class 2 (Brasil, 2005) and in the Ordinance 2914/2011 of the Ministry of Health (Brasil, 2011). Similar results were observed by Madruga et al. (2008) from 1.89 to 4.21 mg/L, Romitelli and Paterniani (2007) from 7.5 to 15 mg/L and Medeiros et al. (2008) from 0.1 to 1.0 mg/L in urban and rural micro basins.

Water samples from the site P3 (upstream) in the Km 119 River showed the highest values of ammoniacal nitrogen (Figure 8) and total nitrogen (9.0 mg/L and 10.6 mg/L on July 3rd, 2013, respectively, Figure 9). pH values of the samples collected on this day was 7.28 for P3 and ammoniacal nitrogen exceeded the maximum value of 3.7 mg/L for pH ≤ 7.5 of the Conama Resolution 357/2005 for Class 2 (Brasil, 2005) and of 1.5 mg/L of the Ordinance 2914/2011 of the Ministry of Health (Brasil, 2011). The presence of ammoniacal nitrogen may be related to raw sewage, recent pollution and intermediate stage of pollution (Sperling, 2005).

The results of ammoniacal nitrogen observed herein are higher than those found by Romitelli and Paterniani (2007) of 0.0001-4.0 mg/L, Medeiros et al. (2008) of 0.08-0.2 mg/L and similar to those of Lima and Medeiros (2008) of 2.0-5.0 mg/L in urban and rural micro basins. Values of total nitrogen were higher than those registered by Siqueira et al. (2012) (0.12 and 0.33 mg/L).

There is no limit set for total nitrogen in the Conama Resolution 357/2005 for Class 2 (Brasil, 2005), but the § 3 of Article 10 describes that the value of total nitrogen (after oxidation) should not exceed 2.18 mg/L for lotic environments in the reference flow in Class 2, when nitrogen is limiting for eutrophication under the conditions set by the environmental agency.

According to ANOVA, there were no significant differences for mean nitrate (p-value 0.6542), but rather

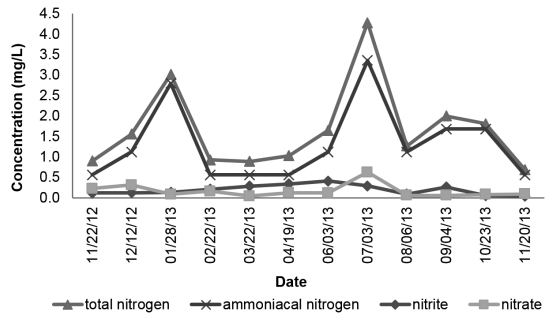


Figure 6. Temporal variation of total nitrogen, ammoniacal nitrogen, nitrite and nitrate (mg/L) of water samples from the Km 119 River (P1, upstream).

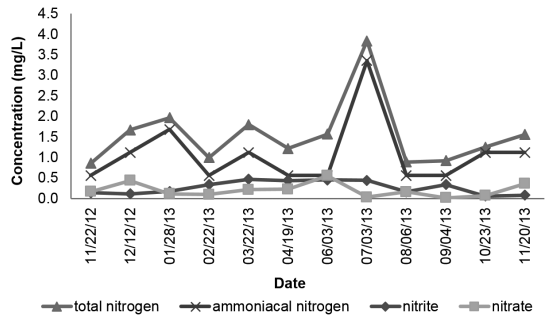


Figure 7. Temporal variation of total nitrogen, ammoniacal nitrogen, nitrite and nitrate (mg/L) of water samples from the Campo River (P2, upstream).

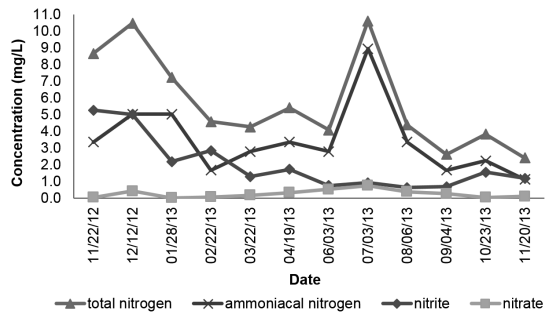


Figure 8. Temporal variation of total nitrogen, ammoniacal nitrogen, nitrite and nitrate (mg/L) of water samples from the Km 119 River (P3, downstream).

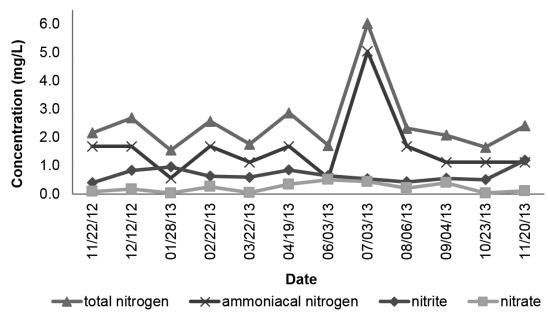


Figure 9. Temporal variation of total nitrogen, ammoniacal nitrogen, nitrite and nitrate (mg/L) of water samples from the Campo River (P4, downstream).

for total nitrogen (p-value 0.0001), ammoniacal nitrogen (p-value 0.00031) and nitrite (p-value 4.01E-06). For total nitrogen, the post-hoc test indicated that the mean difference of 4.0 mg/L occurred between P1, P2 and P4 in relation to P3 with greater variation (6.0-2.0 mg/L) (Table 2). Maximum values showed a greater variation of 5.0 mg/L from P3 (11.0 mg/L) to P1, P2 and P4 (4.0, 4.0 and 6.0 mg/L, respectively). In relation to ammoniacal nitrogen, the post-hoc test identified a mean difference of 2.4 mg/L between P1, P2 and P4 relative t P3, with greater variation (3.5-1.1 mg/L) (Table 2). Maximum values showed a greater variation of 5.6 mg/L from P3 (9.0 mg/L) to P1, P2 and P4 (3.4, 3.4 and 5.0 mg/L, respectively). Considering the nitrite, the post-hoc indicated that the mean difference of 1.8 mg/L occurred between P1 and P3 with greater variation (2.0-0.2 mg/L) (Table 2). Maximum values exhibited a greater variation of 4.9 mg/L from P3 (5.3 mg/L) to P1 (0.4 mg/L).

Moreover, in Figure 10 it can be seen an increase in mean concentration of total phosphorus from upstream towards downstream, from P2 to P4 (0.09 to 0.10 mg/L) in the Campo River, and more sharply from P1 to P3 (0.05 to 0.18 mg/L) in the Km 119 River. Approximately 83% of these results were higher than the limit of 0.1 mg/L of the Conama Resolution 357/2005 (Brasil, 2005) for Class 2 in lotic environment. The results indicate points of contamination, probably due to the disposal of effluents of sewage treatment plants, Km 119 and Campo wastewater treatment plants, in the urban area of the municipality of Campo Mourão and fertilizers used in agricultural activities in the rural area of the basin.

The input of phosphorus in aquatic environments occurs mainly by erosion, punctual discharges of effluents contaminated with these elements, leaching of primary minerals, dissolution of soil compounds and organic matter decay. Moreover, the presence of dumps may be the origin of this element in excess in waters (Sperling, 2005). Rainfall may increase the phosphorus concentration in the water body via runoff and leaching, but also cause dilution and consequent decrease due to increased flow (Ellison and Brett, 2006). The decrease in phosphorus concentration was not observed as a function of rainfall,

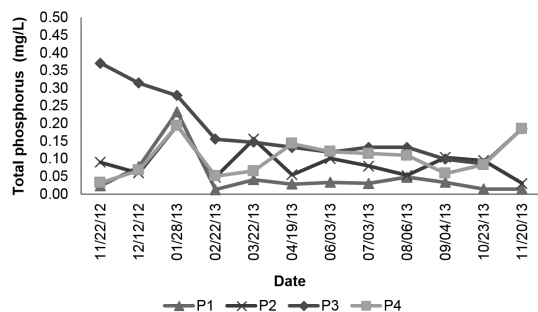


Figure 10. Temporal variation of total phosphorus (mg/L) of water samples from the Km 119 River (P1 and P3) and Campo River (P2 and P4).

once phosphorus concentrations varied in the sampling days with such event.

At the P1, upstream of P3, the non-attendance of the regulation resulted in 8%, corroborating the greater contamination downstream of this site in the 119 km River, followed by 8% at P2 and 50% at P4 in the Campo River. In Table 2, ANOVA revealed significant differences for total phosphorus (p-value 0.0003) and the post-hoc test indicated difference between P1 and P3 with greater variation of 0.13 mg/L (0.18-0.05 mg/L). Maximum values exhibited a greater variation of 0.18 mg/L from P3 (0.37 mg/L) to P1 (0.19 mg/L). Madruga et al. (2008) reported mean values of total phosphorus of 0.01-0.11 mg/L upstream, and 0.02-0.19 mg/L; Borges et al. (2003) of 0.01-0.07 mg/L; Medeiros et al. (2008) of 0.1-1.0 mg/L in urban basins.

Regarding total solids, higher values were verified at P2 (117 mg/L) on June 3rd, 2013 and P4 (136 mg/L) on March 22nd, 2013, corresponding to rainy days with higher river discharges, compared to the other days (Figure 11). As previously emphasized, the presence of sediments from the overflow of retention boxes and from rill erosion on roadsides by the poor maintenance of rural roads leads to increased concentration of total solids in the river water in rainy days (Crispim et al., 2012). Besides that total volatile solids (TVS) predominated in 56%, 60%, 56% and 64% and total fixed solids (TFS) in 44%, 40%, 44% and 36% of the samples. This behavior is associated with the occurrence of organic matter in rivers. Bregunice et al. (2011) and Machado et al. (2007) found similar results when evaluated water quality in urban basins.

In Table 2 are listed the results of ANOVA that indicated significant differences in results of total solids (p-value 0.0086). The post-hoc test identified the difference between P1 and P3, with greater variation of 28 mg/L (68-40 mg/L). Maximum values exhibited a greater variation of 72 mg/L from P4 (136 mg/L) to P1 (64 mg/L).

Figure 12 shows the reduction in mean values of WQI in the Km 119 River, from 74 to 60 (P1 and P3), and in the Campo River, from 68 to 60 (P2 and P4), confirming what was previously discussed for each parameter given the influence of urban (sewage and industrial effluents) and rural (leaching, erosion, runoff) contributions, from

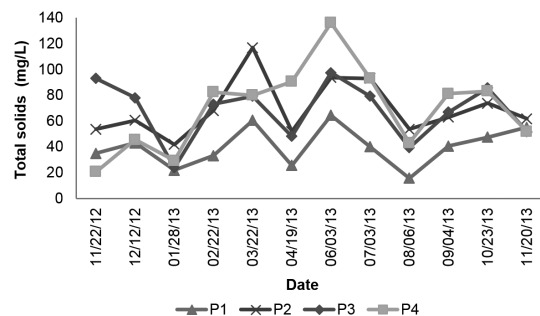


Figure 11. Temporal variation of total solids (mg/L) of water samples from the Km 119 River (P1 and P3) and Campo River (P2 and P4).

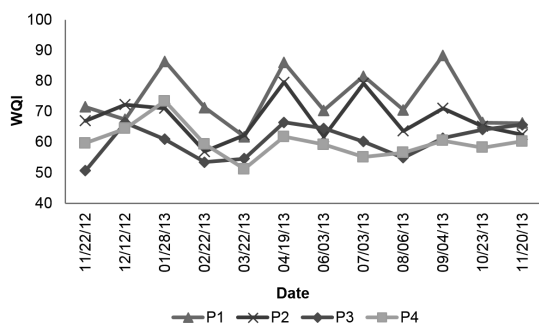


Figure 12. Variation of WQI of water samples of the Km 119 River (P1 and P3) and Campo River (P2 and P4).

upstream towards downstream. The median ranged from 61 to 71, with minimum of 51 at P3 and P4, and maximum of 88 at P1; in other words, the water quality of the rivers varied between average and good, according to WQI classification.

Upstream in the Km 119 River, the WQI resulted in 75% of samples below 83 (3rd quartile); 25% of samples above 67 (1st quartile) and 50% of samples in the range 67-83 (P1); and downstream, at the site P3, resulted in 75% of samples below 65 (3rd quartile); 25% of samples above 55 (1st quartile) and 50% samples in the range 55-65. The values classified the waters of this river as average.

The same classification was observed in the Campo River, with 75% of samples below 71 (3rd quartile); 25% of samples above 62 (1st quartile) and 50% samples in the range 62-71, at the site P2 (upstream); and 75% of samples below 61 (3rd quartile); 25% of samples above 67 (1st quartile) and 50% of samples in the range 58-61 at the site P4 (downstream).

Significant differences were verified for WQI (p-value 0.0001) by ANOVA (Table 2), with differences between P1 and P3, and greater variation of 14 (74-60) by the Tukey's post-hoc test. Maximum values showed a slightly greater variation of 21 from P1 (88) to P3 (67).

4. Conclusions

The behavior of the parameters revealed a higher degree of deterioration in water samples from the sites downstream in the 119 km and Campo Rivers in the Campo River basin, mainly due to the significant influence of rural and urban human activity in this area.

High concentrations of organic matter, fecal coliforms and total phosphorus indicate a deficit of sanitation in the basin, probably due to lack of tertiary treatment for removal of these pollutants in urban areas, and basic sanitation in rural areas.

The results of the Water Quality Index for the rivers Km 119 and Campo indicate that their waters can be classified as of average quality, in 71%, and good quality in 29% of the evaluated sites. The reduction in water quality may be associated with pollution by sewage and

agro-industrial effluents, according to the greater influence of the parameters aforementioned.

The assessment of water quality on the basis of monitored parameters and WQI demonstrates the need to implement measures of urban and rural planning in the region to improve environmental preservation.

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