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Scientific Article

Analysis of total nitrogen and chlorophyll a correlations in reservoirs in Ceará/Brazil

Análise das correlações entre nitrogênio total e clorofila a em reservatórios do Ceará/Brasil

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ABSTRACT

Chlorophyll a (Chla) concentration is an important indicator to characterize algal biomass, reflecting water quality and the level of eutrophication of aquatic environments. This study analyzed 4315 total nitrogen (TN) and Chla samples in 155 reservoirs in Ceará, Brazil. Relationships were obtained between TN and Chla through simple linear regression and classified according to the statistical performance of the coefficient of determination (R^2). The dynamics of these correlations were examined by analyzing the variance between classification groups concerning watershed, reservoir size, coefficient of variability, and trophic state. The concentration of pollutants was influenced by seasonality, which increased significantly from the wet to the dry period in most basins. The coefficients of determination between Chla and TN for the watersheds followed the trends of classic curves in the literature, with satisfactory models ($R^2 > 0.3$) in most reservoirs (53.3%). The variance analysis attested that the models' performance was affected by the basins, the volumetric variation, and the change in the trophic state levels. There was no significant variance of R^2 between reservoirs of different sizes.

Keywords: nutrients; tropical reservoirs; eutrophication; water quality.

RESUMO

A concentração de clorofila a (Cla) é um indicador importante para caracterizar a biomassa de algas, refletindo a qualidade da água e o nível de eutrofização dos ambientes aquáticos. Este estudo analisou 4.315 amostras de nitrogênio total (NT) e Cla em 155 reservatórios do Ceará, Brasil. As relações entre NT e Cla foram obtidas por meio de regressão linear simples e classificadas de acordo com o desempenho estatístico do coeficiente de determinação (R^2). A dinâmica dessas correlações foi examinada mediante a variância entre os grupos de classificação quanto à bacia hidrográfica, tamanho do reservatório, coeficiente de variabilidade e estado trófico. A concentração de poluentes foi influenciada pela sazonalidade, que aumentou significativamente do período chuvoso para o seco na maioria das bacias. Os coeficientes de determinação entre Cla e NT para as bacias hidrográficas seguiram as tendências das curvas clássicas literárias, com modelos satisfatórios ($R^2 > 0,3$) na maioria dos reservatórios (53,3%). A análise de variância atestou que o desempenho dos modelos foi influenciado pelas bacias, pela variação volumétrica e pela mudança nos níveis de estado trófico. Não houve variação significativa de R^2 entre reservatórios de diferentes tamanhos.

Palavras-chave: nutrientse; reservatórios tropicais; eutrofização; qualidade da água.

INTRODUCTION

In recent decades, the bloom of cyanobacteria in lakes and reservoirs has occurred with greater intensity and frequency mainly due to the increase in human activities and global climate change, which is considered an environmental and public health problem on a global scale (BEAVER *et al.*, 2018; MUNOZ *et al.*, 2021; CALY; RODRÍGUEZ; PEÑUELA, 2022). As one of the typical characteristics of eutrophication is the outbreak of harmful algal blooms, chlorophyll a (Chla) is widely used as an indicator to assess the quality and state of eutrophication of water bodies (MA *et al.*, 2021).

Total nitrogen (TN) and total phosphorus (TP) are the main biogenic elements for phytoplankton production, which makes them closely related to the concentration of algal biomass in water and the most important sources of eutrophication (CHEN *et al.*, 2018; MAMUN *et al.*, 2020; MA *et al.*, 2021). However, the relationship between Chla concentration and the nutritional status of reservoirs still has many uncertainties because there are a series of physical-chemical, temporal, environmental, hydrological, and morphological factors that can jointly control bioactivity (KRUK, 2023).

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Thus, discussions about nutrient management strategies to mitigate eutrophication in aquatic environments have focused on identifying the nutrient with the best predictive capacity for algal biomass production (GELETU, 2023; ZHOU *et al.*, 2022). In the Northeast region of Brazil, significant water-level variability and generally higher trophic levels (WIEGAND *et al.*, 2021) imply more complex mechanisms behind eutrophication, making it challenging to predict Chla (CARVALHO; LIMA NETO; SOUZA FILHO, 2022). Thus, understanding the patterns of Chla and nutrient dynamics in these reservoirs is often a prerequisite for reversing current water quality problems and managing reservoir ecosystems (PHAM *et al.*, 2020; LI *et al.*, 2022). Limitation by nitrogen in this region was previously identified through empirical models and linear regression in Wiegand *et al.*'s (2020) studies, which concluded that TN was the most critical predictor of algal growth in 64 of the 101 reservoirs analyzed in Ceará state.

Thus, understanding the patterns of Chla and nutrient dynamics in these reservoirs is often a prerequisite for reversing current water quality problems and managing reservoir ecosystems (LI *et al.*, 2022). Despite the abundance of studies that provide a better understanding of limnology, sources of polluting loads, the eutrophication process, and its relationship with hydroclimatic variables in some reservoirs in the Brazilian semi-arid region (MOURA *et al.*, 2020; RAULINO; SILVEIRA; LIMA NETO, 2021; ROCHA; LIMA NETO, 2021; LIMA NETO *et al.*, 2022), studies that investigate the correlations between Chla and TN are still scarce and local. Therefore, this study aimed to analyze data from 155 reservoirs located in the state of Ceará, Brazil, verify the predictive capability of TN for Chla, and identify the factors that influence the dynamics of these correlations in the studied reservoirs.

METHODOLOGY

Study site and available database

For this study, 155 reservoirs distributed throughout the territory of the state of Ceará were selected (Figure 1 and Supplementary Table 1 - https://abes-dn.org.br/wp-content/uploads/2023/08/Supplementary_material.pdf), which has a territorial area of 150 km², with 175 of its 184 municipalities (95%) inserted in the semi-arid region of the Brazilian Northeast (BRASIL, 2021). As a characteristic of semi-arid regions, the state has great temporal and spatial precipitation variability and high evaporation rates, with stocks accumulated in surface reservoirs as the primary water source (SOUZA *et al.*, 2017).

The research data were obtained through the water quality monitoring and volume measurements of the reservoirs available in the Ceará Hydrological Portal, developed by the Secretariat of Water Resources of the State of Ceará (SRH), the Cearense Foundation of Meteorology and Resources (FUNCEME), and the Water Resources Management Company of the State of Ceará (COGERH) (CEARÁ, 2021a). The database provides data on TN and Chla through water sampling procedures carried out with variable frequency according to the size and strategic importance of the dam and measurements of daily volumetric percentages in each reservoir. The samples, collected 0.3 m from the surface and at strategic points that represent the conditions of each water body, are analyzed *in loco* using portable equipment and/or sent for laboratory analysis.

In this study, TN and Chla a concentration data between the years 2008 and 2021 were selected, considering reservoirs with monitoring data with a

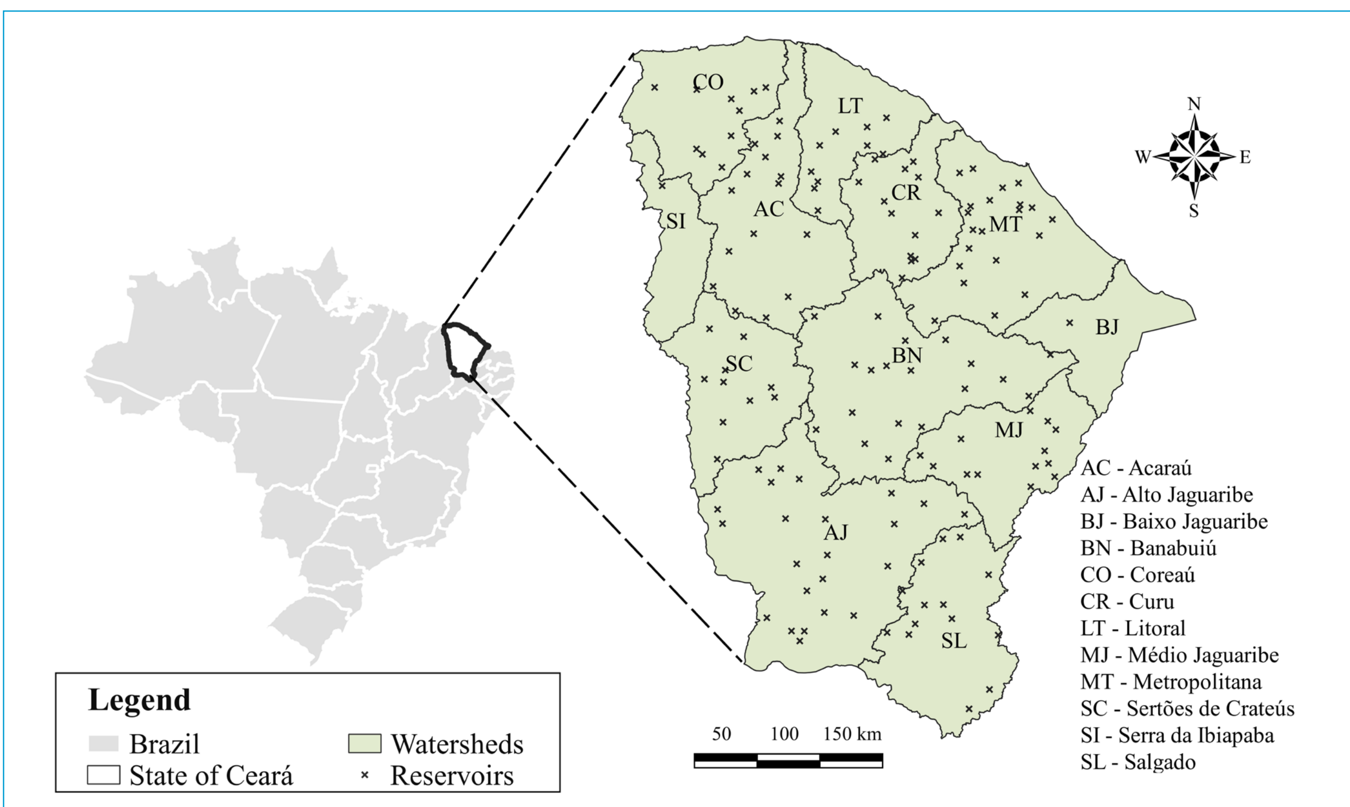

Figure 1 – Location of monitored reservoirs.

number of sample collections greater than 10 and only measurements without null values. In this way, a set of 4315 Chla and TN concentration values was obtained in 155 reservoirs distributed in the 12 hydrographic basins of the state (Supplementary Table 2 - https://abes-dn.org.br/wp-content/uploads/2023/08/Supplementary_material.pdf).

Statistical analyses

The limnological evaluation was performed using descriptive statistics (mean, standard deviation, minimum, and maximum) of TN, Chla, and volume percentage (V). The analysis of the dynamics of the relationship between TN and Chla was performed by obtaining the coefficient of determination (R^2) through simple linear regression and descriptive statistical analysis using (*i*) data from sampling events individually and (*ii*) aggregating the sample data in groups, according to the evaluated criterion (by period, hydrographic basin, volumetric capacity, and trophic state). The data were divided into two periods according to the occurrence of hydrological drought to analyze the TN and Chla variability in relation to the percentage of volume in the hydrographic basins. The years 2008–2012 were classified as a wet period. As of 2012, rainfall in the state was below average, and most reservoirs reached volumetric percentages below 50%; the years 2013–2021 were classified as the dry period (ARAÚJO; BRONSTERT, 2016; WIEGAND *et al.*, 2021).

Linear adjustments were obtained through linear regression for data aggregated by basin and by the reservoir and classified according to the statistical performance evaluation criteria of TN correlations recommended by Moriasi *et al.* (2015) into four groups: very good ($R^2 > 0.7$), good ($0.6 < R^2 \leq 0.7$), satisfactory ($0.3 < R^2 \leq 0.6$), and unsatisfactory ($R^2 \leq 0.3$). The variability of the statistical performance between TN and Chla between the reservoirs was evaluated concerning the influence of the hydrographic basin in which they are inserted, the size of the reservoir, the coefficient of variation of the reservoir volume (CV), and the trophic state index.

With regard to size, the reservoirs were subdivided according to their storage capacity into four groups: strategic (> 500 hm^3), large size (100–500 hm^3), medium size (10–100 hm^3), and small size (1–10 hm^3). The relationship of volume fluctuations in the reservoirs with the performance of the R^2 was evaluated using the coefficient of variability of the annual volumetric percentage (CV), obtained through the relationship between the standard deviation and the average of the average percentage volumes between the years monitored for each reservoir, dividing the reservoirs, according to the observed minimum and maximum limit of variability, into very high ($CV > 1.2$), high ($0.8 < CV \leq 1.2$), medium ($0.4 < CV \leq 1.2$), and small ($CV \leq 0.4$).

The influence of trophic state index on nutrient-Chla dynamics was evaluated using the classification threshold based on mean Chla concentrations (CUNHA; CALIJURI; LAMPARELLI, 2013), defining ultra-oligotrophic when Chla ≤ 2.0 μg×L^{-1}, as oligotrophic when 2.1 < Chla ≤ 3.9 μg×L^{-1}, mesotrophic when 4.0 < Chla ≤ 10 μg×L^{-1}, eutrophic when 10.1 < Chla ≤ 20.2 μg×L^{-1}, supereutrophic when 20.3 < Chla < 27.1 μg×L^{-1}, and hypereutrophic when Chla ≥ 27.2 μg×L^{-1}. The normality between data was verified using the *Shapiro-Wilk* test. As most of the tests between the subgroups did not follow a normal distribution, the data were compared using the non-parametric *Kruskal-Wallis* analysis with *Dunn*'s test of individual significance (*post hoc*), considering the analyses in which $p < 0.05$ as significant.

RESULTS AND DISCUSSION

Limnological and space-time characterization of the variables

The concentrations of TN and Chla nutrients were analyzed for the data obtained in 155 monitored reservoirs. Considering all samples, the mean concentration of TN was 1.996 mg×L^{-1} ± 2.306; for Chla, the mean concentration obtained was 51.831 ± 88.311 μg×L^{-1}. Evaluating the variations in the annual percentage volume of the reservoirs, an average of 40.81 ± 30% was obtained. In Figure 2, which shows the variations in TN (A) and Chla (B) concentrations, it is possible to observe significant differences between the average concentrations between the basins concentration values. For example, the Banabuiú and Médio Jaguaribe basins had the highest average concentrations for both TN (2.749 and 2.983 mg×L^{-1}, respectively) and Chla (83.382 and 66.359 μg×L^{-1}). This high concentration of TN can be attributed to the high density of reservoirs in these basins, which, according to Freire, Costa, and Lima Neto (2022), are the state highest reservoirs density basins with 0.470 and 0.270 reservoirs×km^{-2}, respectively.

The high density of reservoirs can affect water quality because the existence of several small reservoirs favors the trapping of nutrients due to sedimentation and biological capture (FREIRE; COSTA; LIMA NETO, 2022; LI *et al.*, 2022; LIMA NETO; WIEGAND; ARAÚJO, 2011). Similarly, the lowest means of TN and Chla were identified in Serra da Ibiapaba (0.631 mg×L^{-1} and 3681 μg×L^{-1}, n = 39), which has a much lower number of water bodies than what was verified in the other hydrographic regions of the state, which is mainly due to its sedimentary hydrogeological characteristic (CEARÁ, 2021b).

By analyzing TN and Chla variability regarding the percentage of available volume in the reservoir (Figure 3), during the wet period, the average volume for all basins was greater than 50% (65.9%), while, in the dry period, the average found was 30.9%. Regarding TN, the average concentration increased from 1.133 mg×L^{-1} (*n* = 599) in the wet period to 2.135 mg×L^{-1} in the dry period (*n* = 3715).

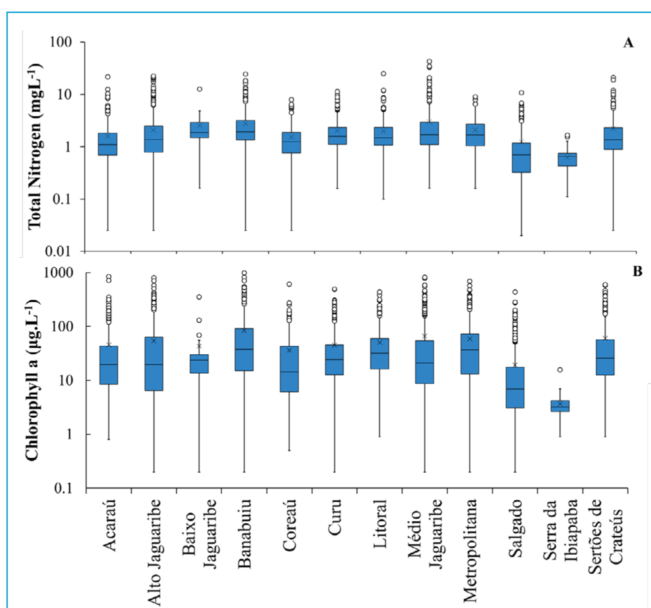

Figure 2 – Variation of (A) total nitrogen and (B) chlorophyll a in Ceará watersheds, on linear-log scale.

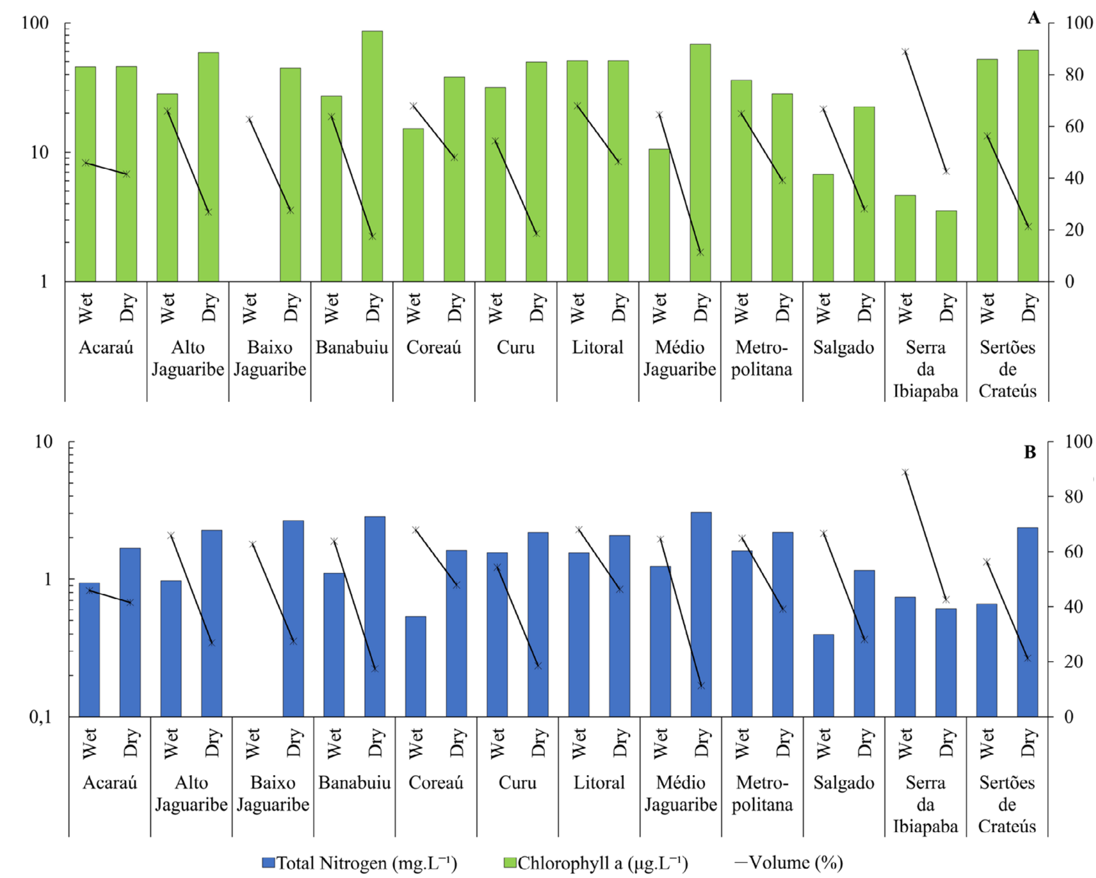

Figure 3 – Variation of the volumetric percentage and average concentrations of (A) Chla and (B) TN in the wet (2008–2012) and dry (2013–2021) periods in the monitored basins.

Except for Serra da Ibiapaba (0.741–0.611 mg×L^{-1}) and Baixo Jaguaribe (which does not have samples concentration data for the wet season), a significant increase in nitrogen concentration was observed in all basins.

Similarly, for all hydrographic regions, except for the Serra da Ibiapaba basin, an increase in Chla from the wet to the dry period was observed, with the average concentration of Chla increasing from 29.649 to 55.420 µg×L^{-1}. Similar results regarding the influence of climate change on the concentration of nutrients and biomass were found in other studies in tropical reservoirs (CAVALCANTE; ARAÚJO; BECKER, 2018; ROCHA JUNIOR *et al.*, 2018; FREIRE; SOUZA FILHO, 2022), showing that reservoirs with inflows below average during periods of drought may show an increase in the trophic state due to the decrease in the dilution of the concentration in the system (GÁMEZ; BENTON; MANNING, 2019).

Chla prediction and performance of simple regression models

The analysis of the coefficient of determination between TN and Chla through simple linear regression for the entire data set resulted in a satisfactory statistical model ($R^2 = 0.448$; $n = 4315$; p-value < 0.05). Similarly, the models between TN and Chla obtained for each watershed resulted in satisfactory determination coefficients (p-value < 0.05), with the lowest value identified in Serra da Ibiapaba ($R^2 = 0.123$; p-value = 0.454) (Figure 4). Comparing the models obtained with classic literature curves, most basins, except for Serra da Ibiapaba, present trends similar to the curves proposed by Nürnberg (1996) ($R^2 = 0.38$) and Pridmore, Vant, and Rutherford (1985) ($R^2 = 0.53$). The classical curves serve as an essential foundation for understanding nutrient cycling processes, facilitating the identification of general patterns and trends within the studied basins. However, as these models were derived from data collected in specific regions, nutrient cycling may display considerable variations influenced by diverse factors such as climatic conditions, lake characteristics, and land-use practices within the respective watersheds. For example, the curves developed by Prairie, Duarte, and Kalff (1989) differ from the studied basins because the model suggested by the authors was developed for 133 lakes that, despite the high concentration of nutrients, had low concentrations of Chla, showing limitations regarding the prediction of high concentrations, which was not observed in the studied basins.

The curves show Chla's response to TN variations. In all basins, except for Serra da Ibiapaba, the positive coefficient in the equation demonstrates that the availability of TN in the water favors the increase of phytoplankton biomass. The descending behavior of the resulting model curve for Serra Ibiapaba indicates that the increase in TN causes a reduction in Chla. In this basin, characterized by high water transparency (CEARÁ, 2017), most measurements were classified as oligotrophic or mesotrophic, conditions where TP is usually the limiting nutrient (LIANG; SORANO; WAGNER, 2020; ROCHA; MESQUITA;

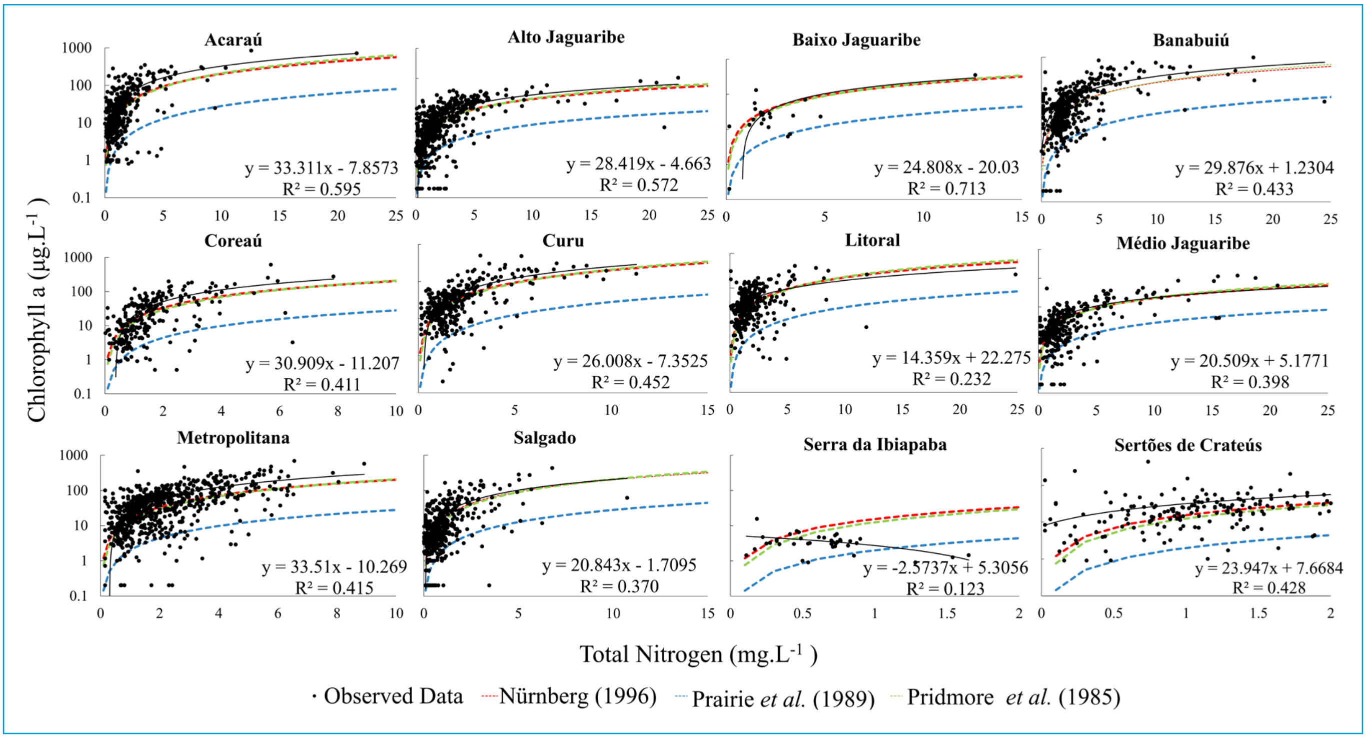

Figure 4 – Comparison between the coefficients of determination between TN and Chla in the studied basins and classic literature models.

LIMA NETO, 2020). In this type of system, phosphorus significantly regulates the Chla concentration, even while TN remains at higher concentrations (ATIQUE; AN, 2020).

By analyzing the simple regression values developed for each reservoir, among the R^2 classified according to the statistical performance criterion proposed by Moriasi *et al.* (2015), 46.45% of the reservoirs under study ($n = 72$) fit the unsatisfactory classification (Supplementary Table 3 - https://abes-dn.org.br/wp-content/uploads/2023/08/Supplementary_material.pdf). Thus, most reservoirs (53.55%, $n = 83$) achieved satisfactory (n = 45) or superior performance (good, n = 17; very good, n = 21). The R^2 intervals found corroborate the results found in the classic studies by Prairie, Duarte, and Kalff (1989) ($R^2 = 0.69$), Canfield *et al.* (1984) ($R^2 = 0.78$), and Pridmore, Vant, and Rutherford (1985) ($R^2 = 0.53$), where strong correlations were obtained between log transformed Chla and TN values in lakes.

Concerning analyses in reservoirs, assessing the probability of eutrophication and harmful cyanobacterial blooms, Thi Hoang Yen *et al.* (2021) analyzed two reservoirs during a prolonged period of drought, identifying correlations between TN and Chla with $R^2 = 0.550$ and 0.603. Stepanova (2021), by analyzing the Chla-nutrient ratios in a eutrophic reservoir, observed positive correlations of $R^2 = 0.570$ indicating that in eutrophic reservoirs and/or subjected to high hydroclimatic variations, TN can be a satisfactory predictor of Chla. However, the predictive ability of the TN was unsatisfactory in approximately 46% of the reservoirs. Other reservoir studies have also reported positive, but less satisfactory, correlations (FILSTRUP; DOWNING, 2017; ATIQUE; AN, 2020; JARGAL *et al.*, 2021; MAMUN *et al.*, 2020; MAMUN; KIM; AN, 2021). In these, the correlations between TN and Chla identified are classified with unsatisfactory statistical performance, with Chla being better correlated with other nutrients, as in the case of TP limitation or external factors (air temperature, turbidity, climatic variability, depth, and light). Thus, as the dynamics between TN and Chla can be influenced by several factors and complex processes in these reservoirs, generally subject to high hydroclimatic variability and where the diversity of pollution sources allows space-time heterogeneity in TN dynamics, the patterns of Chla dynamics may not always be characterized by simple linear models with only one input variable as a predictor (GUO *et al.*, 2021).

Using the classification criteria suggested by Cunha, Calijuri and Lamparelli (2013), the reservoirs were classified according to their trophic state using the average concentration of Chla. We identified 105 reservoirs classified as hypereutrophic, 15 supereutrophic reservoirs, 18 eutrophic, 16 mesotrophic, and only one reservoir with an average classifiable as oligotrophic (Supplementary Table 4 - https://abes-dn.org.br/wp-content/uploads/2023/08/Supplementary_material.pdf). Furthermore, it was observed that the R^2 values increased significantly according to the intensification of the trophic state, having identified significant differences between the trophic classes through the *Kruskal-Wallis* test ($H(4) = 47.813$, $p < 0.05$) (Supplementary Table 5 - https://abes-dn.org.br/wp-content/uploads/2023/08/Supplementary_material.pdf). The highest number of satisfactory or superior R^2 was found in hypereutrophic reservoirs, with 69.5% of R^2 being greater than 0.3 (p-value < 0.05). The best fits found in the eutrophic and hypereutrophic classes are associated with the decreasing trend of TP limitation with increasing Chla concentration. In oligotrophic reservoirs with lower concentrations of Chla, TP is generally the limiting nutrient. However, when the concentration of Chla in the aquatic environment increases, making it hypereutrophic, a TN co-limitation or limitation is more likely (LIANG; SORANNO; WAGNER, 2020). In addition, high phosphorus concentrations, characteristic of hypereutrophic environments, may imply a reduction in TN supply in the tropogenic zone due to excessive planktonic nitrogen use, favoring TN limitation (PHILLIPS *et al.*, 2008). The limiting nutrient change under different conditions of Chla concentration or climatic conditions was also verified in the studies by Yan *et al*. (2016), Wiegand *et al*. (2020), and Zhou *et al*. (2022).

With regard to correlations between data in the same hydrographic basin (Supplementary Figure 1 - https://abes-dn.org.br/wp-content/uploads/2023/08/Supplementary_material.pdf), the Alto Jaguaribe, Curu, and Médio Jaguaribe basins had the highest percentage of reservoirs with satisfactory or superior statistical performance. The correlations between mean TN and Chla in these basins (Supplementary Table 6 - https://abes-dn.org.br/wp-content/uploads/2023/08/Supplementary_material.pdf) were $R^2 = 0.465$ ($n = 16$ reservoirs), $R^2 = 0.417$ ($n = 13$ reservoirs), and $R^2 = 0.445$ ($n = 15$ reservoirs). The *Kruskal-Wallis* test (H(11) = 20.822; $p = 0.03$) confirmed the influence of the watershed on the linear correlations between TN and Chla. Land use in the basin area plays a relevant role in the entry of sediments and nutrients into the beds of water bodies. Urban occupation, agricultural crops, and deforestation, responsible for causing changes in the volume of surface runoff, water temperature, increase in algae production, and decrease in oxygen concentration in watercourses, occur with varying intensity in each watershed (CHEN *et al*., 2018; LOPES *et al*., 2019). Thus, each basin may be subject to different anthropic pressures, resulting in different polluting sources and anthropogenic inputs of nutrients.

Regarding the variability of TN and Chla correlations concerning size (Supplementary Figure 2A - https://abes-dn.org.br/wp-content/uploads/2023/08/Supplementary_material.pdf), the *Kruskal-Wallis* test (H(3) = 1.553; $p = 0.629$) and *Dunn's* post hoc test did not indicate significant differences between the correlations of reservoirs with different storage capacities. The averages of the correlations of the groups were similar, and the unsatisfactory statistical performance was evenly distributed among the classes (50, 52.63, 43.04, and 49.06%, respectively), thus verifying that size did not have a significant impact on the dynamics of R^2 between TN and Chla.

By analyzing the influence of variability in the annual volumetric percentage (Supplementary Figure 2B - https://abes-dn.org.br/wp-content/uploads/2023/08/Supplementary_material.pdf), estimated based on the coefficient of variation on the correlations between TN and Chla, a similar performance was identified between reservoirs with different coefficients of variability. This fact was confirmed through the *Kruskal-Wallis* variance test, which identified significant differences between the groups with different volumetric variability coefficients (H(3) = 9.658; $p = 0.02$), mainly between the high groups ($p = 0.002$) and very high ($p = 0.035$) with the medium variability group. Reservoirs with a high coefficient of variability have greater dispersion in the volume data, indicating possible extreme events of fluctuation in the water level in the reservoirs, generally considered responsible for causing more significant impacts on the chemical quality of the water, especially on the primary productivity in lakes and reservoirs (HARA; ATIQUE; AN, 2020). In periods of prolonged drought, the water level is reduced, increasing the concentration of nutrients and making the aquatic environment susceptible to cyanobacterial blooms and eutrophication processes (COSTA; ATTAYDE; BECKER, 2016; ROCHA JUNIOR *et al*., 2018).

CONCLUSION

Through the analysis of data obtained for 155 reservoirs located in the state of Ceará, Brazil, the ability of TN to predict Chla was examined, verifying the factors that influence the dynamics of the correlations. The concentration of the parameters varied between the basins, identifying that basins with denser networks of reservoirs have higher average concentrations of Chla and TN. In addition, the dynamics of Chla and TN showed a difference in seasonality governed by fluctuations in the volumetric percentage of water in the reservoirs, with an increase in the average concentrations of pollutants in most basins during the dry period, which has a lower average volume than the wet period.

The correlation models between TN and Chla found were satisfactory for all basins except for Serra da Ibiapaba, following, in all cases, the trends of classic models suggested in the literature, where the increase in the availability of nutrients in the aquatic environment favors the phytoplankton production, represented by ascending curves. Regarding the performance of the reservoirs, 53.55% ($n = 83$) of the reservoirs had satisfactory or superior performance, with the highest average R^2 in the Alto Jaguaribe, Curu, and Médio Jaguaribe basins.

Regarding the influence of the investigated factors on the linear adjustments between TN and Chla, a variance was observed in the performance of the determination coefficients regarding the influence of the hydrographic basin and the volumetric variability coefficient, indicating that possible extreme events of water level fluctuation in the reservoirs favor the increase in the concentration of nutrients in the reservoirs, making TN a better predictor in reservoirs with high variability. In addition, it was found that the trophic state of the reservoir influences the predictive capacity of nitrogen, identifying that, in oligotrophic and mesotrophic environments, TN is not the main predictor of biomass, indicating the need to investigate other factors in predicting the complex processes associated with Chla concentrations.

AUTHORS' CONTRIBUTION

Guimarães, B.M.D.M.: Conceptualization, Formal Analysis, Investigation, Methodology, Writing – Original Draft. Lima Neto, I.E.: Conceptualization, Formal Analysis, Writing – Review & Editing, Supervision, Project Administration.

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