Evaluation of the aquatic life quality of the Floriano river in Maringá-PR

Avaliação da qualidade da vida aquática do Ribeirão Floriano em Maringá-PR

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Abstract

With the urban and social development of cities, residents who live in the vicinity of streams and valleys begin to suffer the consequences of the continuous release of sewage. The objective of this work was to evaluate the water quality of Floriano river, located in the Maringá-PR city. For that, four points, denoted by P_1, P_2, P_3 and P_4, were chosen. For COD analysis, all samples showed the same concentration, being less than 15 mg L^{-1}, however, in relation to BOD_5 in the summer period, the points P_2, P_3 and P_4 were within the expected limit of 2.0 mg L^{-1} for Class II surface water, according to Brazilian legislation. Regarding the analysis of the Escherichia coli count, the highest values found for the biological contamination of the stream were at points P_2 and P_3, equivalent to 2000 CFU/mL and 424 CFU/mL, respectively, in the spring period. These two points are located close to industrial laundries that may be associated with the release of effluents from these companies. In the analyses, high concentrations of copper (Cu), aluminum (Al) and nickel (Ni) were determined, showing an equitable distribution of human action throughout the course of the stream. These results suggest the need to implement environmental monitoring programs in surface waters in the Maringá city rivers.

Keywords: Heavy metals; pesticides; physicochemical analyses; chlorophyll.

Resumo

Com o desenvolvimento urbano e social das cidades, os moradores que residem nas proximidades de riachos e vales passam a sofrer as consequências do lançamento contínuo de esgoto. O objetivo deste trabalho foi avaliar a qualidade da água do Ribeirão Floriano, localizado no município de Maringá-PR. Para tanto, quatro pontos, denotados por P_1, P_2, P_3 e P_4, foram escolhidos. Para a análise de DQO todas as coletas realizadas apresentaram a mesma concentração, sendo inferior a 15 mg L^{-1}, porém, em relação ao DBO_5 no período do verão os pontos P_2, P_3 e P_4 mostraram-se dentro do limite esperado, 2.0 mg L^{-1}, para águas superficiais de Classe II, de acordo com a legislação. Em relação a análise da contagem de Escherichia coli os maiores valores encontrados, para a contaminação biológica do ribeirão, foram nos pontos P_2 e P_3, equivalentes a 2000 UFC/mL e 424 UFC/mL, respectivamente, no período da primavera. Estes dois pontos estão localizados próximos a lavanderias industriais que podem estar associados a lançamento de efluentes advindos destas empresas. Nas análises, foi determinado concentrações elevadas de cobre (Cu), alumínio (Al) e níquel (Ni), evidenciando uma distribuição equitativa da ação antrópica em todo o curso do ribeirão. Estes resultados sugerem a necessidade da implantação de programas de monitoramento ambiental em águas superficiais nos rios do município.

Palavras-chave: Metais pesados; pesticidas; análises físico-químicas; clorofila.

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Introduction

Due to population growth and the consequent increase in environmental pollution and degradation of natural resources, water, the source of life, is becoming a limited resource (MENDES; CHAVES; CHAVES, 2018). Environmental pollution is caused by various reasons, including: deforestation, lack of soil conservation, silting, plantations, road construction, urban expansion, irregular land use and occupation, as well as the introduction of agricultural chemical waste emissions and their packaging (CARVALHO *et al.*, 2015; PRAT; MUNNÉ, 2000).

The study of surface and groundwater quality and pollutants is an important tool for environmental monitoring, especially in the conservation and protection of bodies of water for drinking and sewage (BASSO; CARVALHO, 2017).

Monitoring various water quality parameters (physical, chemical, and microbiological) over time can evaluate land use and land cover conditions related to watersheds (ANDRIETTI *et al.*, 2016). These variables are compared to parameters established by current legislation, which enable the classification of water bodies. In Brazil, the classification of water is defined by the National Council on the Environment (CONAMA, 2005).

The Hydrological Basin of Ivaí, one of the mainsprings of Paraná, has a total area of 36,540.00 km^2, corresponding to approximately 19% of the area of the state, the Floriano stream in Maringá, is a sub tributary of the Pinguim stream, which has its mouth in the Ivaí River, its study and evaluation of environmental conditions provide reliable information for the public and private authorities to act directly in the preservation of this important spring (PARANÁ, 2010).

To preserve the environmental conditions of surface water, it is necessary to evaluate the quality of raw water aiming its use for public supply, through the parameters pH, dissolved oxygen (DO), biochemical oxygen demand (BOD$_5$), turbidity, total dissolved solids (TDS), temperature (T), total phosphate, total nitrogen and fecal coliforms (CETESB, 2018). Therefore, the present study aims to evaluate the water quality index of Floriano river in Maringá-PR through physical, chemical and microbiological analysis from its source to its mouth in Pinguim river.

Materials and methods

Study area

Currently Maringá-PR is the third largest municipality in the state of Paraná, with an estimated population of 436,472 inhabitants and a territory of 487,012 km^2, where it has 83% of the city's sewage treatment volume, occupying the 21st position in the state (IBGE, 2021). Floriano river, in Maringá, is one of the sub tributaries of Pinguim river, which has its mouth in Ivaí river, one of the main springs of Paraná (PARANÁ, 2010).

Four collection points, P$_1$, P$_2$, P$_3$, and P$_4$, described in the Table 1, were defined along the 18.3 km stretch of Floriano river, with its source located near the industrial zone of Maringá, and a large part of its course is located in the rural zone, as can be seen in Figure 1.

Point P$_1$ is located at the source of Floriano river, in the surroundings of the point occurs the predominance of agriculture, with some nearby residences that use this outcrop for supply. Points P$_2$ and P$_3$ were intentionally selected due to the proximity of industrial laundries and agricultural activities. The last collection point P$_4$ was selected due to the predominance of agricultural activities and near this location occurs the junction of Floriano and Pinguim rivers.

Collecting samples

The samples were collected superficially between 15 to 30 cm below the water surface during the summer, winter and spring periods in the year 2021. The days selected for the collections were determined according to the guidance of the National Guide for Collection and Preservation of Samples (CETESB, 2011), which suggests a period of 24 hours without the occurrence of rain preceding the collection. The collections were performed throughout 2021 in three seasons, summer, winter and spring, and in each period collected on the same day for the different points, P$_1$, P$_2$, P$_3$ and P$_4$.

The water samples were collected in 500 and 1000 mL amber flasks, properly sterilized, stored in thermal boxes with ice for preservation of the samples, until they were transported to the Interdisciplinary Laboratory of Biological and Chemical Analysis - LIABQ and Environmental Laboratory - LABSAM, for proper storage and further analysis.

The values obtained for the concentrations of the collection points and months were submitted to statistical analysis of variance (ANOVA).

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Table 1 – Description and geographic coordinates of the collection points at Floriano river - PR

Collection points	Distance between the points (m)	Collection points characteristics	Geographical coordinates		
			Latitude	Length	Height (m)
P$_1$	0	Industrial	23°28'44.73"S	51°59'22.00"W	481.72
P$_2$	3.103	Rural	23°30'14.08"S	51°59'52.97"W	420
P$_3$	5.657	Rural	23°32'17.98"S	52° 1'27.08"W	362
P$_4$	8.680	Rural	23°35'57.35"S	52° 1'52.24"W	320

Source: The authors.

Figure 1 – Collection points located in the Floriano river in the Maringá city - PR
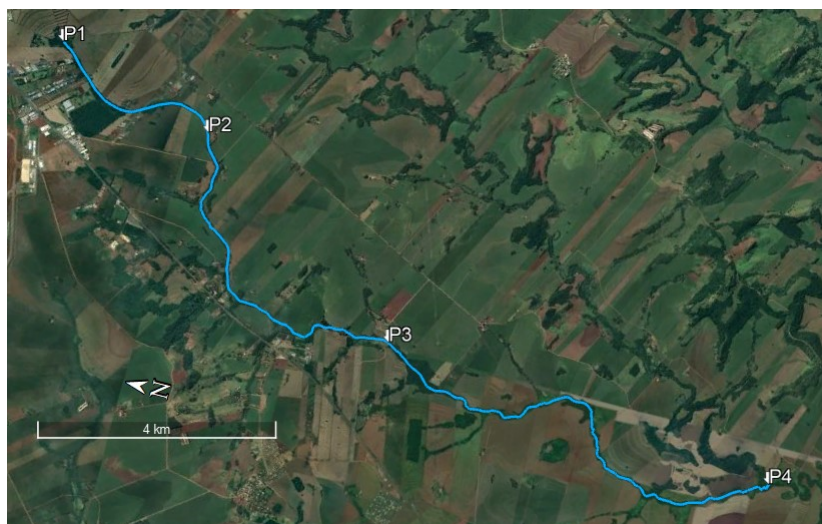
Source: Adapted from Google Earth (2021).

This statistical treatment was performed using the Statistica® v. 7.0 software (STATSOFT, 2007).

Physical, chemical and microbiological analysis

Physical-chemical analysis

The physical-chemical analyses were performed according to methodologies described in the Standard Methods for the Examination of Water and Wastewater, following the methodology of the American Public Health Association (APHA) and the parameters of electrical conductivity (μS cm^{-1}), DO (mg L^{-1}), pH, T (ºC), turbidity (NTU), STD (mg L^{-1}) and oxidation and reduction potential, were performed in situ by means of a portable multiparameter HORIBA U50 probe (APHA, 2012).

Analysis of phosphorus, total nitrogen and metals

The phosphorus analysis was determined by the colorimetric method (APHA, 2012), while the total nitrogen analysis was performed by the classic Kjeldahl Method (IAL, 2008).

To determine the concentration of metals (copper, zinc, cadmium, chromium, nickel, lead), 500 mL of each water sample was transferred to erlenmeyers, reducing the volume to 50 mL under heating, and then adding 10 mL of concentrated nitric acid for acid digestion under heating at 300°C for 4 hours (repeat the procedure 2 times). After this process, at room temperature, 50 mL of distilled water and 5 mL of concentrated nitric acid were added. Then the solution was filtered, collecting the filtrate directly into a 100 mL volumetric flask, completing the volume with ultra purified water, Arium® Mini, Satorius.

The readings of the metal concentrations were performed in an optical emission spectrophotometer employing inductively coupled argon plasma (ICP-OES) iCAP PRO XP, Thermo Fisher. For the analysis, a calibration curve was prepared at the following concentrations: 0.01 mg L^{-1}, 0.05 mg L^{-1}, 0.5 mg L^{-1}, 0.8 mg L^{-1} and 1 mg L^{-1} from the multi-element standard (Sigma-Aldrich). To eliminate the matrix effect, a 5 % nitric acid aqueous solution was used as a blank. The results obtained were compared with the limit concentrations for water and food, established by Brazilian legislation (CONAMA, 2005).

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Determination of surfactants, chlorophyll and biochemical oxygen demand (BOD)

Surfactants analyses were performed using method 5540 C - Standard Methods (suitable for raw, treated, or drinking water) and their concentrations determined by spectrophotometer in the UV-Vis region at 652 nm (APHA, 2012).

Chlorophyll-a (CL) was determined according to the method of Wetzel and Likens (1991) and its readings by spectrophotometer in the UV-Vis region at wavelengths of 665 and 750 nm, applied the calculation method of Lorenzen (1967) for the identification of concentrations in μg L^{-1}.

To determine BOD, the samples were incubated at 20 ºC and then measurements were taken in a laboratory outside Unicesumar, following the procedure described in Standard Methods (APHA, 2012), method 5220 B.

Fecal coliform determination

Fecal coliforms were determined using the most probable number method, which is the estimate of the density of bacteria in a sample calculated from the combination of positive and negative results. The analyses were performed in a laboratory outside Unicesumar, following the procedure described in Standard Methods (APHA, 2012), method 9222 B.

Determination of pesticides and phenols

Extraction and chromatographic analyses of the water samples were performed by preconcentration and purification of the samples by Solid Phase Extraction (SPE), with Bond Elut Nexus cartridge as adsorbent and a Supelco Visiprep SPE vacuum system. The concentration factor for the water samples was 500, as established by the method applied at the Paraná Institute of Technology - TECPAR (APHA, 2012).

For phenols analysis, 15 mL of water samples were transferred to a 20 mL flask, incubated for 30 minutes at 80 °C and analyzed by headspace and GC-MS technique.

The GC-MS analyses were performed on a gas chromatograph (model Agilent 7890B) coupled to a mass spectrometer (model Agilent 5977A MSD), equipped with an Agilent HP-5MS UI column with a 5% phenyl methyl siloxane phase (30.0 m × 250 μm i.d. × 0.25 μm film thickness) and one with an automatic injector (CTC PAL Control). For proper separation of the analytes in the GC-MS system, the following optimized oven temperature programming was performed: initial temperature of 92 °C held for 2.5 min, then ramp of 15 °C min^{-1} to 175 °C held for 13 min, and ramp of 20 °C min^{-1} to 280 °C and held for 15 min. The other conditions of the analysis were: injection volume 1.0 μL, carrier gas flow (He, purity 99.99999) 1.0 mL min^{-1}, electron impact ionization of 70eV, and temperatures of the ionization source 230 °C, the quadrupole 150 °C, the transfer line 280 °C, and the injector 250 °C. Data acquisition was performed by MassHunter software and qualitative analysis of the mass spectra by NIST library 11.

Results and discussions

Physical, chemical and microbiological analysis

Table 2 presents the triplicate mean of the physico-chemical and microbiological results from the four collection points in the summer, winter, and spring periods.

After the collection of samples at different times of the year and in four different points along the Floriano river, Table 2, it is clear that the concentration of DO had higher values than the minimum allowed by the resolution, which requires DO, in any sample, not less than 5 mg L^{-1} O$_2$, and all analyses showed concentration of COD below 15 mg L^{-1}, indicating that these points are part of class II water bodies, responsible for the supply of human consumption after treatment, irrigation, aquaculture and fishing activity (CONAMA, 2005).

The BOD$_5$ concentration values (Table 2) are associated with the amount of organic load present in the sample, in the summer period for P$_2$, P$_3$ and P$_4$, the BOD$_5$ concentration was within the expected limit of 2.0 mg L^{-1} for Class II surface waters (CONAMA, 2005). However, the collection points in the winter and spring periods showed concentrations lower than 2 mg L^{-1}, indicating that these areas receive a load of organic matter well above the self-depuration capacity. As for P$_1$, the BOD$_5$ concentrations lower than the 2 mg L^{-1} limit may be intrinsically related to the location of the point (spring), with a predominance of agriculture and some residences in its surroundings, which may be discharging untreated sewage.

The Escherichia coli count in surface water is essential to verify the degree of microbial contamination of these waters, and the presence of fecal coliforms indicates the risk of occurrence of other pathogenic microorganisms, responsible for the transmission of waterborne diseases, such as typhoid fever, paratyphoid fever, bacillary dysentery and cholera (SALES, 2005).

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Table 2 – Physical-chemical and microbiological values found in the water samples from Floriano river

Periods	Analysis	P_1	P_2	P_3	P_4
Summer					
	DQO (mg L^{-1})	14.98 ± 1.85	13.78 ± 0.067	14.05 ± 0.41	14.75 ± 0.0048
	DBO$_5$ (mg L^{-1})	1.57 ± 0.088	2 ± 2.31	2 ± 0.54	2 ± 0.043
	OD (mg L^{-1})	13.78	14.59	16.27	15.86
	Escherichia coli (UFC m L^{-1})	1 ± 0.42	11 ± 0.52	4 ± 0.145	7 ± 0.136
Winter					
	DQO (mg L^{-1})	13.87 ± 0.31	12.87 ± 0.009	13.08 ± 0.12	12.56 ± 0.003
	DBO$_5$ (mg L^{-1})	1.98 ± 0.11	1.87 ± 0.12	1.75 ± 0.098	1.81 ± 1.67
	OD (mg L^{-1})	20.24	17.03	10.46	24.68
	Escherichia coli (UFC mL^{-1})	1 ± 1.15	11 ± 0.19	4 ± 0.77	3 ± 0.71
Spring					
	DQO (mg L^{-1})	13.25 ± 0.083	12.46 ± 0.13	11.98 ± 0.16	12.57 ± 0.057
	DBO$_5$ (mg L^{-1})	1.87 ± 0.193	1.69 ± 0.25	1.55 ± 0.02	1.72 ± 0.021
	OD (mg L^{-1})	16.76	15.53	12.26	15.41
	Escherichia coli (UFC mL^{-1})	88 ± 0.0175	2000 ± 0.027	424 ± 0.08	353 ± 0.07

Results expressed as average $\pm$ coefficient of variation of the triplicates.
Source: The authors.

According to the Ordinance No. 518/2004 of the Ministry of Health (ANA, [2021]), water must be tested for potability; furthermore, the ordinance recommends that the standard bacterial count should not exceed 500 CFU/mL. The highest values found for biological contamination of the stream (Table 2) were at P_2 (2000 CFU/mL) followed by P_3 (424 CFU/mL) in the spring period, these two points are located near industrial laundries that may be associated with effluent discharge (MANOEL, 2013).

Phosphorus is an important nutrient in biological processes and its excess can cause eutrophication of waters. The highest incidences of phosphorus are in the sanitary sewage discharges, in agricultural activities due to the use of fertilizers and pesticides (ANA, 2013). Figure 2 shows the concentrations of phosphorus in the four sampling points in the three periods of the year.

Through Figure 2 it is possible to verify that the points P_2, P_3 and P_4 in the spring period showed higher concentrations of total phosphorus, these points are close to industrial laundries and agricultural activities, however, according to the maximum tolerance limits established for Class Waters, for phosphorus concentration is 0.1 mg L^{-1}, thus all samples are in accordance with the legislation (CONAMA, 2005).

The analysis of total nitrogen includes ammoniacal nitrogen and organic nitrogen and, like phosphorus, nitrogen is important for the aquatic environment, making it more fertile and enabling greater development of living beings that use it, especially algae, accelerating the process of eutrophication. Figure 3 shows the concentration of total nitrogen obtained at the four sampling points during the three seasons of the year.

The results of total nitrogen analysis for P_1 in summer, winter and spring (0.0467 mg L^{-1}, 0.0506 mg L^{-1} and 0.0545 mg L^{-1}, respectively) did not show great variations in their concentrations and, thus, did not present significant differences (p>0.05) in the samples collected in different seasons of the year. As observed for P, the spring period showed the highest concentrations of total nitrogen in the four sampling sites, with P_3 showing the highest concentrations, due to its location. The values of total N2 varied from (0.047 mg L^{-1} and 0.13 mg L^{-1}), being below the MRL of 2.18 mg L^{-1} (CONAMA, 2005).

Another very important parameter to be analyzed to assess the trophic state of aquatic environments is chlorophyll-a, being one of the pigments responsible for the photosynthetic process representing up to 2% of the dry weight of organic material in planktonic algae (PASSOS; MUNIZ; OLIVEIRA, 2018). Figure 4 shows the results of chlorophyll-a concentration in the four sampling points in different periods.

The corresponding values of chlorophyll-a concentrations represented by Figure 4, refer to a response of the water body to the causative agent, thus indicating the level of algae expansion at the site.

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Figure 2 – Phosphorus concentration at the four sampling points in the summer (blue color), winter (red color) and spring (green color) periods.
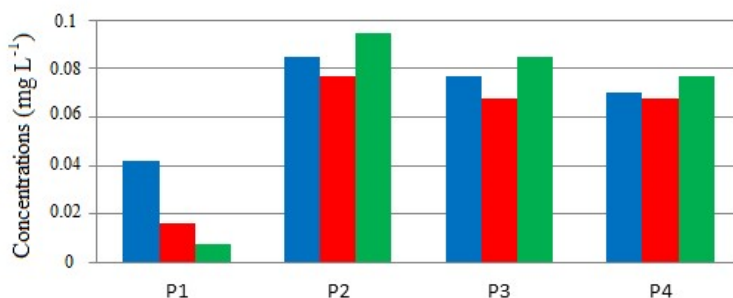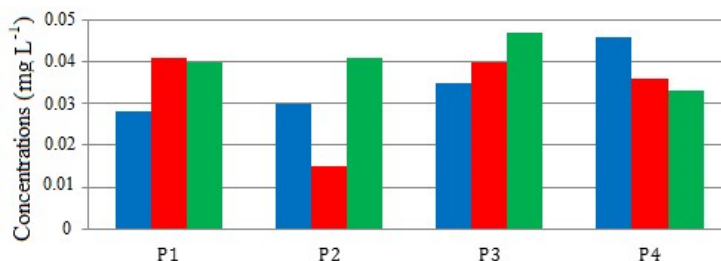

Source: The authors.

Figure 3 – Nitrogen concentration at the four sampling points in the summer (blue color), winter (red color) and spring (green color) periods.
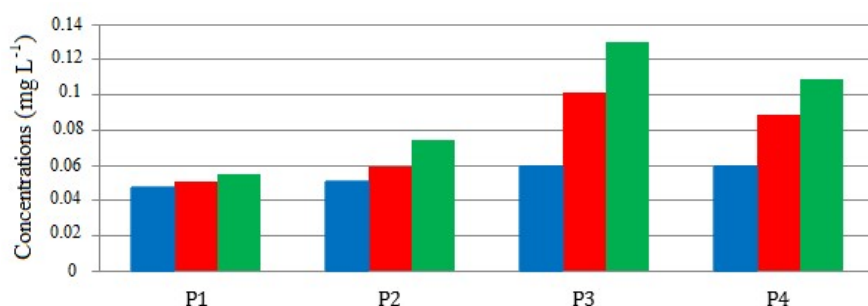
Source: The authors.

Figure 4 – Chlorophyll-a concentration at the four sampling points in the summer (blue color), winter (red color) and spring (green color) periods.
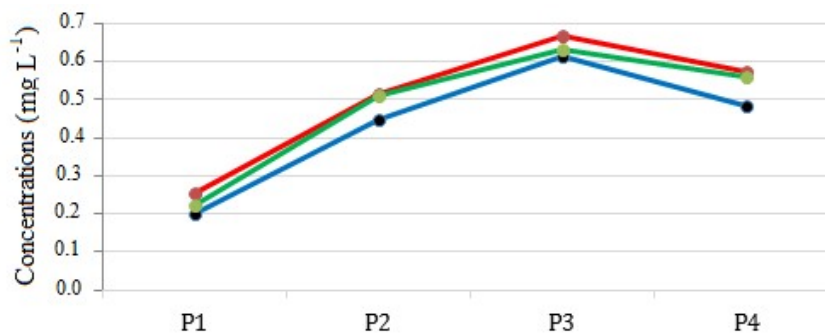

Source: The authors.

However, according to the legislation (CONAMA, 2005) for class waters the chlorophyll level cannot exceed 30 μg L^{-1}, analyzing the results obtained we can verify that the maximum chlorophyll concentration reached was approximately 0.05 μg L^{-1} for P$_3$, in the spring period, indicating low level of algae growth at the site.

Surfactants are amphiphilic compounds, having in their chain a hydrophobic part and a hydrophilic part. The hydrophobic (non-polar) part is a chain that contains between 10 and 20 carbon atoms. The hydrophilic (polar) part can be of two types: that ionizes in water or that does not ionize in water (TONDO, 2010).

Figure 5 presents the surfactants concentrations collected at four different points at different times of the year. According to CONAMA (2005), the MRL for the surfactant concentration substances in freshwater that reacts to Methylene Blue is 0.5 mg LAS/L for class II.

According to the evaluation of surfactants presented in Figure 5, it is possible to verify that all samples analyzed in P$_3$ showed values above the limit determined, the excess values are probably due to the laundry industry activity and agricultural activities that is located near this collection point that release high amounts of synthetic detergents, as well as the use of pesticides causing higher levels (TERSARIOL, 2015).

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Figure 5 – Surfactants concentration at the four sampling points in the summer (blue color), winter (red color) and spring (green color) periods.

Source: The authors.

Metals

Metals are found in natural sources such as rocks, soils, and volcanic activities, transported by leaching processes, erosion, and rainfall runoff (RIETZLER; FONSECA; LOPES, 2001).

Metal pollution can cause serious long-term damage, such as cardiovascular and neurological diseases and even cancer (AGUILLAR *et al*., 2020). Due to the diversity of sources that it is possible to find metals, it is necessary to evaluate the concentration of each metal along the Floriano river, which are shown in Table 3, as well as the limits established by CONAMA (2005).

Iron is a metal found naturally in aquatic environments and soil erosion, as well as indirect sources such as industrial sectors, minerals, household sewage and agricultural inputs. The concentration of iron varied from (0.458 - 35.65 mg L^{-1}), and in P$_4$ in the summer and spring periods there was the highest incidence of this metal due to the region having agricultural activities, thus occurring soil management and consequently driving the carriage of this element along with the sediments to this location. Analyzing the collection periods, in the winter period it was obtained the lowest concentrations of iron stipulated within the maximum residue level (MRL) for class II hydric bodies (CONAMA, 2005).

Manganese is widely found in industrial effluents and runoff from agricultural areas, the concentration of manganese in the analyzed periods varied (0.035 - 1.01 mg L^{-1}), with the highest concentration found in the summer period at P$_3$. In this place are located agricultural activities and industrial laundries, thus, the maximum concentration obtained exceeded the MRL (CONAMA, 2005). Similar behavior can be observed in P$_4$, where in all collections Mn concentrations higher than allowed were found, requiring the control of the region to avoid water consumption, because high concentrations can cause problems to the central nervous system (LIMA; LIMA; FEREIRA, 2013).

The Ni concentrations were within the MRL for P$_1$ in all collection periods, for the other points collected (P$_2$, P$_3$ and P$_4$) the concentrations exceeded the maximum allowable values in all periods. These values above the MRL should be attributed as a result of runoffs, agricultural activities and effluents around the region (CONAMA, 2005).

The Pb concentrations ranged from (0.0015 - 0.010 mg L^{-1}), being within the MRL for class II waters (CONAMA, 2005). Its monitoring is necessary due to the damage it can cause to the central nervous system, in addition to affecting blood and kidney (CDC, 2012). As for Zn concentrations varied (0.011 - 4.40 mg L^{-1}), where in the P$_1$ spring period was found the highest concentration and with a value of more than 2,444 % above MRL for class waters (CONAMA, 2005). Therefore, for the points and periods collected that exceeded the MRL, Table 3, what occurred is related to sites with the presence of agricultural activity and consequently a contamination through fertilizers that are probably rich in zinc, effluent discharge or runoff from agricultural and urban areas (CETESB, 2018).

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Table 3 – Metal content determined in water samples and maximum allowable limits

Sample	Elemen	Summer	Winter	Spring	MRL* mg L^{-1} class II
		Concentration (mg L^{-1})			
P$_1$					
	Al	8.40	2.99	7.94	0.1
	Hg	0.000583	0.000560	0.000551	0.001
	Zn	0.24	0.19	4.40	0.18
	Pb	0.010	0.0047	0.0040	0.01
	Fe	0.45800	1.11	3.40	0.3
	Cu	0.03350	0.010	0.027	0.009
	Mn	0.070	0.059	0.10	0.1
	Ni	0.0062	0.016	0.13	0.025
	Cr	0.0043	0.0068	0.025	0.05
P$_2$					
	Al	8.35	4.08	24.43	0.1
	Hg	0.000561	0.000571	0.000610	0.001
	Zn	0.51	0.052	0.15	0.18
	Pb	0.010	0.0065	0.0021	0.01
	Ni	0.35	0.063	0.31	0.025
	Fe	2.70	1.20	7.72	0.3
	Mn	0.163	0.035	0.293	0.1
	Cr	0.17	0.011	0.593	0.05
	Cu	0.23	0.042	0.011	0.009
P$_3$					
	Al	13.65	3.10	66.52	0.1
	Hg	0.000533	0.000654	0.000535	0.001
	Zn	0.26	0.53	0.50	0.18
	Pb	0.009	0.0034	0.0048	0.01
	Ni	0.027	0.048	0.083	0.025
	Mn	1.01	0.32	0.39	0.1
	Fe	7.55	1.90	14.44	0.3
	Cr	0.021	0.075	0.158	0.05
	Cu	0.035	0.032	0.064	0.009
P$_4$					
	Al	15.65	8.82	90.13	0.1
	Hg	0.000598	0.000617	0.000545	0.001
	Zn	0.011	0.091	0.32	0.18
	Ni	0.099	0.041	0.311	0.025
	Pb	0.0015	0.010	0.0038	0.01
	Mn	0.803	0.266	0.707	0.1
	Fe	17.85	3.7	35.85	0.3
	Cr	0.15	0.010	0.71	0.05
	Cu	0.05034	0.034	0.133	0.009

*MRL = maximum residue level

Source: The authors.

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Therefore, for the points and periods collected that exceeded the MRL, Table 3, what occurred is related to sites with the presence of agricultural activity and consequently a contamination through fertilizers that are probably rich in zinc, effluent discharge or runoff from agricultural and urban areas (CETESB, 2018).

Al is a very abundant metal in the earth's crust, impacting positively on the economy, however, high concentrations in water and ingestion by humans can cause neurological problems (FERREIRA; PIAI; MUNOZ, 2008).

In relation to the points and periods collected the concentration of Al varied from 2.99 - 90.13 mg L^{-1}, all being above the MRL for class II waters (CONAMA, 2005). The spring period showed an increasing increase in aluminum concentration in the points collected, this increase can be attributed to the occurrence of rainfall (acid pH), leading to greater solubility of this metal (FREITAS; BRILHANTE; ALMEIDA, 2001; SANCHES FILHO *et al.*, 2009). Similar behavior was reported by Justus *et al.* (2020).

The Cr concentrations ranged from 0.0043 - 0.71 mg L^{-1}, Table 3, exceeding in its great majority (P_2, P_3 and P_4) the MRL for class waters (CONAMA, 2005). The major source of Cr comes from industrial effluents (FREITAS, 2006). Hg is a global pollutant of great concern due to its wide applicability, mobility and toxicity, which comes from natural and anthropic sources. The results were evaluated according to the Ordinance No. 2914/2011 of the Ministry of Health, which sets the limit of 0.001 mg L^{-1}, analyzing the values obtained, Table 3, it was possible to verify that all samples showed results within the MRL and thus the springs are protected with respect to contamination by total mercury (OLIVEIRA *et al.*, 2011).

Based on the results, it was possible to observe that the methods of detection of metals in hydric bodies exceed the MRL for some elements, being important the environmental monitoring in the surface beds, making it possible to investigate toxic levels of certain elements. Furthermore, high concentrations of Cu and Al were found in all points, P_1, P_2, P_3 and P_4, as well as high levels of Ni in points P_2, P_3 and P_4, showing an equitable distribution of anthropic action throughout the course of the river.

Pesticides and phenols

The monitoring of pesticides, especially in the environment near their application, is an important environmental indicator that guides public policies and control actions (LOPES; ALBUQUERQUE, 2018).

Table 4 presents the pesticides identified and quantified in the collection points throughout the summer, winter, and spring periods. In the analysis, it was possible to identify the following pesticides or their derivatives at the respective sample points: P_1 and P_4: 1,4-dichlorobenzene, Mesitylene and Toxaphene; P_2: 1,4-dichlorobenzene, Mesitylene Toxaphene and Permethrin. P_3: 1,4-dichlorobenzene, Mesitylene, Molinate and Toxaphene.

The presence of substituted benzene hydrocarbon compounds at the collection points may be related to the presence of petroleum derivatives, such as gasoline, as well as to the raw material used in the production of pesticides. These compounds are highly toxic substances used on a large scale in the chemical and petrochemical industries.

The presence of Toxaphene, an organochlorine characterized by its toxicity, persistence and ability to bioaccumulate (OLIVEIRA, 2011). Molinate is a highly toxic herbicide that causes alteration in the reproductive system and cancer (CABRERA; COSTA; PRIMEL, 2008). Furan TCDF is highly toxic because of its neurotoxic effects besides leaving residues in the water and along with Toxaphene its use is prohibited in Brazil. Methyl mercaptan is used in the manufacture of some pesticides (VIEIRA, 2013).

The results obtained emphasize the need for the implementation of environmental monitoring programs in the region, as they contaminate the soil, food and water (surface and groundwater).

Phenols are highly toxic and bioaccumulative substances in the aquatic environment. Due to its high solubility in water, it causes a reduction in the amount of dissolved O_2 and directly affects the aquatic ecosystem, so the monitoring of this compound around steel, textile, pharmaceutical and other regions is important (CUNHA; AGUIAR 2014; SINGH *et al.*, 2020). Of the collection points and periods, only in P_2 (summer and winter) and P_3 (spring) were identified the presence of phenols, as shown in Table 5.

Through the results, see Table 5, only P_2 in the summer period exceeded the MRL of 0.010 mg L^{-1} for class water bodies (CONAMA, 2005). This increase can be attributed to the discharge of waste made by industrial plants located around this point.

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Table 4 – Limit of quantification by the chromatographic method and MRL

HT (min)	Compounds	Pesticides (μg L^{-1})	MRL* μg L^{-1}
3.62	1,4-dichlorobenzene	0.05 - 0.06	0.3
4.29	Mesitylene	0.10 - 0.15	5.0
4.96	Toxaphene	0.15 - 0.50	0.0002 - 0.21
4.52	Mesitylene	0.15 - 0.44	5.0
8.20	Molinate	0.06 - 0.07	6.0
11.60	Methyl Mercaptan	0.09	0.0005 - 0.08
12.76	Furan TCDF	0.04	0.10
24.13	Permethrin I	2.21 - 2.25	20.0

*MRL = maximum residue level

Source: The authors.

Table 5 – Concentration of phenolic substances acquired at the collection points

Periods	Sample	Retention time (min)	Compound	[Phenol] mg L^{-1}
Summer				
	P$_1$	-	-	-
	P$_2$	22.95	2-metoxi-4-(2-propenyl) Phenol	0.0339
	P$_3$	-	-	-
	P$_4$	-	-	-
Winter				
	P$_1$	-	-	-
	P$_2$	23.02	2-metoxi-4-(2-propenyl) Phenol	0.0012
	P$_3$	-	-	-
	P$_4$	-	-	-
Spring				
	P$_1$	-	-	-
	P$_2$	-	-	-
	P$_3$	27.14	2,4-di-t-butyl-nitroPhenol	0.0011
	P$_4$	-	-	-

Source: The authors.

Conclusion

Monitoring the Floriano river region through physical, chemical and microbiological analyses was of utmost importance for the quality of the water in this place, and through the results acquired it is necessary to implement environmental monitoring programs in the region.

A general analysis of the results obtained shows that the water fits in Class III waters, desirable for bathing, but with the presence of pesticides (Toxaphene and methyl mercaptan) outside the MRL and also with high concentrations of the metals Cu, Al and Ni.

Therefore, monitoring is essential to prevent the increase in the concentration of these substances, making it unsuitable for human and animal consumption and for soil and plantation irrigation.

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