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SPACE-TIME AND NICTEMERAL VARIATION OF NITRATE (NO_3) ON THE SURFACE AND BOTTOM OF THE WATER COLUMN, AT TWO POINTS WITH DIFFERENT FRAMEWORKS, IN THE JACUÍ DELTA, LAKE GUAÍBA, RS, BRAZIL

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Abstract. In the present work, nitrate in surface and bottom water was evaluated at two specific points in the Jacuí Delta, the upper course of Lake Guaíba, a set of sixteen islands, channels, swamps, and ponds formed by the meeting of the Jacuí, Gravataí, Sinos e Caí, in Porto Alegre, RS. It is noteworthy that close to the collection points, raw water is collected by the Municipal Department of Water and Sewers (DMAE) in this source. One of the points is located on the left side of the stream with the greatest urban influence and another point on the right side with the greatest rural influence. At each point, surface and bottom water samples were obtained for nitrate analysis (NO_3-) for 24 hours, totaling 12 samples from each horizon. After the collections, the values of (NO_3-) were verified in the laboratory, totaling four sampling campaigns (September, November 2019, and in January and February 2020), contemplating the spring and summer seasons. Through the analysis of variance, significant differences were detected between the points and between the sample campaigns. The analyzed points showed inverse behaviors for each campaign. The left side of the Jacuí Delta receives the greatest contribution from the Gravataí River with considerable input of organic load. Regarding the temporal variation, the average concentration decreased between campaigns, and between points, the averages were higher in November, January, and February in the Navegantes channel, which is a strong indication of the organic matter that comes from the Gravataí River. For the point on the right bank of the flow with the greatest influence of the Jacuí River, the average value was significantly higher in the 1st sampling campaign (September). This temporal oscillation was probably influenced by temperature variation, rainfall events, wind and wave performance, production and decomposition processes, among others.
Keywords: Nitrate; Delta of Jacuí; Guaíba Lake; water quality; nictemeral

1. INTRODUCTION

The high demand for freshwater worldwide for domestic, industrial supply, food production through irrigated agriculture, demonstrates how, at present, human activities are dependent on the availability of this natural resource (Esteves and Menezes 2011). In large urban centers, in particular, citizens are completely dependent on the availability of water, insufficient quantity and quality for all activities, whether individual or collective.

In Brazil, a few years ago, water resource management was not a priority issue in any of the planning spheres and not even in the scientific sphere, a situation that possibly was due to the great abundance of water in most of the national territory (Resende 2002). Still, according to the author, when analyzing the distribution of water on the planet, even based on very generic estimates, the worrying conclusion is reached that it is an exhaustible (non-renewable) natural resource and much scarcer than can imagine.

According to Kurata and Kira (1995), the quality of water in rivers is different from the quality of lakes. The water undergoes notable changes when entering lakes, and this mixture is not a simple continuous process, but a complex one, strongly influenced by the topography of the estuaries, the quantity, and speed of river waters, water temperature, lake currents, if any. , wind and wave actions.

Water pollution is related to the addition of substances or forms of energy that, directly or indirectly, alter the nature of the body of water in such a way that it harms the legitimate uses that are made of it (Von Sperling 1996).

For Resende (2002), part of the water quality problems is due to the contamination of water sources by nutrients, especially by nitrogen in the form of nitrate (NO_3-), agriculture being an important polluting source. The enrichment of water with nutrients causes damage to the environment and to human health itself. In urban areas, the main sources responsible for nitrate contamination are associated with the disposal of solid waste (poorly constructed dumps and sanitary landfills, in inappropriate places) and, mainly, with sanitation systems, of which the septic and black septic tanks stand out. , as well as leaks from sewage collection networks (Varnier 2019).

Of the various forms of nitrogen present in nature, ammonia (NH_3) and, in particular, nitrate (NO_3^-) can be causes of loss of water quality (Resende 2002). Adult people can ingest relatively high amounts of nitrate without further damage. However, this compound is associated with diseases, such as methemoglobinaemia or blue baby syndrome, in which babies under six months of age may suffer from asphyxiation, which can lead to death (Von Sperling 1996; Resende 2002; Varnier 2019). Nitrate can also be related to some types of cancer (eg lymphatic, gastric) or even problems in the reproductive system, in humans and animals. Several studies have been carried out to assess the relationship between nitrate and cancer, although they are not considered conclusive and definitive regarding this aspect (Varnier 2019).

In a water body, the determination of the predominant form of nitrogen can provide information about the pollution stage, when it refers to the most remote pollution is associated with nitrogen in the form of nitrate (Von Sperling 1996). Nitrate is a compound whose occurrence in the water column and the sediment are linked to the production and decomposition processes. As a consequence, its vertical distribution in the aforementioned compartments can still occur due to the thermal behavior and gas dynamics, especially oxygen, in it (Esteves and Amado 2011).

The spatial and temporal characterization of the quality of a body of water, through a monitoring program, requires different efforts (Coimbra 1991). The planning purposes include, in addition to other information, the provision of available water-quality potentially to meet current and future needs, determination of quality variation in specific periods, to detect and measure trends, and propose preventive actions.

According to Martins et al. (2019), the study of nictemeral variations is important for understanding the dynamics of the environment. The authors observed the nictemeral variation for all parameters evaluated in the study, highlighting that the evaluated water is collected and served for public supply in the municipality of Porto Alegre.

To collaborate with subsidies for the understanding of the processes occurring in the deltaic system, the present study analysed the nictemeral and space-time variation of nitrate (NO3-) in water.

2. MATERIAL AND METHODS

The Guaíba River Basin is located to the east of the State of Rio Grande do Sul, covering an area of 2,523.62 km², with a total population estimated at 1,293,880 inhabitants (Rio Grande do Sul 2017).

Lake Guaíba has a surface area of 496 km^2, and is formed by the Jacuí (84.6%), Sinos (7.5%), Caí (5.2%), and Gravataí (2.7 /%) rivers, also receiving the contribution of several streams located on its banks (Rossato and Martins 2001). In its northern part, the Delta del Jacuí system is located, with an area of 47.18 km² (Menegat et al. 2006).

Due to the relevant ecological, economic, and scenic beauty of the delta system, in 1976 the Delta do Jacuí State Park (PEDJ) was created, which had its limits expanded in 1979 (Rio Grande do Sul, 2014). In 2005, State Law No. 12,371 (Rio Grande do Sul 2005) created the Delta do Jacuí State Environmental Protection Area (APAEDJ), located in the Municipalities of Porto Alegre, Canoas, Nova Santa Rita, Triunfo, and Eldorado do Sul, with an area of 22,826.39 ha (twenty-two thousand, eight hundred and twenty-six hectares and thirty-nine areas), in which, in 14,242.05 ha (fourteen thousand, two hundred and forty-two hectares and five areas), is Delta do Jacuí State Park was inserted as an Integral Protection Unit.

The importance of PEDJ is in the conservation of a large extent of wetlands and their functions and the protection of the water dynamics of the delta system, favoring the continuity of the sedimentation processes and the supply of nutrients from the rivers that are part of the delta system, collaborating in mitigating floods and the consequences of drought (Rio Grande do Sul 2014). The sampling points of the present work are located on the Left Channel (P1 - Canal Navegantes) and Right Channel (P2 - Canal Jacuí) both in the Jacuí Delta, Guaíba Lake, Porto Alegre, and Eldorado Sul respectively, RS (Figure 1). in the left margin of the Navegantes channel, it is in a nearby area, but not inserted in the PEDJ.

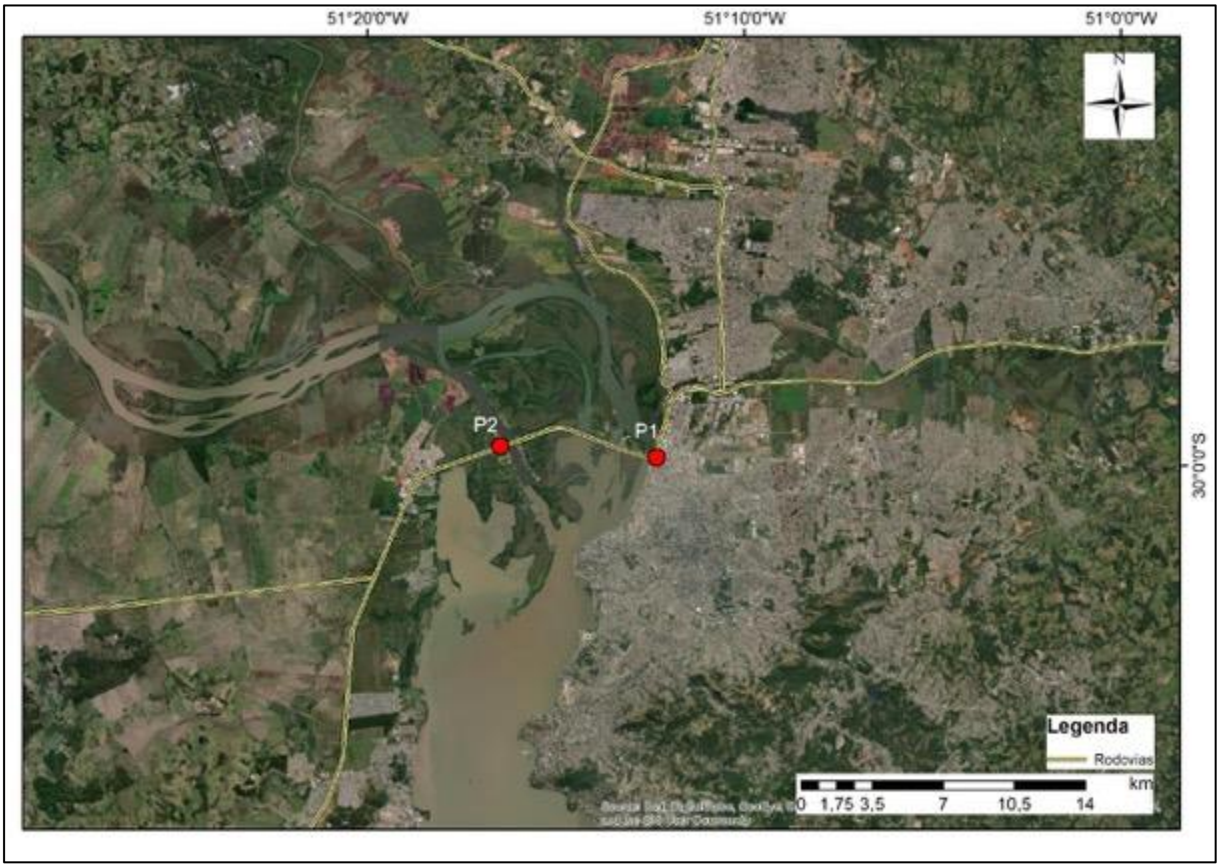

Figure 1. Location map of the water sampling points in the Jacuí Delta, P1 Canal Navegantes and P2 Canal Jacuí, Lake Guaíba, RS, Brazil.

Sample campaigns nitrate (NO_3^-) were carried out in September and November 2019, January and February 2020. The samples were obtained with a horizontal Van Dorn bottle at two depths, including surface and bottom water. The collections were carried out with an interval of two hours, during the 24 h period. To carry out the chemical characterization, 300 ml of each horizon were collected, and packed in cooled thermal boxes, and sent to the laboratory. The analyses were performed according to methodologies of the Standard Methods for Examination of Water and Wastewater (APHA / AWA / WEF, 2012).

Simple variance analyzes (ANOVA) were performed to compare the variables between depths and time. When the ANOVA was significant, the averages were compared using the Bonferroni Post Hoc test with a 95% confidence interval ($p < 0.05$).

3. RESULTS AND DISCUSSION

3.1 Spatio-temporal analysis

During the sampling campaigns, the rainfall regime decreased considerably, in November, month of the second campaign, the drought started in the Rio Grande do Sul (Figure 2). The January and February campaigns continued to show irregularities in rainfall in much of the southern region, including decrees of public calamity in several municipalities due to the lack of rain. The water levels at the collection points followed the rainfall decline, and at the sample point of the Navegantes channel (P1) the average depths were in the sequence (3.26m), (4.15m), (2.40m), and (2, 20m), and for the Jacuí channel (P2) medium depths (2.86m), (3.40m), (2.40m) and (2.30m). Also noteworthy is the phenomenon of water barring governed by the wind from the south quadrant and the tides that dam the waters of Lagoa dos Patos, When we separate the variable (NO_3^-) into groups, almost all of them show normal behaviour, except the bottom layer of the Canal do Jacuí in November and the surface layer of the two channels in January. We noticed that there is an Outlier that is a point of influence in the model, which is the observation of 9 am on the surface of the Jacuí River, in September.

Analysing the graph (figure 3), it was noticed a tendency towards a decrease in the amount of NO_3 as months go by, in both locations, with a significant difference in September.

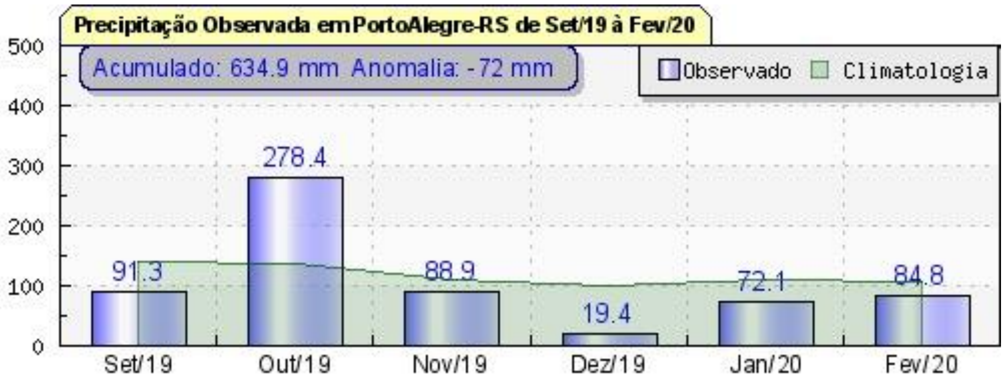

Figure 2. Monthly rainfall (Observed) and historical average (Climatology) for the period. (Source: SOMAR)

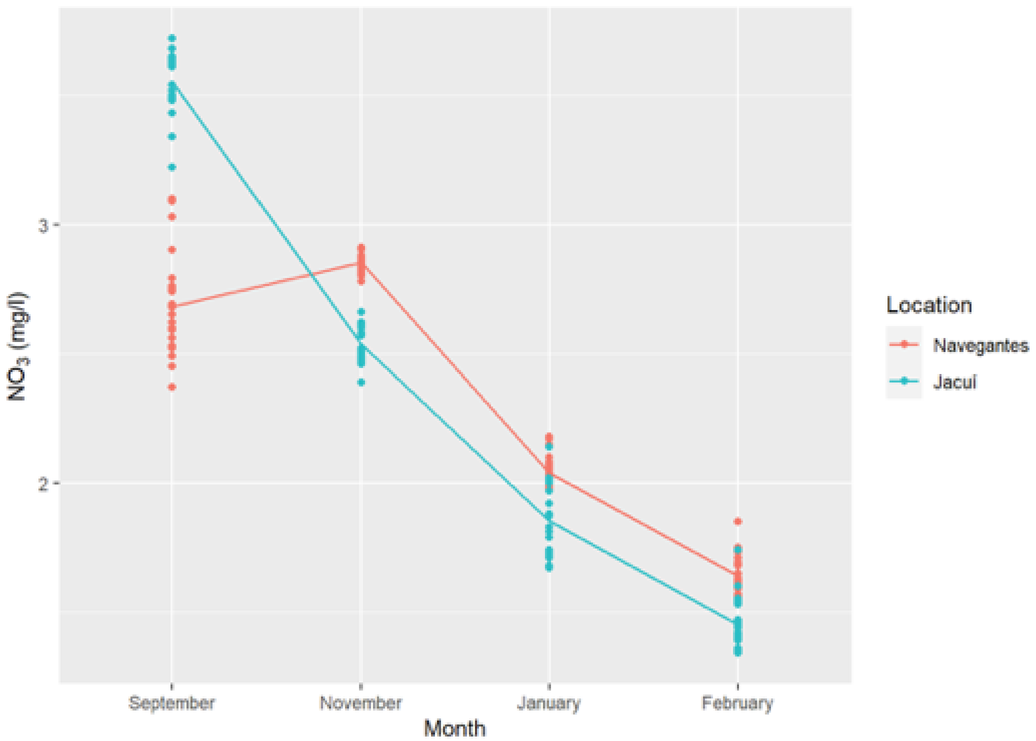

Figure 3. Interaction graph Month x Location of the Nitrate parameter (NO_3^-) (mg / L), September and November 2019, and January and February 2020 Navegantes channel and Jacuí channel, Jacuí Delta, RS, Brazil

Analyzing the month x depth graph (figure 4), it was noticed that there does not seem to be an influence of depth on the amount of (NO_3^-), as the surface and bottom lines remain together.

Figure 5 shows a small difference in the concentration values of (NO_3^-), according to the depth, with the levels increasing in Jacuí in the measure of the deepest layer and decreasing in the Navegantes channel. However, the error bars are crossing and the change is very small, according to the scale, which may indicate that it is not a significant change.

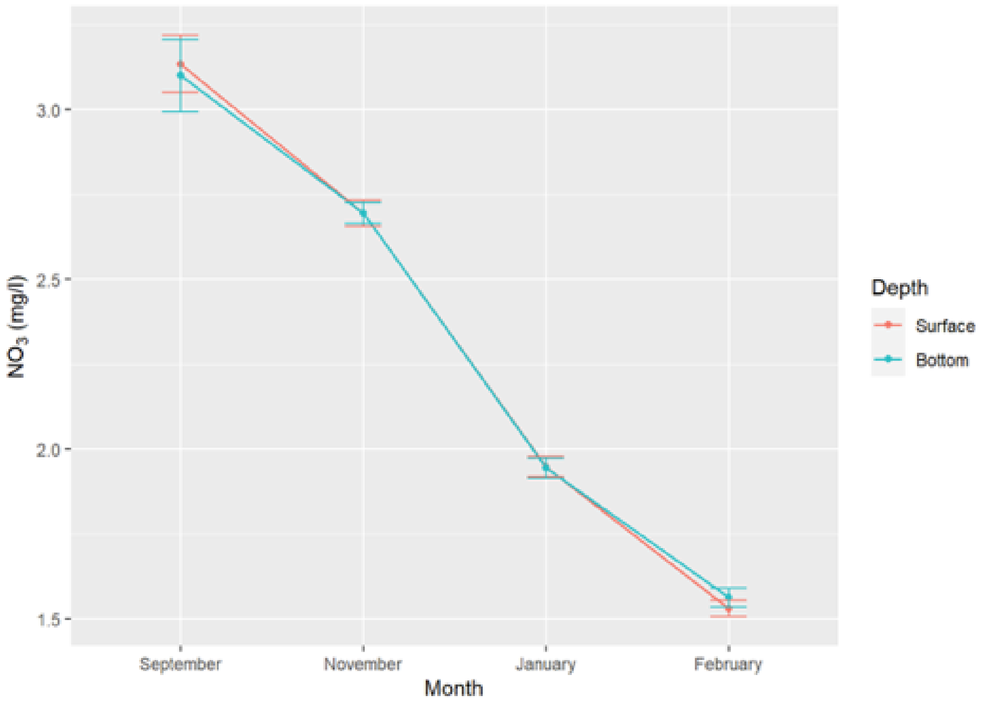

Figure 4. Interaction graph Month x Depth of the nitrate parameter (NO_3^-) (mg / L) in the Surface and Bottom layers, September and November 2019, and January and February 2020, Navegantes channel and Jacuí channel, Delta do Jacuí, RS, Brazil

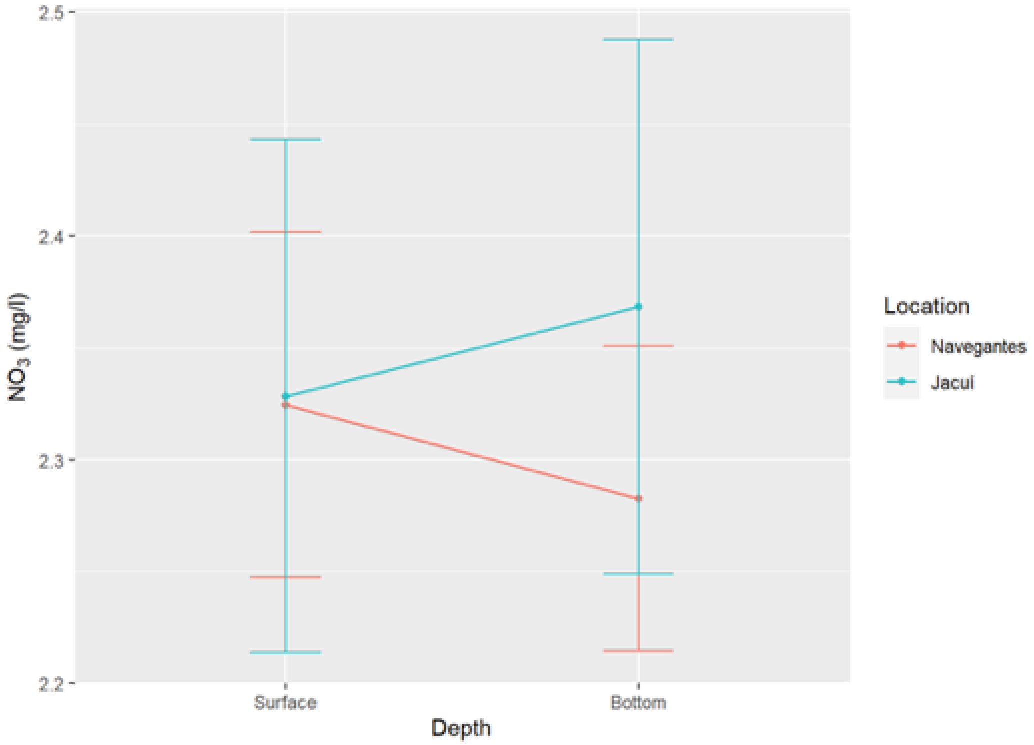

Figure 5. Interaction graph Depth x Location of the nitrate parameter (NO_3^-) (mg / L) in the Surface and Bottom layers, Navegantes channel and Jacuí channel, Delta do Jacuí, RS, Brazil

Three mixed ANOVAS were carried out, an adequate test for repeated intra-subject measurements (several measurements at different times in the same channel, month, and depth) and inter-subject (the same variable measured in different locations, months, and depths), with the main purpose of verifying the influence of time on measurements, but none of the tests showed Time to be an influential variable. Running the model, we arrived at the following ANOVA results for month and location (Table 1).

Table 1. Month x Location Interaction

	Sum Sq	Df	F	p-value
(Intercept)	172,646	1	14695.32	<2.2e-16
Month	22,946	3	651.05	<2.2e-16
Local	9,100	1	774.59	<2.2e-16
Month: Location	11,057	3	313.73	<2.2e-16

The models are in line with what was analysed in the graphs. There is the influence of months on the present amount of NO_3^- and also of the place, generating the interaction between month and place perceived in figure 2. However, it is important to consider the Outlier highlighted above. From a cross-sectional approach to the data, it could be verified, from the graphs and ANOVA, that there is the influence of the months on the level of NO_3^- and the place where it was measured, so that the lowest concentrations occur in the Jacuí channel and in February, followed by January, November, and September (except the Navegantes channel - P1, in the latter case).

An interaction was also detected between the Local and Month variables, which means that the variation between NO_3 concentrations - month to month depends on each location. It is possible to infer that the variation in each location depends on the month in which the collection was made. No significant difference was detected in the depths assessed, and, therefore, it is not possible to assume that there is a difference in measurements according to the measured depth. The graphs corroborate this result, as the data are practically overlapping when comparing the depths for months.

Regarding the location, although in the Jacuí channel there is an increase in the concentration of NO_3^- in the bottom, compared to the surface and in the Navegantes channel there is a decrease in that same case, the standard error bars indicate a high variation, in this case, probably caused by the measurement outside the September curve in Navegantes (P1).

When we run the mixed ANOVA for the Month and Hour effect, we get the following results (Table 2).

Table 2. Depth x Location interaction

	Sum Sq	Df	F	p-value
(Intercept)	259,377	1	567.7861	<2e-16
Depth	0.042	1	0.0921	0.7618
Local	0.000	1	0.0007	0.9783
Prof. : Local	0.080	1	0.1761	0.6752

In particular, in the test with months as a variable between subjects, the significance of the months was shown, as already perceived in the cross-sectional analysis and interaction with the time, that is, there is a difference in the measurements in each month, but depending on the time there are greater differences or smaller (those closest to Graph 6 do not show any significant difference, such as January to February at 1 am).

Of all campaigns, the phenomenon of the average concentration being higher than the previous campaign was observed only once. This episode of concentration above the previous month was at the point of the Navegantes channel (P1), not following the trend of average values of the Jacuí channel, which only occurred after the second campaign (figure 3). Also noteworthy is the temporal variability in the collection points and between them, which evidences correlated with rainfall. In a study by Andrade et al. (2018) limnological parameters of the delta region were analyzed. It was found that the locations differ significantly in the parameter of total nitrogen. Also, the authors also pointed out how the Navegantes - P1 channel had the highest average values for the entire period analyzed, and for the same authors, the Gravataí river and its low environmental quality directly affects the navigator’s channel. Andrade and Giroldo (2014) found in Canal Navegantes - P1, nitrate values significantly lower in the summer season, when compared to the winter season, while chlorophyll values were higher in the summer when compared to the other seasons of the year. year. In the first campaign (September) the average values were higher in the Jacuí channel, with the upper and lower limits of concentrations in the layer close to the sediments, the maximum value attributed is 3.72 mg / L in the bottom layer, also highlighted values higher mean values for the surface layer, for this same point, the lowest concentration value was found, of 1.34 mg / L in the last campaign (February).

3.2 Nictemeral variation

The nictemeral variation was observed mainly in the bottom layer in the period that involved this study (figure 5), considering the depths of the evaluated water column, significant differences ($p < 0.05$) of the column were detected in September at 19 : 00, 23:00 and 07:00, and November at 11:00, 19:00 and 21:00 on the Navegantes channel, and for the Jacuí channel the significant difference was in September at 11:00 and 17:00 in the bottom layer.

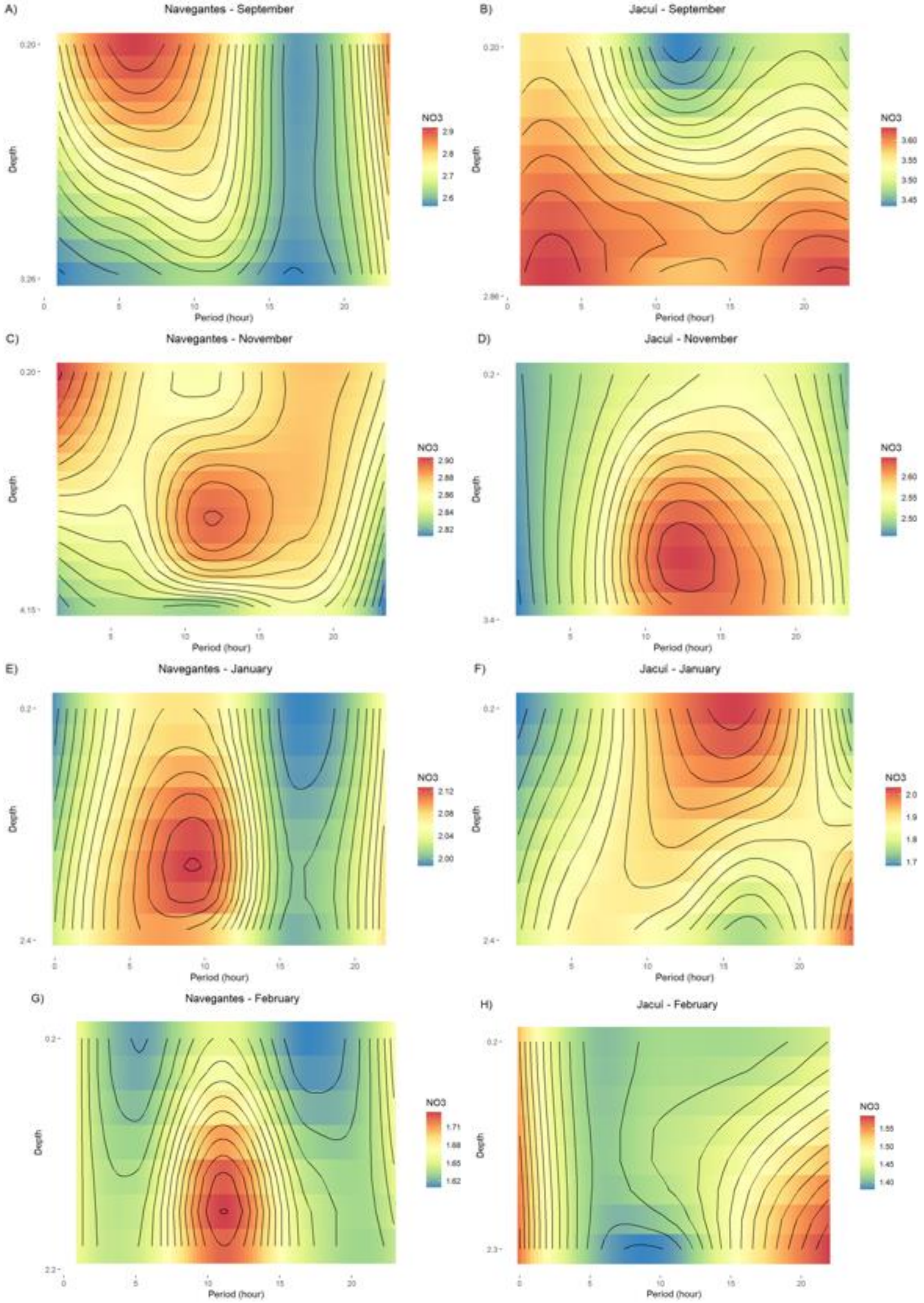

Figure 6. Nictemeral variation of nitrate recorded in surface water and bottom water, in September, November 2019, January and February 2020, Delta do Jacuí, RS, Brazil.

The nictemeral variation followed a pattern of maximum and minimum values very close in November, January, and February in the Navegantes channel - P1, and September and November in the Jacuí channel - P2. In September, it showed three peaks of concentration in the superficial layer 3.10 mg / L at 9:00 am, 3,03 mgl / L at 11:00 pm and 3,09 mg / L at 7:00 am. There was a significant inversion and variation from bottom to surface in the month of January at night, with a peak of 2.14 mg / L at 23:00 in the Jacuí channel. It should be noted that all values obtained in the study were below 10 mg / L, fixed as the maximum limit for the water quality standard required by CONAMA Resolution No. 357/2005 (Brazil 2005) and also for the nitrate potability standard for human consumption, established by Consolidation Ordinance No. 5/2017 (Brazil 2017) of the Ministry of Health (MS), which is 45 mg / L nitrate.

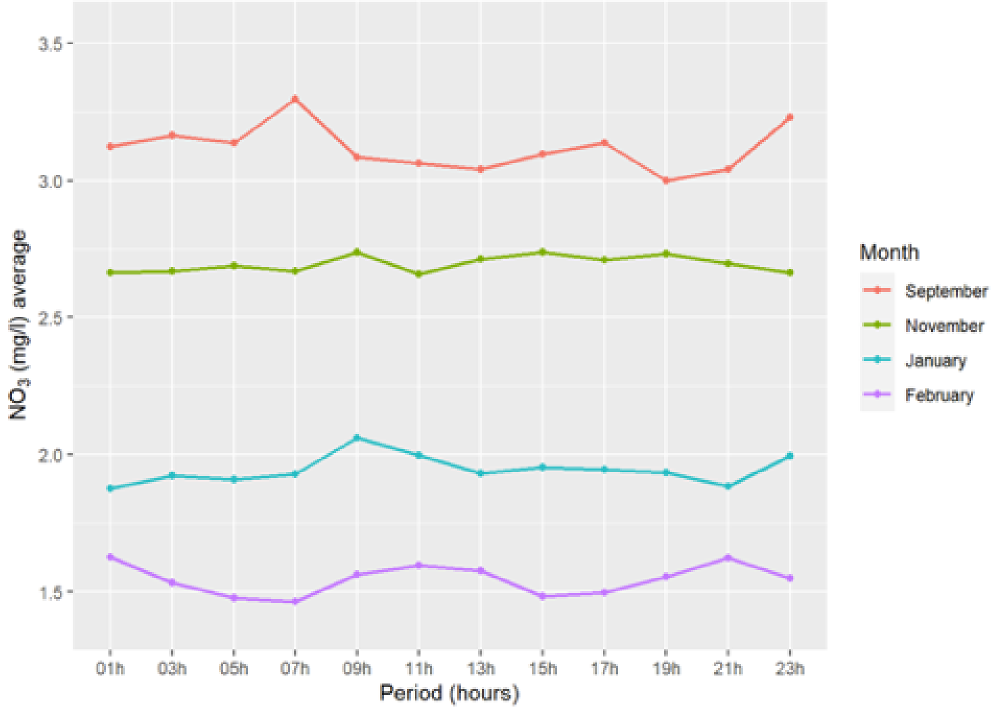

Figure 7. Graph of nictemeral average in each period, separated by Month, of nitrate registered in September, November 2019, January, and February 2020, Delta do Jacuí, RS, Brazil.

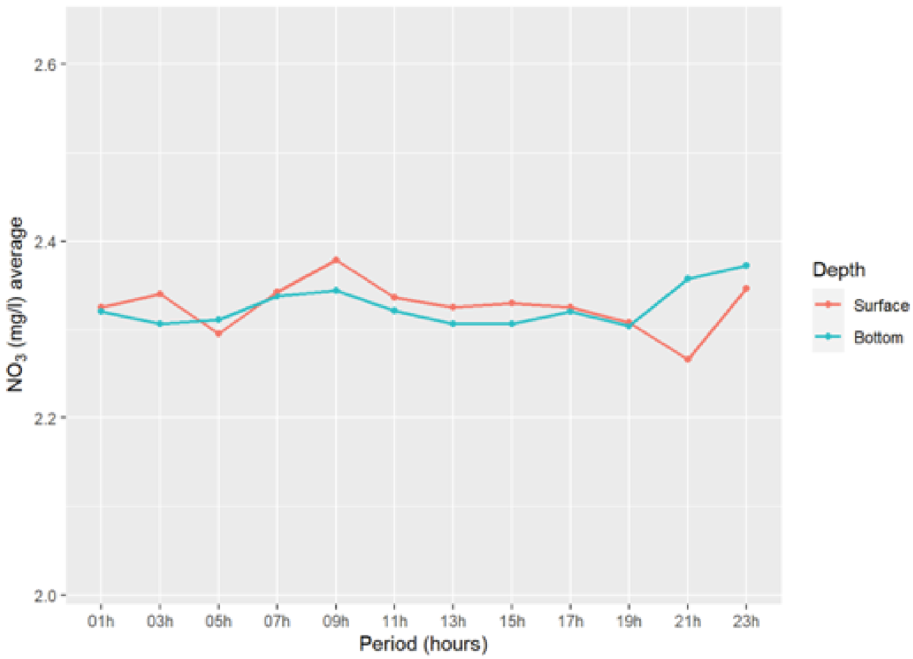

Figure 8. Graph of nictemeral average in each period, separated by Depth, of nitrate registered in the Surface and Bottom layer, in the Jacuí channel and Navegantes channel, Delta do Jacuí, RS, Brazil.

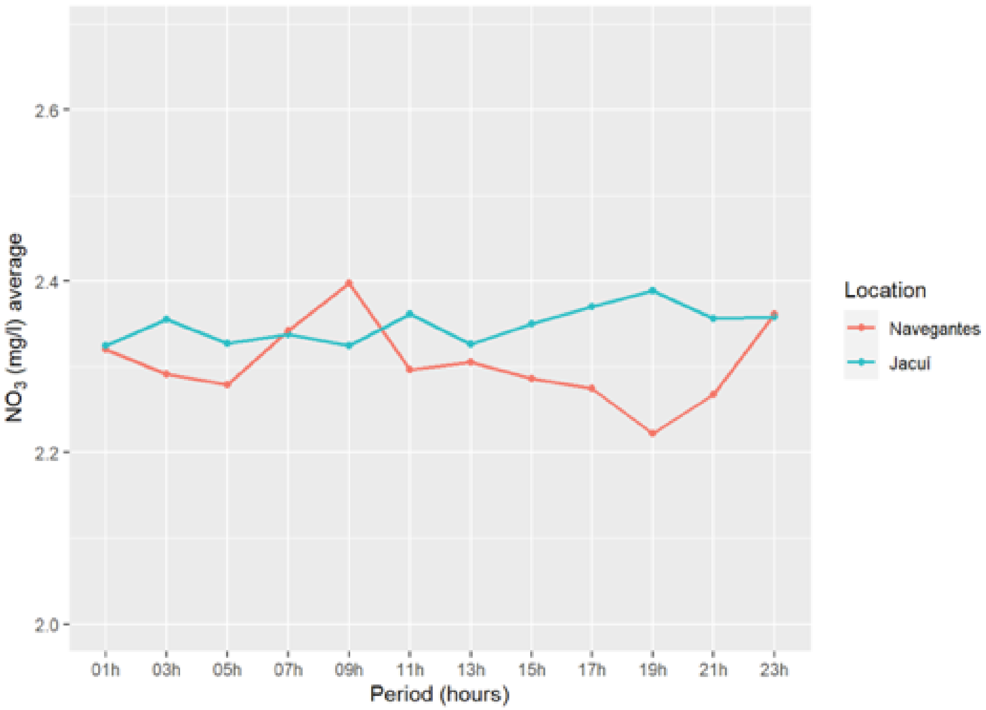

Figure 9. Graph of nictemeral average in each period, separated by Location, of nitrate registered in the Jacuí channel and Navegantes channel, Delta do Jacuí, RS, Brazil.

Starting with a longitudinal approach, considering the times of measurement of the level of (NO_3^-), it was noticed from the graphs that there is a big difference in the measurements in each month (figure 7), as we had already detected, but these measurements very little about the time. This also happens when compared by depth (figure 8) and a little less when compared by location (figure 9), because in the Navegantes channel it seems to show higher measures around 9 am, when compared with measures in the late afternoon.

4. CONCLUSION

During the development of the study, the concentrations showed spatial and seasonal heterogeneity, probably related to the period of warmer seasons and with a greater photoperiod (spring and summer) and to a drought that hit the region during the study period.

The nictemeral variation was verified for all campaigns. It should be noted, however, that these values are per that contained in CONAMA Resolution No. 357/2005 (Brazil 2005). Higher values were observed in the month of September in the Jacuí channel, probably due to the transition period of the wet season.

The average concentrations were higher for most of the period studied in the Navegantes channel, except for September, coinciding with the region with the highest concentration of population and the most compromised quality and currently classified as class 4 to reach class 3 as recommended by the framework . The data presented does not present restrictions for the noblest uses.

Probably the integration of several factors and processes influenced the results obtained, such as the production and breathing processes, and the hydrological and meteorological forces. It is noteworthy that the present work was carried out in the spring and summer with a strong drought, and even though there was a concentration of pollutants due to drought, still the values did not exceed those defined in CONAMA, and that for greater inferences it is necessary conducting additional sampling campaigns in the wet season (autumn and winter).

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