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Seasonal assessment of water quality parameters in Mirim Lagoon, Rio Grande do Sul State, Brazil

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Abstract: This paper aimed at to evaluate the qualitative effects of climatic seasonality in a subtropical lagoon, using Discriminant Analysis, as well to identify the most sensitive and responsible parameters for these changes. The Mirim Lagoon watershed is one of the main transboundary basins in South America and is of great economic importance for the region because its waters are used for irrigation of rice fields and for the potable water supply to populations close to it, in this way, these uses may affect the quality of the basin waters. The data used in the study were provided and collected by the Mirim Lagoon Development Agency. Water quality parameters were selected in a five-year database and submitted to statistical tests that demonstrated their distinctions throughout the climatic seasons. The results showed that the parameters temperature, pH, dissolved oxygen, biochemical oxygen demand, total nitrogen and total phosphorus differ statically between the four climatic seasons. Were also identified four discriminative parameters between the seasons, being them dissolved oxygen, biochemical oxygen demand, total nitrogen and total phosphorus. In this way, it can be concluded that the seasonality mainly affects anthropogenic pollution sources such as agricultural activities and domestic discharges.

Key words: discriminant analysis, seasonality, subtropical lagoon, water pollution, water resources

INTRODUCTION

The quality of surface water depends to a large extent on the nature and extent of the impact resulting from the use and coverage of the soil in its environment (Singh et al. 2009). The pollution and wastewater discharges can be considered as deposits of chemical elements, which results in a decrease in the quality of the water (Julien & Shah 2005, Lobato et al. 2008, Anteneh et al. 2017). According to Li et al. (2018a), in a lagoon there are fewer water changes, causing deficiency in their self-cleaning and contributing to a higher nutrients concentration. Basatnia et al. (2018) comment that ponds are affected by the rates of water gains and losses, such as evaporation, precipitation, surface runoff and groundwater inflow, generating changes in their quality parameters.

The quality of surface water bodies is related to natural factors such as hydrological regime and water temperature, besides anthropogenic activities related to soil use and pollutant load (Liu et al. 2016). One of the effects of high water temperatures, together with the presence of high concentrations of nutrients, is the occurrence of cyanobacteria blooms (Adioff et al. 2018).

The waters of Mirim Lagoon are mainly used for irrigation of rice sinks, in addition to the extraction for human consumption of the counties of Pelotas and Rio Grande, acting as a reservoir of freshwater (Oliveira et al. 2015). Coradi et al. (2009) related the occurrence of laminar erosion in the Mirim Lagoon with the withdrawal of vegetation cover in rural areas. The use of synthetic organic compounds by agricultural activity, such as fungicides and herbicides, has a negative influence on water resources, especially those used for public supply (Cabrera et al. 2008). In addition, several factors influence its characteristics such as wind, tides, river discharges, water balance between evaporation, precipitation, and surface heat (Oliveira et al. 2015). Thus, the surface water quality of this water body is negatively impacted by seasonal variations in the concentration of pollutants, being essential knowledge and evaluation of their characteristics for the preservation of natural resources.

This scenario explains the importance of studies in this area, to optimize future policies and monitoring programs, aimed at a more efficient management (Coradi et al. 2009, Duan et al. 2016, Hajigholizadeh & Melesse 2017).

However, the creation of a water quality monitoring system with adequate efficiency is difficult, since it is necessary to identify and measure, as much as possible, the variables that would express the qualitative changes of the water bodies (Jung et al. 2016). The surface water quality data encompasses several parameters, making their analysis complex (Moura et al. 2010).

Multivariate statistics allow reducing the data complexity and discards redundant information, being used to explain correlations between observations. The Discriminant Analysis (DA) technique has been universally used to determine the parameters that discriminate the water quality between the seasons (Boyacioglu & Boyacioglu 2017). According to Gulgundi & Shetty (2018) and Kumar et al. (2018), DA aims to increase the similarity between the group (season) and the variance within it, producing significant results. In this way, the technique is adequate to define the seasonal variation of surface water quality, evidencing its critical and significant parameters, as shown by several studies (Bilgin 2015, Nosrati 2015, Anteneh et al. 2017, Hajigholizadeh & Melesse 2017, El-Mezayen et al. 2018).

Therefore, the aim of this paper was to evaluate the qualitative effects of climatic seasonality in Mirim Lagoon, located in Rio Grande do Sul State, Brazil, as well to identify the most sensitive and responsible parameters for these changes, which may interfere negatively in the quality of the water used to irrigation and human suplly in the region.

MATERIALS AND METHODS

Study site and data acquisition

With a total area of 62,250 km², which 47% is located in the Southern the Rio Grande do Sul State and 53% in Uruguay, the Mirim Lagoon Watershed (MLW) is located between the geodesic coordinates 31°31’ and 34°35’ south latitude and 53°31’ and 55°15’ west longitude (Coradi et al. 2009) (Figure 1). Köppen classifies the climate of the region as subtropical of hot and humid summer of the type Cfa and average temperatures above 22°C in the hottest times and inferior to 18°C in the colder months, the average annual precipitation is of 1,450mm (Alvares et al. 2013).

The watershed in question is one of the main transboundary basins in South America and is of great economic importance for the region because its waters are used for irrigation of rice fields and for the potable water supply to populations close to it, in this way, these uses may affect the quality of the basin waters (Oliveira et al. 2015).

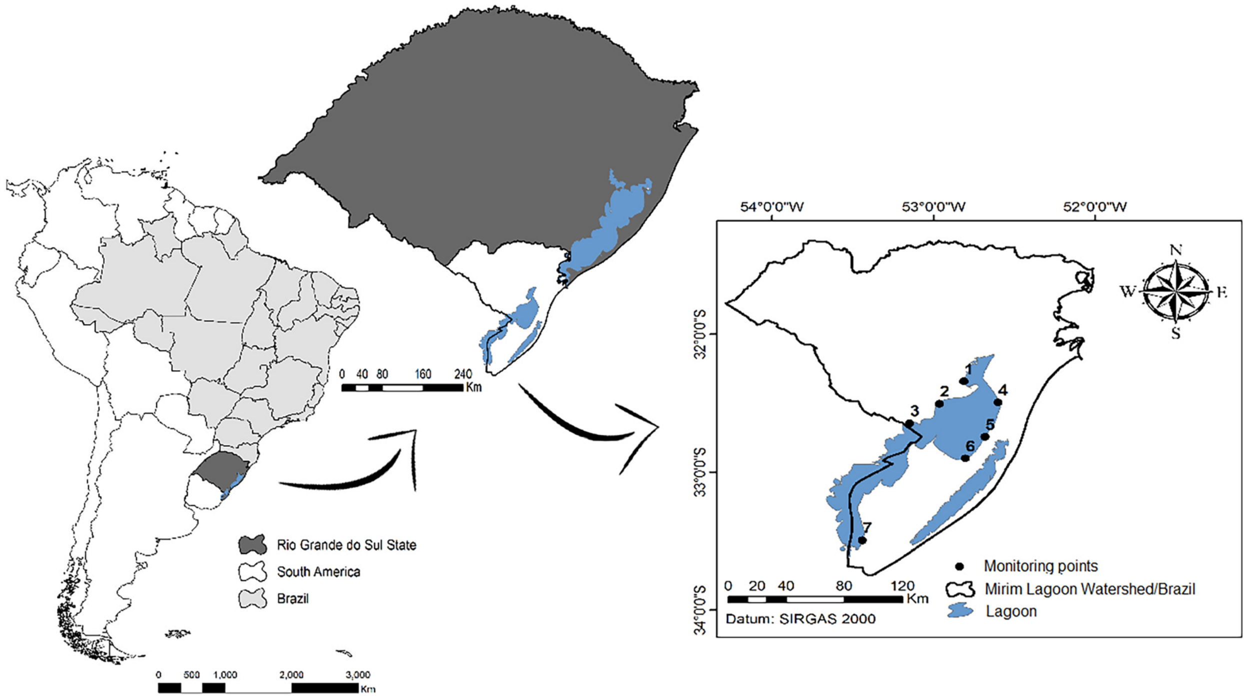

Figure 1. Geographic localization of Mirim Lagoon Watershed and its monitoring points.

The data used in the study were provided and collected by the Mirim Lagoon Development Agency (ADLM 2018), preserving the samples and the analytical protocols according to the methodologies described in APHA (2005). The monthly samples were collected during the period of June 2013 and December 2017, totalizing 33 campaigns in each of the following monitoring points: 1 - Praia do Pontal; 2 - Fazenda Bretanha; 3 - Fazenda São Francisco; 4 - Capilha; 5 - Curral Alto; 6 - Vila Anselmi; e 7 - Porto Santa Vitória. The selected water quality parameters were: temperature (T), turbidity (Tb), pH, electrical conductivity (EC), dissolved oxygen (DO), biochemical oxygen demand (BOD), total nitrogen (TN), total phosphorus (TP) and total solids (TS). The data set was divided in groups between the four seasons of each year: spring (October to December), summer (January to March), autumn (April to June) and winter (July to September).

Data analysis

Statistical analyzes were used to identify the seasonal variation of water quality, based on the qualitative variables analyzed in this study. The data set was subjected to descriptive analyzes (minimum, maximum, mean and standard deviation), box-plot graphs, univariate analysis of ANOVA variance and multivariate discriminant analysis (DA). All statistical analyzes were performed with the aid of IBM SPSS v. 20 software.

The normal distribution of data is an essential requirement for multivariate statistical analyzes because they are only valid if the standard deviations are close to zero (Gulgundi & Shetty 2018). The normality of the data was verified by the Kolmogorov-Smirnov test, based on the descriptive results by the method, which had to be significative $p>0.025$ (2-tailed), according to SPSS.

The descriptive analyzes were applied to systematize the results and to determine if the seasonality interferes with the mean concentrations of the quality variables. Through the box-plot graphs it was possible to indicate the distribution or population format of the data with maximum value, third quartile, median value, first quartile and minimum value; being possible to identify extreme values (Jung et al. 2016).

The univariate analysis of variance (ANOVA) was used to verify the significance between the means or dispersion of the variables within the groups, in other words, if the variables have seasonal temporal differences with significance level of 5% ($p<0.05$), being essential for the adjustment of the model (Colling et al. 2010, Bilgin 2015). The ANOVA was used since there are several independent metrical variables and wide approach of the analysis in recent studies of water quality characterization (Piratoba et al. 2017, Thebaldi et al. 2017, Tormam et al. 2017).

The statistical power of the study was also calculated to validate the results, proving the significant effect of the analysis, based on the database used (Potvin & Schutz 2000). Statistical power is defined by Park & Schutz (1999) as the probability of detecting a significant effect where there is a true effect on the population, assessing whether the analysis is likely to detect a treatment effect. The software used in this paper performed the statistical power calculation by the Pillai's Trace, Wilks' Lambda, Hotelling's Trace and Roy Largest Root methods.

Discriminant Analysis (DA) is part of multivariate statistics and was used to define the water quality parameters that discriminate between the groups. This method is based in dependent (quantitative) and independent (qualitative) variables, which generates the discriminant functions. In this work, DA was applied using the climatic seasons as the dependent variables and the water quality parameters as the independent variables. The resulting function was obtained by the Stepwise method, which is considered one of the most adequate and provides a better adjustment of the variables, as reported in several studies that used the same analysis for space/time evaluation (Aris et al. 2013, Anteneh et al. 2017, Boyacioglu & Boyacioglu 2017, Hajigholizadeh & Melesse 2017).

The Box M test was applied to compare the covariance matrix equality, since more than one metric parameters was used. In order to verify the methods significance, the Wilks Lambda was used, from the normal data distribution (Hair Jr. et. al. 2009), showing the function ability to separate the groups (Hajigholizadeh & Melesse 2017). In other words, this method has as aim generate a function, based in observed data, that better separates the climates seasons (Boyacioglu & Boyaciaoglu 2009).

Sentinel-2, a European Space Agency (ESA) satellite images, was used in the land use and coverage mapping, using a 10m spatial resolution, with a mosaic of six scenes dated 2016. The Maximum Likelihood (MaxLike) was used, which is a supervised method of statistical classification that estimates the class pixels distribution, based on Bayesian statistics (Brasileiro et al. 2016). The MaxLike method is widely used in literature studies, since the user can define sample areas of which class, ensuring a good result precision (Ladwig et al. 2018, Bentes et al. 2017).

RESULTS AND DISCUSSION

Multivariate statistical methods used in water quality studies are highly susceptible to non-normal distributions due to the influence of particularly rare extreme events (Anteneh et al. 2017). Therefore, in this work, water quality parameters were submitted to the normality test

Kolmogorov-Smirnov, confirming the normal distribution ($p>0.025$), as shown in the Table I footer, provided by SPSS software.

Regarding the statistical power of the study, the value of 0.906 was obtained, that is, 90.6%. This result goes according to the convention adopted by studies found in the literature, that the statistical power should be at least 80%, validating the founded results (Jones et al. 2003).

The basic descriptive statistics for all water quality parameters in the four seasons are presented in Table II, and the box-plot graphs, used to explore and graphically interpret the seasonal variations, are presented in the Figure 2.

The pH average values, ranging between 7.37 and 7.94, which are present in fall and spring, respectively, indicated that the Mirim Lagoon's water is strictly alkaline. These values were in accordance with the studies presented by Thebaldi et al. (2017), Basso & Carvalho (2007) and Amâncio et al. (2018), who evaluated the increase of pH with rainy seasons, fact that may be due to the greater dissolved compounds dilution. The EC mean values varied between 116.68 a 139.95 $mScm^{-1}$, being the highest variation in summer and autumn.

The CONAMA N°357/2005 resolution is a document prepared by the Brazilian Environment Ministry in order to classify and determine guidelines for surface water bodies classification and to effluents discharge. Based on this resolution, the pH values fit into class one – since the lower class the better the quality – once they are within the range of 6.0 to 9.0 (Brazil 2005).

The DO variations can occurs seasonably owing to temperature and biological activity. Ojok et al. (2017) founded high DO concentrations in Rwizi River, Uganda, being justified by the photosynthetic activities concentrations increase of aquatic plants and bacteria because

Table I. Kolmogorov-Smirnov normality test result.

	Temperature	Turbidity	pH	Electrical Conductivity	Dissolved Oxygen	Biochemical Oxygen Demand	Total Nitrogen	Total Phosphorus	Total Solids	Organic Matter
Kolmogorov-Smirnov Z	0.807	0.612	0.522	0.391	0.886	0.783	0.444	0.674	0.620	0.455
Asymp. Sig. (2-tailed)	0.533	0.848	0.948	0.998	0.413	0.572	0.989	0.753	0.837	0.986

Table II. Descriptive statistics of water quality samples collected at Mirim Lagoon.

Parameter	Unit	Season	Average	Standard Deviation	Minimum	Maximum
Temperature (T)	°C	Summer	25.90	1.39	24.25	27.93
		Autumn	14.26	2.06	11.69	16.43
		Winter	17.25	1.42	15.64	19.77
		Spring	23.22	1.29	21.02	25.21
Turbity (Tb)	NTU	Summer	45.75	12.28	32.56	69.29
		Autumn	59.53	41.00	22.56	132.77
		Winter	44.86	16.41	23.88	73.46
		Spring	51.39	12.32	33.04	72.01
pH	-	Summer	7.81	0.14	7.61	7.98
		Autumn	7.37	0.29	6.93	7.70
		Winter	7.91	0.23	7.45	8.08
		Spring	7.94	0.11	7.74	8.07
Electrical Conductivity (EC)	mS cm^{-1}	Summer	116.68	22.75	93.97	159.07
		Autumn	135.09	37.20	94.18	197.48
		Winter	139.95	16.26	121.30	168.00
		Spring	131.54	9.09	122.38	144.58
Dissolved Oxygen (DO)	mg L^{-1}	Summer	7.14	0.66	5.80	7.76
		Autumn	7.57	0.39	6.71	7.89
		Winter	7.64	0.24	7.25	7.99
		Spring	6.92	0.38	6.45	7.44
Total Nitrogen (TN)	mg L^{-1}	Summer	1.31	0.41	0.86	1.86
		Autumn	3.09	0.51	2.42	3.81
		Winter	2.09	0.61	1.29	3.23
		Spring	1.67	0.48	1.27	2.49
Total Phosphorus (TP)	mg L^{-1}	Summer	0.61	0.30	0.30	1.19
		Autumn	0.57	0.23	0.32	0.82
		Winter	0.95	0.29	0.47	1.27
		Spring	0.83	0.20	0.49	1.12
Total Solids (TS)	mg L^{-1}	Summer	173.36	17.33	157.43	200.14
		Autumn	182.38	29.62	140.80	220.60
		Winter	172.93	26.85	140.39	220.81
		Spring	184.27	21.56	153.00	221.86
Biochemical Oxygen Demand (BOD)	mg L^{-1}	Summer	1.78	0.47	1.37	2.81
		Autumn	1.42	0.28	1.10	1.81
		Winter	2.54	0.22	2.14	2.81
		Spring	1.74	0.45	1.18	2.47

temperature rises. Therefore, to use DO as an indicator of surface water quality, seasonal variations should be considered. The obtained values, according to Table II, were defined as satisfactory for quality class one in CONAMA resolution since they are greater than 6.0 mgL^{-1} (Brazil 2005). This indicates the good aeration and photosynthesis capacity by the algae in Mirim Lagoon.

An inverse relationship is observed between T and TN, which in the highest temperature averages, found in the summer and spring seasons (25.90°C and 23.22°C, respectively), were found the lowest averages of TN (1.31 mgL^{-1} in summer and 1.67 mgL^{-1} in spring). This fact can be justified by the seasonal influence of water temperature variation on biochemical decay rates (Mikan et al. 2002). The nitrification and denitrification rates decrease with decreasing temperature, because of this, NO_3 and NH_4 are less efficiently removed from the water, so their concentrations remain relatively high. An opposite picture occurs when the water temperature rises, decreasing these compounds concentrations in the water (Anteneh et al. 2017).

According to Vega et al. (1998), the TN rising level is attributed to inorganic fertilizers used in agricultural areas. The study area is characterized by an intense agriculture activity, once their water is captured for rice crops irrigation (Oliveira et al. 2015, Albertoni et al. 2017). In this way, it is possible to relate the TN fall in the water at the end of rice crop, reducing the leaching residues caused by the plantations, as also observed by Tormam et al. (2017) in the same study area and evidenced by Cunha et al. (2013), who evaluated the Cuiabá Lagoon water quality, located in a nearby area.

The TP higher average values were observed in spring and winter seasons (0.83 mgL^{-1} and 0.95 mgL^{-1}, respectively). The phosphorus increasing concentration is related to agricultural activities, due to fertilizer into the water bodies, since it is a necessary nutrient for growth of plants (Sulaiman et al. 2018). Based on the land use and coverage mapping (see Figure 3), these statements can be verified since most of the area around the Mirim Lagoon is occupied by grassy fields and agriculture, mainly of rice cultivation (Fia et al. 2009). Domestic and industrial wastewater rich in phosphorus and other chemicals are released into the water and do not degrade easily, so after a long period, the lakes ecological environments are compromised (Yang et al. 2018).

Lagoons are ecosystems more vulnerable to human pollution, such as excess nutrients, especially phosphorus (Cunha et al. 2013). According to Pereira et al. (2009), nitrogen and phosphorus concentrations may be higher in densely populated areas due to domestic, industrial and agricultural discharges.

The TP results did not meet the limit of Brazil (2005), referring to class three for lentic environments, having the highest maximum average equal to 0.95 mgL^{-1}, in winter season. This result shows the importance and necessity of more specific studies on phosphorus concentration in the Mirim Lagoon, as well as monitoring its pollution source.

BOD is one of the most important parameters to identify the organic carbon load in fluvial system and to indicate the anthropogenic sources influence on water quality, i.e. it is a verification parameter of the organic pollution degree of the water bodies (Singh et al. 2009, Kumar et al. 2018). In this study, we observed a discrepant increase in BOD concentration in winter (Figure 2). This increase was also verified in the Cunha et al. (2013), Abreu & Cunha (2017) and Basso & Carvalho (2007) studies, being related to the rainy season, characteristic of winter in the Mirim Lagoon region, because this period provides greater nutrient input from

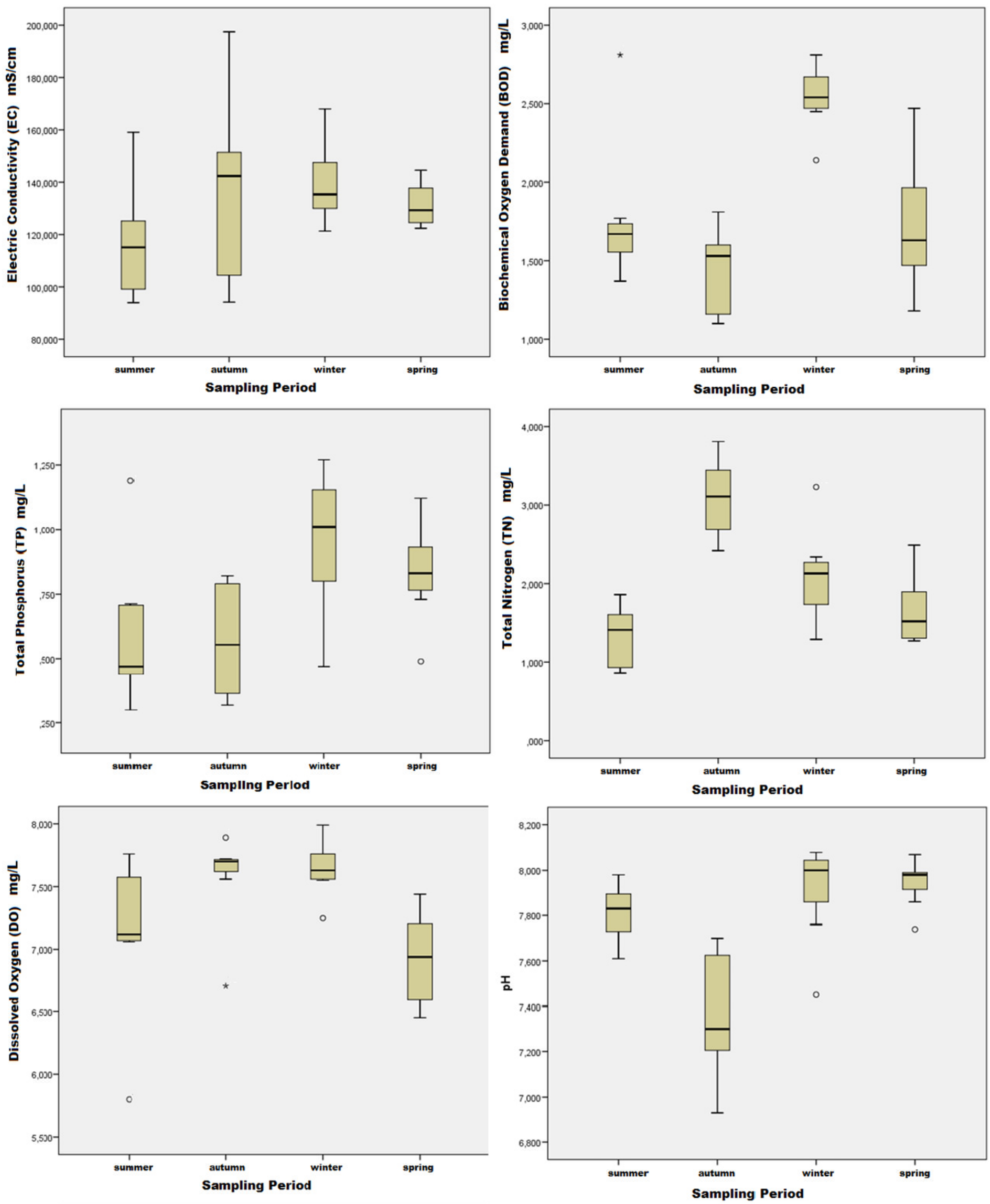

Figure 2. Time variation of monitored water quality variables in Mirim Lagoon.

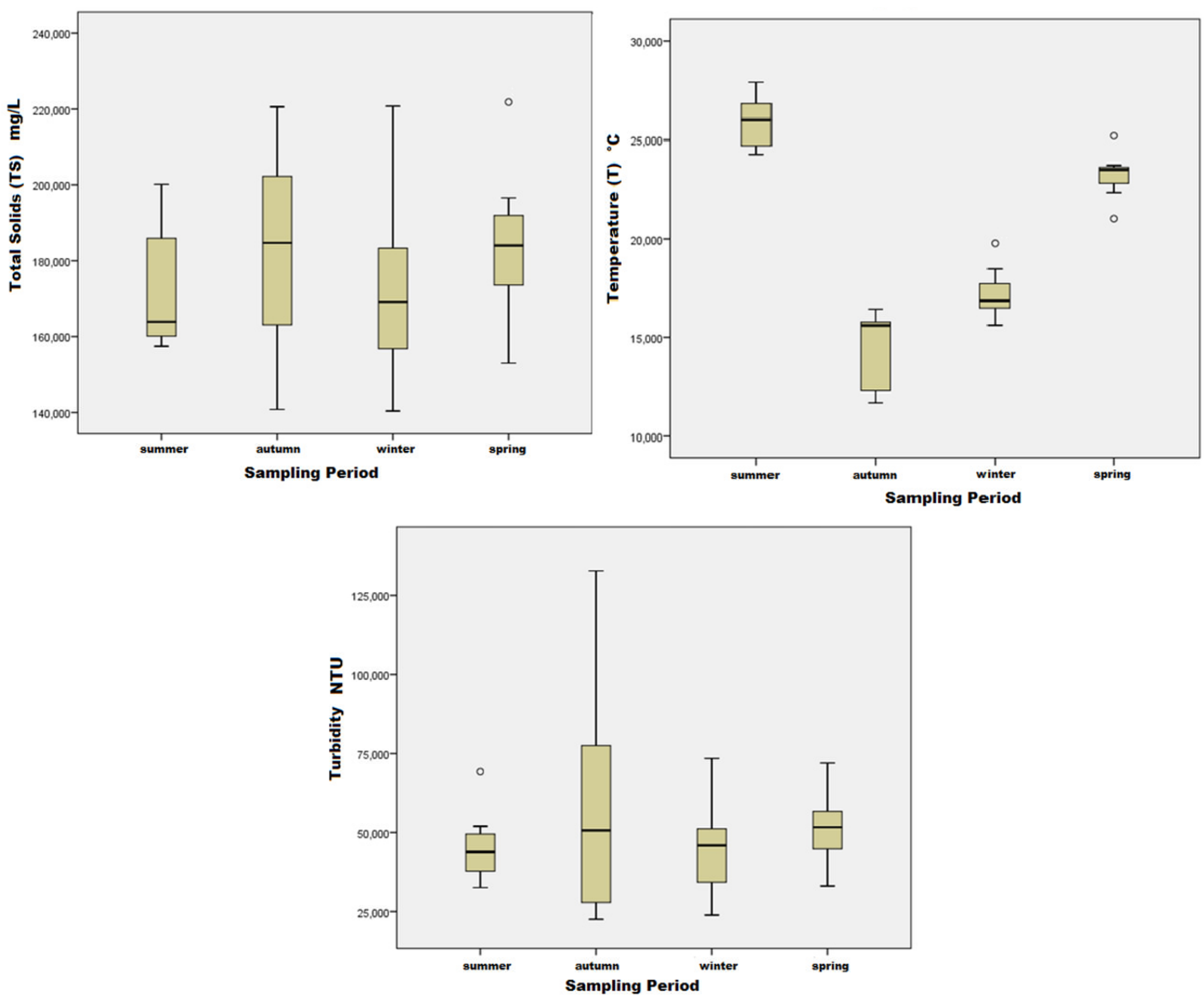

Figure 2. Time variation of monitored water quality variables in Mirim Lagoon. (continuation)

soil to water. The BOD freshwater limit to class one of CONAMA resolution is 3 mgL^{-1}, so the observations are included in it (Brazil 2005).

The TS observations presented the lowest average in the winter period, which may be associated to the season higher rainfall volume. This parameter also falls the class one of CONAMA resolution, since it does not reach the 500 mgL^{-1} limit (Brazil 2005).

In Table III are showed the results of ANOVA statistical test to each one of the parameters. The T, pH, DO, BOD, TP and TN values were statistically significant ($p<0.05$), there was a seasonal difference of these water quality parameters according to the proposed analysis. The pH parameter was also significant in the studies of Bilgin (2015).

The hydrographic basin under study is located in the subtropical climate region, characterized by four well defined seasons, where temperature variations can cause changes in the lakes metabolism, ecosystem and biodiversity, due to chemical, physical and biological variations throughout the year (Cunha et al. 2013). In this work, the difference between the temperature averages was 11.64°C, generating the highest F value among the ANOVA test parameters. The pH significance is explained by the lowest values in dry periods, so it is verified the climatic variation influence, as showed in Table II (Thebaldi et al. 2017).

The DA analysis identified the most important parameters that influenced the water quality variations in the lagoon. In the

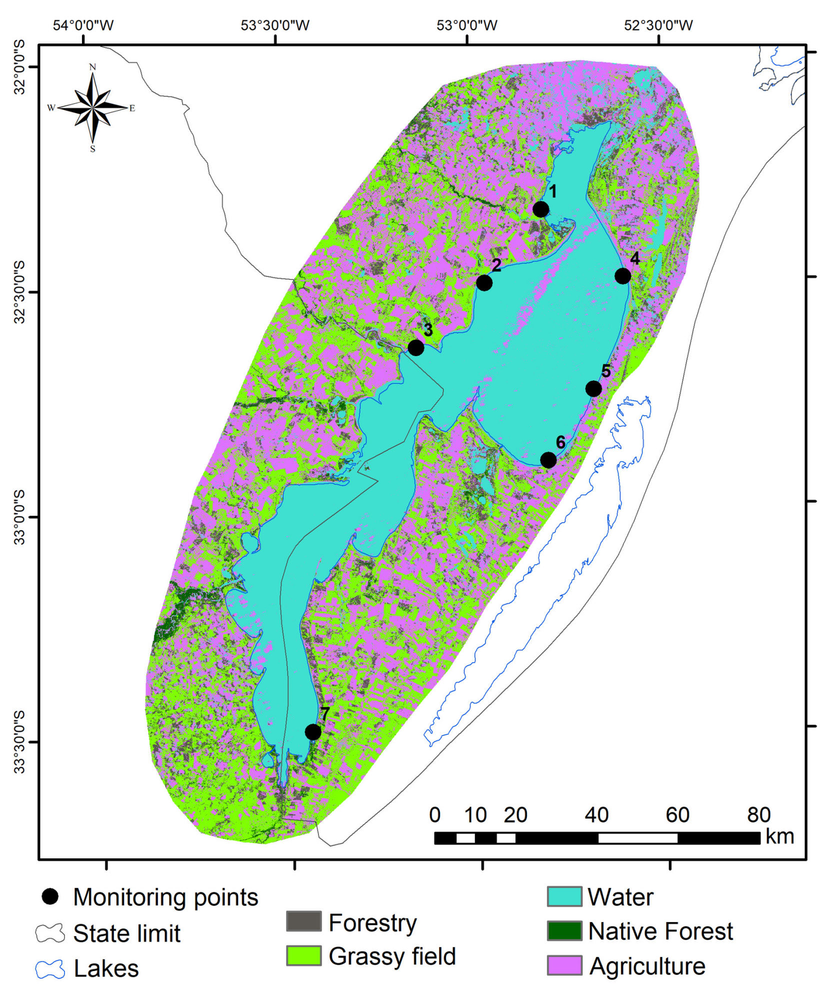

Figure 3. Land use and occupation in the vicinity of Mirim Lagoon.

Table III. ANOVA applied to the water quality database in Mirim Lagoon.

Parameter	Sum of squares	Df	Mean square	F	Significance (p)
Temperature (T)	599.174	3	199.725	81.194	0.000
Turbity (Tb)	956.294	3	318.765	0.566	0.643
pH	1.465	3	0.488	11.723	0.000
Electrical Condutivity (EC)	2114.691	3	704.897	1.254	0.312
Dossilved Oxygen (DO)	2.514	3	0.838	4.268	0.015
Biochemical Oxygen Demand (BOD)	4.717	3	1.572	11.452	0.000
Total Nitrogen (TN)	12.348	3	4.116	15.999	0.000
Total Phosphorus (TP)	0.696	3	0.232	3.504	0.031
Total Solids (TS)	737.550	3	245.850	0.416	0.742

Table IV. Discriminant functions obtained for the water quality database in Mirim Lagoon.

Function	Eigenvalue	Variance (%)	Cumulative (%)	Canonical Correlation
1	5.739	81.2	81.2	0.923
2	1.171	16.6	97.8	0.734
3	0.156[a]	2.2	100.0	0.367

Table V. Values of the Wilks Lambda and Chi-Square tests obtained for the water quality database at Mirim Lagoon.

Functions test	Wilks Lambda	Chi-square	Df	Significance (p)
1 through 3	0.059	65.036	12	0.000
2 through 3	0.399	21.155	6	0.022
3	0.865	3.331	2	0.189

Table VI. Coefficients of the discriminant functions obtained for the seasonal variation of water quality in Mirim Lagoon.

Functions	DO	BOD	TN	TP
1	0.637	-0.985	0.929	-0.547
2	0.328	0.544	0.426	0.340

analysis, the seasons were inserted as the grouping variables and the quality parameters as the independent variables to generate the classification functions. In canonical correlation (Table IV), the eigenvalues for the first two functions were greater than the unit (function 1 = 5.739 and function 2 = 1.171) and for the third function the value was less than unit. Therefore, only the first two functions can be used to evaluate the dominant character in the data set (Kumar et al. 2018). Functions one and two alone account for 97.8% of the total variance between groups, in which the first function presents 81.8% of the variance. In this study, we chose to consider only function one in most significant parameters' verification in groups discrimination, due to its high contribution. This decision was taken based on what presented by Hajigholizadeh & Melesse (2017) and Boyacioglu & Boyacioglu (2017).

The Wilks Lambda values and Chi-square are presented in Table V, so that they represent the discriminatory ability of functions. The Wilks Lambda is used to compare the groups based in their averages and measures the correlation between the dependent and independent variables, the values varying between zero and one; the closer to zero, the more separated are the average values, i.e., a good distance between groups (Kumar et al. 2018). Since the Chi-square test has the inverse relationship, they should result in higher values (Boyacioglu & Boyacioglu 2017).

The Box M test evaluates the group covariance equality, being the best result that the log determinants are equal or practically equal (Hair Jr. et al. 2009). In this work, the values for summer, winter, spring and autumn were equal to -8.562, -12.325, -10.432 and -8.240, respectively. The Box M value should be insignificant ($p>0.05$), as a result the significance was 0,249, so the functions used are satisfactorily discriminatory.

Thus, based on the studies by Aris et al. (2013), Hajigholizadeh & Melesse (2017), Boyacioglu & Boyacioglu (2017) and Anteneh et al. (2017), the stepwise method was applied to obtain a resulting function, in order to select the parameters that best represent the groups discrimination. This method indicated four discriminative water quality parameters (Table VI), being BOD as the most important parameter, followed by TN, TP and DO. In other words, these parameters account for most of the likely seasonal variation in water quality. Anteneh et al. (2017) made studies of seasonal evaluation of surface water quality in two basins of Central Ethiopia, where DO and TN were found among the five variables of the discriminant function. Kumar et al. (2018) and Xia et al. (2018) also found similar results, as the dissolved oxygen.

El-Mezayen et al. (2018) conducted studies in Mediterranean Egypt using twelve parameters of water quality, being verified the seasonality influence in variables such as temperature, turbidity and nutrients. These parameters resulted in higher concentrations in the seasons: winter, summer and spring, respectively. In Australia, Li et al. (2018b) results in only NH4-N not having temporal variations, between twenty-two parameters, obtaining among the main discriminating parameters the water temperature, turbidity, alkalinity and dissolved oxygen. Cunha et al. (2013) and Amâncio et al. (2018) studied a subtropical lagoon and verified the existence of seasonal variations in their physical, chemical and biological characteristics, due to climatic season being well defined and the presence of industries and agricultural areas.

CONCLUSIONS

The results showed that the parameters temperature, pH, dissolved oxygen, biochemical oxygen demand, total nitrogen and total phosphorus differ statically between the four climatic seasons. Were also identified four discriminative parameters between the seasons, being them dissolved oxygen, biochemical oxygen demand, total nitrogen and total phosphorus.

In this way, it can be concluded that the seasonality mainly affects anthropogenic pollution sources such as agricultural activities and domestic discharges, like in BOD, TN and TP concentrations. It is evident the need to know the seasonal water quality variations, in order to allow the adoption of water resources management measures geared to the specific problems faced in the study areas.

The methodology used was successful in Mirim Lagoon allowing inferring about the main variables of water quality that should be monitored, mainly due to their seasonal variability. It is important to highlight the importance of this study in directing future analyzes of water quality in the lagoon, reducing logistic planning time for monitoring and costs with laboratory analysis. However, specific studies, such as the presence of pesticides or antibiotics in water, analyzes with other variables of water quality, should be requested depending on the need of the management agencies.

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