Revista Ciência Agronômica, v. 51, n. 1, e20196800, 2020
Centro de Ciências Agrárias - Universidade Federal do Ceará, Fortaleza, CE
www.ccarevista.ufc.br

Scientific Article
ISSN 1806-6690

Balance of nitrogen and phosphorus in a reservoir in the tropical semi-arid region[1]

Balanço de nitrogênio e fósforo em um reservatório na região semi-árida tropical

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ABSTRACT - In relation to the process of eutrophication of water reservoirs, it is necessary to understand the nitrogen and phosphorus supply, as well as they contribute to the eutrophication process. The aim of this research was to quantify the input and the balance of phosphorus and nitrogen, as well as to identify the effect of climate seasonality on dynamics of these nutrients in a reservoir. The campaigns took place from April/2008 to Dec/2012 at the Orós reservoir, located in the semi-arid region of Brazil. Based on dataset it was possible to calculate the inflow and outflow of total nitrogen (TN) and total phosphorus (TP). The reservoir becoming a storage place for the nutrients transported by the flow of water from the drainage network. A total of 176 Mg of nitrogen and 230 Mg of phosphorus were retained in the reservoir. The TN and TP retained in the reservoir can lead to the water being compromised by eutrophication, increasing the financial cost of water treatment and compromising water availability for consumption use (human, livestock, irrigation and industry). Because it is a predominantly agricultural basin, and the nutrients show a similar input trend in the reservoir, it is believed that the primary source of nutrients is agriculture and livestock, also wastewater from cities around reservoir. There has been an increase in nutrient input of over time. Reservoirs in semi-arid regions are unique as regards nutrient load during dry periods, since even without fluvial input, nutrient concentrations generally remain steady or increase.

Key words: Nutrients source. Mass balance. Chlorophyll-a. Semi-arid eutrophication. Water quality.

RESUMO - A eutrofização dos reservatórios de água aumenta os custos de tratamento para sua utilização nos múltiplos uso, portanto é necessário conhecer o aporte do nitrogênio e do fósforo, uma vez que estes contribuem com o referido processo. Portanto, objetivou-se com esta pesquisa quantificar o aporte e o balanço do fósforo e nitrogênio; bem como identificar o efeito da sazonalidade climática na dinâmica desses nutrientes em reservatório. No período de abr/2008 a dez/2012 foram realizadas 21campanhas de coleta de água no reservatório Orós, localizado no semiárido brasileiro, Ceará, Brasil. Tendo-se por base os dados de campo foram calculados o fluxo de entrada e saída de nitrogênio total (NT) e fósforo total (PT). Foi identificado que o reservatório se mostrou como um sumidouro dos nutrientes transportados pelo escoamento superficial, com uma retenção de 176 Mg de NT e 230 Mg de PT durante o período de estudo. A retenção de NT e PT pelo reservatório pode resultar no comprometimento da qualidade das águas pela eutrofização, aumentando os custos para disponibilizar uma água de qualidade para os diferentes usos. Por se tratar de uma bacia hidrográfica predominantemente agropecuária e os nutrientes apresentarem a mesma tendência de aporte no reservatório, acredita-se que a fonte primaria dos nutrientes seja a agricultura e a pecuária. Houve aumento do aporte de nutrientes ao longo do tempo. Os reservatórios de regiões semiárida são peculiares quanto a carga de nutrientes em períodos secos, pois mesmo sem aporte fluvial é comum manutenção e/ou aumento das concentrações de nutrientes.

Palavras-chave: Fontes de nutrientes. Balanço de massa. Clorofila-a. Eutrofização semi-árida. Qualidade da água.

DOI: 10.5935/1806-6690.20200020
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Received for publication 27/06/2019; approved on 23/11/2019
[1]Parte da Dissertação de Mestrado do segundo autor, apresentada ao Programa de Pós-Graduação em Ecologia e Recursos Naturais, Universidade Federal do Ceará
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INTRODUCTION

The accelerated growth in population, coupled with the uncertainty of the spatial and temporal distribution of rainfall in semi-arid environments (ANDRADE *et al*., 2016), results in the water deficit always present in these regions (KAMPF *et al*., 2016; VAROL, 2013). As a way of minimising water scarcity in semi-arid areas, governments adopt a practice of reservoir building to store surface runoff. Records of dam construction to meet the man's water demands date from 1000 BC. During the processes of water runoff and storage, a large quantity of nutrients is transported and deposited in the reservoirs (JORDAN *et al*., 2012; MOURA; VALENTI; HENRY-SILVA, 2016; SANTOS *et al*., 2016a; SANTOS *et al*., 2016b). In the Brazilian semi-arid region, climate variability, the long water retention time and high rates of evapotranspiration, added to anthropic action upstream of the basin, contribute to an increase in nutrient concentrations, in the water column, and acceleration of the eutrophication process of the aquatic ecosystem (GONZÁLEZ; ROLDÁN, 2019).

A greater contribution to the nutrient load in waterbodies increases the net production of the ecosystem, shifting the system towards autotrophy (BECKER *et al*., 2010), with the proliferation of phytoplankton (ROCHA; ANDRADE; LOPES, 2015; YANG *et al*., 2012). Among the nutrients that influence the eutrophication of aquatic ecosystems, nitrogen and phosphorus have the greatest contribution (MACEDO; SIPAÚBA-TAVARES, 2018). Nitrogen (N) is an important element for the formation of living organic matter. The main sources of N for continental aquatic ecosystems are the biological fixation of nitrogen by phytoplankton (BECKER *et al*., 2010); rainfall (GIESE *et al*., 2011); the input of domestic and industrial effluent (LI *et al*., 2015) and farming activities (ESTEVES, 2011).

The importance of phosphorus as a nutrient is due to its participation in the fundamental processes of living beings, such as energy storage, the structuring of cell membranes, and cellular metabolism (ESTEVES, 2011). In aquatic systems, phosphorus is a limiting element, compared to the availability of other nutrients (ROCHA; ANDRADE; LOPES, 2015). The availability of phosphorus has a positive influence on phytoplankton biomass (ROCHA; ANDRADE; LOPES, 2015), which compromises the photic layer and triggers the process of eutrophication. Phosphorus is assimilated biologically only in the form of phosphate. The phosphate present in aquatic ecosystems has natural and artificial origins: rocks in the drainage basin, atmospheric precipitation, organic and inorganic fertiliser residue, and domestic and industrial sewage (VAROL, 2013).

It can therefore be inferred that the input of nutrients in an artificial lake increases the eutrophication potential in the waterbody, in addition to altering the ionic balance present in the reservoir (PAULA *et al*., 2010). In rural environments, the greatest supply of nutrients in waterbodies originates in widely spread sources such as farming areas. Evaluating nutrient behaviour in water-supply reservoirs is an indispensable part of monitoring water quality (VIDAL; CAPELO NETO, 2014). Understanding nutrient balance is important to ensure quality of a water body. The aim of this research therefore, was to quantify the input and the balance of phosphorus and nitrogen, as well as to identify the effect of climate seasonality on dynamics of these nutrients in a reservoir in the semi-arid region of Brazil.

MATERIAL AND METHODS

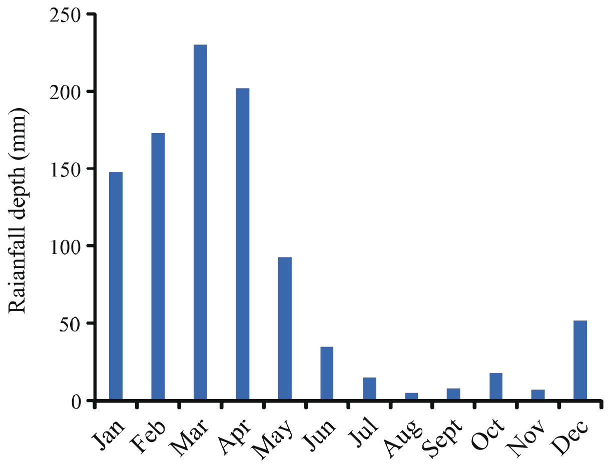
Study Area

The Orós reservoir is inserted in the Upper Jaguaribe river basin, which drains an area of 25,242 km^2. It is a strategic reservoir in the management of water resources by the State, with the capacity to store 1.94 billion m^3, and a regularised mean flow rate of 5.63 m^3 s^{-1} (COMPANHIA DE GESTÃO DOS RECURSOS HÍDRICOS DO CEARÁ, 2010). Among the multiple uses of the water stored in the reservoir, the most important is the supply to the populations of the Mid and Lower Jaguaribe, and the metropolitan region of the state capital, Fortaleza, corresponding to a population of 3.12 million people (INSTITUTO BRASILEIRO DE GEOGRAFIA E ESTATÍSTICA, 2017). The perenialisation of the River Jaguaribe by the Orós dam also supplies the irrigated fields of the lower and upper Jaguaribe basins, for food production, fish farming and tourism. The climate zone of the region is BSw'h', a hot semi-arid climate with maximum rainfall in the Autumn and average monthly temperature above 18 °C. The average historical rainfall in the region (Iguatu, Icó, Quixelô, Orós municipality stations) is 823 mm, with 86% of it being concentrated from January to May (Figure 1), of which around 25% is recorded in March. The average potential evaporation is around 1988 mm year^{-1}.

The area around the river basin of the Orós reservoir has several uses (ARRAES; ANDRADE; SILVA, 2012), which may influence the nutrient balance of the waters in the reservoir. The four most important types of land use in the areas surrounding the reservoir are: Open vegetation (45%), Degraded area (28%), Dense vegetation (12%) and Crops (6%). The main human settlements close to the reservoir are Iguatu city with 100000 inhabitants and the villages of

Suassurana, Santa Clara, and Barreiro, with a total of 6000 habitants.

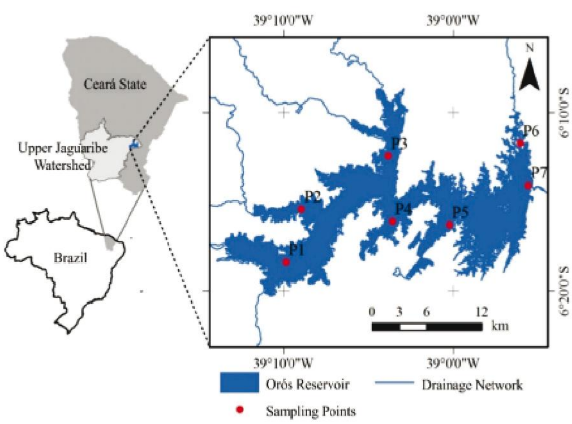
Figure 1 - Average monthly precipitation of the region. Historical dataset: 1978-2018). Stations: (Iguatu, Icó, Quixelô, Orós municipality)



Data set

During the period of study, from April 2008 to December 2012 (56 months) twenty collection campaigns (each three months) were carried out at seven water quality monitoring stations (P1, P2, P3, P4, P4, P5 and P7). These stations represent the principal entries into the Orós reservoir (Figure 2). Stations P1 to P6 represent inputs, while P7, located in the spillway of the reservoir, represent the outputs. A total of 140 samples (20 campaigns x 7 seasons) were collected.

Figure 2 - Sampling stations in the Orós reservoir, Iguatu, Ceará



Hydrochemistry Characteristics

The physical-chemical variables of the water column were obtained in situ. Dissolved oxygen with winkler method (Azide modification)-iodometry. The electrical conductivity and pH of water samples were carried out with the ECTestr and pHTestr (Oakton®). The transparency with a Secchi disk. The Total Nitrogen (TN) and Total Phosphorus (TP) analyses were conducted by standard methods for surface waters (AMERICAN PUBLIC HEALTH ASSOCIATION, 2005).

Samples were filtered immediately after collection and frozen for later analysis, filters were used to obtain the concentration of the total suspended solids in the water (TSS). To quantify chlorophyll-a, filtered samples were stored frozen and transported to the laboratory where quantification was obtained in a spectrophotometer according to standard method (AMERICAN PUBLIC HEALTH ASSOCIATION, 2005). The Principal Component Analysis (PCA) was used to describe the relationships between variables. The analyses were performed by SPSS Software, v.16.

Nutrient Balance

To calculate the nutrient balance in terms of flow, P1 was considered an entry point and P7 an exit point (Figure 2). The choice to consider only P1 as an entry point, is because this point represents the input of the River Jaguaribe, which drains 98% (24,900 km^2) of the tributary basin of the Orós reservoir. Inflow and outflow were based on the continuity equation (Equation 1) and showed the balance of the material analysed throughout the reservoir.

$$dS/dt = I - Q \tag{1}$$

Where: S = volume (m^3); t = time (s); I = inflow rate(m^3 day^{-1}); Q = outflow rate (m^3 day^{-1}).

The inflow rate was calculated considering the daily variation in the volume stored in the dam, obtained from daily elevation readings, and the relationship to evaporation, precipitation and the flow rate released by the dam. All the information was provided by the (COMPANHIA DE GESTÃO DOS RECURSOS HÍDRICOS DO CEARÁ, 2013). Equation 2 was used to estimate the input flow rate, represented by I:

$$V_{t+1} = V_t + I - E_t - S_t - R_t \tag{2}$$

Where: V_{t+1} = volume for the current time (m^3); Vt = volume for the previous time (m^3); I = total inflow to the reservoir (m^3 day^{-1}); Et = evaporation for a given time (m^3 day^{-1}); St = spill (m^3); Rt = withdrawal (m^3 day^{-1}). Rearranging the terms, we have Equation 3:

$$I = \Delta V + E_t + S_t + R_t \quad (3)$$

The term ΔV (m³) was obtained from the ELEVATION x VOLUME table. Values for *Et* were based on daily evaporation. The term *Rt* is the flow rate released by dam, determined by the operating routine of the reservoir. This flow rate considers the volume stored during the rainy season and the demands throughout the basin including perenialisation of the River Jaguaribe, human supply and the irrigated perimeters. Data for the ELEVATION x VOLUME table and the flow rate released by the dam were provided by Companhia de Gestão dos Recursos Hídricos do Ceará (2013). The discharge volume (*S*) was estimated based on elevation of the spillway crest (200 m). If the elevation flow <200 m, the discharge is zero ($S = 0$). If >200 m, the discharge is given by Equation 4:

$$S = C.\ L.\ (H - H_{sp})^{1,5} \quad (4)$$

Where: C = the discharge coefficient (varies according to the shape of the spillway, here 2.1 was used); L = spillway width (180 m); H = flow elevation; H_{sp} = spillway elevation crest (200 m).

Once the daily input flow rates were determined, the mean inflow rate between the collection campaigns was calculated from the sum of the daily flow rates divided by the number of days in each period. The daily output flow rate was obtained through the operating routine of the reservoir. Calculating the sum of the daily flows divided by the number of days in each period provided the mean output flow rate. Knowing the values of the entry and exit flow rates of the reservoir, the inflows and outflows were calculated using Equation 5:

$$Flow = [N] \times Flow\ Rate/1000 \quad (5)$$

Where: *Flow* = input flow or output flow (kg day^{-1}); [*N*] = nutrient concentration (mg L^{-1}); *Flow Rate* = entry or exit flow rate (m^3 day^{-1}).

RESULTS AND DISCUSSION

Hydrochemistry Characteristics

The high input of TSS found in P1 and P2 (Table 1), the main tributaries of the reservoir, is a result of agricultural activity in the reservoir basin (LOPES *et al*., 2014; ROCHA; ANDRADE; LOPES, 2015). Another source that contributes to the input of TSS is fish farming (P5) (Table 1). This activity is a direct source of nutrients with the highest values for chlorophyll-a, contributing directly to the increase in eutrophication. The mean value of 8.2 for pH may be associated with intense photosynthetic activity due to the high availability of solar energy (ROCHA; ANDRADE; LOPES, 2015), or to salts and nutrients that come from agricultural activities and fish farming (SANTOS *et al*., 2016a).

Values for chlorophyll-a and DO throughout the body of water are, respectively, greater than the value permitted (10 µg L^{-1}) and (>5 mg L^{-1}) under Brazilian legislation (BRASIL, 2005). The lower values for SRP recorded in the area of fish farming might be explained by the high assimilation of the phytoplankton community (ROCHA; ANDRADE; LOPES, 2015).

The Orós reservoir reflects conditions of nutrient input and consequent eutrophication. This situation tends to worsen when the volume in the reservoir decreases during the dry season or in situations of severe drought (ROCHA; ANDRADE; LOPES, 2015). Reservoirs in semi-arid regions are unique as regards nutrient load during

Table 1 - Mean value for the attributes monitored in the surface waters of the Orós reservoir in the northeast of Brazil during the monitoring period (April 2008 to December 2012)

Point	pH	TSS (mg L^{-1})	SRP (mg L^{-1})	Chlorophyll-a (µg L^{-1})	DO (mg L^{-1})	Temperature (ºC)	Secchi (m)
P1	8.2 ± 0.5	19.99 ± 20.36	0.06 ± 0.04	13.64 ± 12.27	6.80 ± 2.09	29.3 ± 2.3	0.45 ± 0.15
P2	8.3 ± 0.5	20.56 ± 24.23	0.04 ± 0.05	18.85 ± 16.10	7.30 ± 2.43	29.8 ± 2.3	0.60 ± 0.19
P3	8.1 ± 0.5	9.79 ± 9.60	0.06 ± 0.03	31.70 ± 10.62	7.12 ± 2.41	29.9 ± 1.8	3.02 ± 6.94
P4	8.2 ± 0.4	6.69 ± 3.38	0.05 ± 0.00	22.07 ± 10.91	7.89 ± 2.00	30.0 ± 1.8	0.84 ± 0.13
P5	8.1 ± 0.5	12.75 ± 15.24	0.01 ± 0.00	35.22 ± 16.81	6.66 ± 2.43	30.6 ± 1.7	0.96 ± 0.17
P6	8.2 ± 0.5	8.15 ± 5.38	0.02 ± 0.02	20.17 ± 18.64	7.07 ± 1.75	29.1 ± 1.5	1.14 ± 0.58
P7	8.2 ± 0.5	10.88 ± 18.22	0.03 ± 0.02	22.16 ± 16.15	6.58 ± 1.75	28.6 ± 1.6	1.28 ± 0.53

DO Dissolved Oxygen, SRP Soluble Reactive Phosphorus, TSS Total Suspended Solids, P1 - River Jaguaribe, P2 - River Faé, P3 - River Madeira, P4 - Stream deep, P5 - Fish farming, P6 - River Santarém, P7 - Spillway dry periods, since even without fluvial input, nutrient concentrations generally remain steady or increase due to water evaporation. A study carried out by Molisani *et al*. (2013), found that 97% of the incoming load is retained in the hypolimnion, and when the depth of the reservoir decreases, this favours resuspension of the material on the bottom, increasing the nutrients in the column.

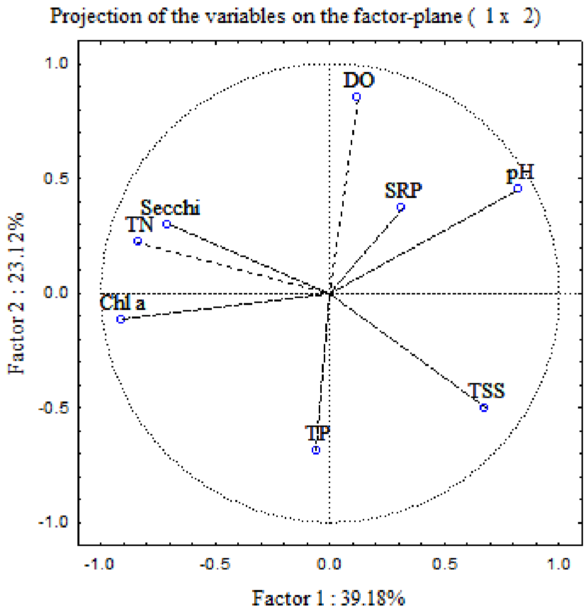
Components PC1, PC2 and PC3 of the principal component analysis (PCA) account for 84% of the processes occurring in the reservoir (Table 2 and Figure 3). PC1, explaining 39% of the internal structure of the data (variability), proves to be a nutritional component, since the highest loads are expressed by the total nitrogen (TN), chlorophyll-a and transparency (Secchi), the latter not so strongly as the others. Besides, they showed a strong relationship with each other (Figure 3). It is known that the main natural sources of nitrogen are rain, Organic Matter - OM (diffuse source) and biological fixation by bacteria (ROCHA; ANDRADE; LOPES, 2015). The high loads that make up PC1 are indicative of an environment rich in nutrients, and may indicate the presence of cyanobacteria (ROCHA; ANDRADE; LOPES, 2015), since transparency is low, and chlorophyll-a is high (Table 2). Studies carried out in the reservoir during the same period found the frequency of groups of cyanobacteria to be between 50% and 60% in the collected samples (ROCHA; ANDRADE; LOPES, 2015). The group of Cyanophyceae became dominant irrespective of the rainfall regime. Such behaviour shows the existence of other sources as fish farming and/ wastewater contaminating the water supplying the Orós reservoir.

Table 2 - Loading and total variance in the principal component analysis (PCA) for water of the Orós reservoir, Brazil during the monitoring period (April 2008 to December 2012)

Variables	Components		
	PC1	PC2	PC3
TN	0.940		
Clorofilla-a	0.873		
Secchi	0.757		
pH	-0.726		
SRP		0.860	
DO		0.812	
TP			0.939
TSS			0.710
Eigenvalues	3.135	1.850	1.730
% of variance	39.18	23.14	21.62
Cumulative (%)	39.18	62.32	83.93

TN Total Nitrogen, SRP Soluble Reactive Phosphorus, DO Dissolved Oxygen, TP Total Phosphorus, TSS Total Suspended Solids

Figure 3 - Biplot of the hydrochemical attributes in the Orós reservoir throughout the during the monitoring period (April 2008 to December 2012)



TN Total Nitrogen, TP Total Phosphorus, DO Dissolved Oxygen, SRP Soluble Reactive Phosphorus, TSS Total Suspended Solids

It was expected that phosphorus would show a positive correlation with chlorophyll. One explanation for this relationship not occurring in the principal component analysis would be the hypothesis that nitrogen functions as a limiting factor. The nutrient TP, always being present, would not influence the growth of the cyanobacteria (Figure 3), since the strong relationship with the TSS would act to buffer the soluble fraction due to the high capacity for adsorption with the fine fraction (WU *et al*., 2016). This hypothesis is reinforced by the high positive correlation between TP and TSS in PCA 3 (Table 2). The inverse relationship of TP with DO (Figure 3) and SRP seen in PC2 (Table 2) can be explained by the degradation process of the organic matter, which releases phosphate into the water column (SANTOS *et al*., 2016b).

Nutrient Balance

The concentrations of total nitrogen (TN) in the waters of the Orós reservoir were always at acceptable values for human consumption (≤10 mg L^{-1}), according to a Ministry of Health ordinance (BRASIL, 2012). These low concentrations are explained by the fact that nitrogen displays rapid mineralisation (ESTEVES, 2011). The mean values were recorded in the following order P3>P5>P4>P6>P2>P1>P7, showing that the highest concentrations do not occur in the main tributary, P1 (Table 3), as expected, but at P3. The highest concentrations

Table 3 - Descriptive statistics for Total Nitrogen (TN) concentrations (mg L^{-1}) in the surface waters of the Orós reservoir in the northeast of Brazil during the monitoring period (April 2008 to December 2012)

Point	Wet Season				Dry Season			
	Min	Max	$\bar{X}$ ± SD	CV (%)	Min	Max	$\bar{X}$ ± SD	CV (%)
P1	0.305	2.304	0.932 ± 0.559 a	60.0	0.085	1.887	0.782 ± 0.515 a	65.9
P2	0.306	1.507	0.942 ± 0.335 a	35.5	0.085	1.429	0.829 ± 0.432 a	52.1
P3	0.962	1.886	1.317 ± 0.479 a	36.4	1.057	1.393	1.171 ± 0.192 a	16.4
P4	0.167	3.177	1.672 ± 2.128 a	127.3	0.641	0.922	0.817 ± 0.154 a	18.8
P5	0.220	1.866	1.290 ± 0.765 a	59.3	0.835	1.507	1.092 ± 0.363 a	33.2
P6	0.262	3.381	1.162 ± 0.919 a	79.1	0.047	1.642	0.697 ± 0.446 a	64.0
P7	0.305	2.275	0.981 ± 0.517 a	52.7	0.048	1.702	0.660 ± 0.453 a	68.7

P1 - River Jaguaribe, P2 - River Faé, P3 - River Madeira, P4 - Stream deep, P5 - Fish farming, P6 - River Santarém, P7 – Spillway. The different letters indicate statistical difference between seasons in each point ($p<0.05$). It was applied test of normality Shapiro-Wilk, applied test t at normal distribution and Mann-Whitney test in nonparametric data

recorded at point P3, P5 and P4 are related to fish farming in cages (Figure 4), expressing enrichment of the water by fish feed residue (MACEDO; SIPAÚBA-TAVARES, 2018). The lower CV recorded at P3 shows that TN input was constant irrespective of the time of year.

The mean concentration of phosphorus at all points (Table 4) was higher than the standard limits determined for human consumption by Conselho Nacional do Meio Ambiente (CONAMA) Resolution No 357/2005, which stipulates a maximum of 0.02 and 0.03 mg L^{-1} in lentic environments for classes I and II freshwater, respectively (BRASIL, 2005). These results express water enrichment by this nutrient. The highest mean concentration was recorded at P1, the main tributary of the reservoir, the River Jaguaribe. The CV greater than 130% identifies high temporal variability in the input of phosphorus to the reservoir.

This high variability expresses the seasonal effect between the wet/dry seasons on the concentration of nutrients delivered to the reservoir by surface runoff. The average concentration during wet season did not differ statistically ($p<0.05$) from the dry season average (Table 4). Since the drainage network of the River Jaguaribe consists of ephemeral courses, the highest nutrient concentrations occur with the maximum flow rates registered during the rainy season (Tables 3 and 4). During dry season, the water input to the Orós reservoir is limited to the regulated water of reservoirs upstream (minimum

Figure 4 - Fish farming in the Orós Reservoir, Ceará, Brasil, (Author: Lopes, Jul/2009)

Table 4 - Descriptive statistics for Total Phosphorus (TP) concentrations (mg L^{-1}) in the surface waters of the Orós reservoir in the northeast of Brazil during the monitoring period (April 2008 to December 2012)

Point	Wet Season				Dry Season			
	Min	Max	$\overline{X} \pm SD$	CV (%)	Min	Max	$\overline{X} \pm SD$	CV (%)
P1	0.026	1.407	0.376 ± 0.492 a	130.8	0.020	1.829	0.280 ± 0.550a	196.0
P2	0.044	0.695	0.238 ± 0.209 a	87.8	0.019	0.285	0.108 ± 0.099a	92.2
P3	0.032	0.514	0.242 ± 0.198 a	81.7	0.060	0.207	0.159 ± 0.067 a	42.0
P4	0.089	0.190	0.140 ± 0.071 a	51.1	0.103	0.360	0.177 ± 0.122 a	69.0
P5	0.110	1.281	0.459 ± 0.555 a	121.1	0.060	0.333	0.175 ± 0.114 a	65.4
P6	0.030	0.486	0.197 ± 0.178 a	90.5	0.006	0.211	0.083 ± 0.074 a	89.1
P7	0.017	0.304	0.125 ± 0.095 a	76.4	0.003	0.208	0.078 ± 0.750 a	96.4

P1 - River Jaguaribe, P2 - River Faé, P3 - River Madeira, P4 - Stream deep, P5 - Fish farming, P6 - River Santarém, P7 - Spillway. The different letters indicate statistical difference between seasons in each point ($p<0.05$). It was applied test of normality Shapiro-Wilk, applied test t at normal distribution and Mann-Whitney test in nonparametric data

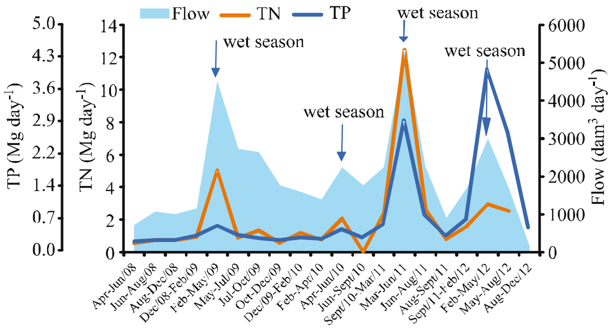
discharge), since the drainage network is composed of ephemeral or intermittent channels. Due to the absence of natural flow, we believe that the input of nutrients during dry season comes from grey waters generated by the cities and villages located around the reservoir.

Phosphorus enrichment of the surface runoff originating in agricultural areas has already been discussed by various researchers (JORDAN *et al*., 2012; VAROL, 2013). The highest phosphorus concentrations at P1 (0.280 mg L^{-1}) during dry season are due to the wastewater flow from Iguatu city (100,000 habitants) which is 20 km away from the Orós reservoir. Unregulated land use and nonexistent or inefficient wastewater treatment have increased nutrient concentration in many reservoirs of the Americas (GONZÁLEZ; ROLDÁN, 2019). Possible low values for P near the dam can be explained by the sedimentation of fine particles and by adsorption (WU *et al*., 2016). P accumulation in the sediment depends on the hydrochemistry influencing remobilisation (ESTEVES, 2011), since conditions of anoxia influence the availability of phosphorous in the water column. The greater the oxidic conditions, the greater the retention of sediment and, consequently, the lower the availability in the column.

Input of the nutrients TN and TP showed the same trend throughout the study period, registering higher intake during the rainy season (Figure 5). The highest nutrient concentrations being associated with the maximum flow rates (BECKER *et al*., 2010) show that nutrient intake originates with surface runoff from areas of farming and livestock (VAROL, 2013; WU *et al*., 2016).

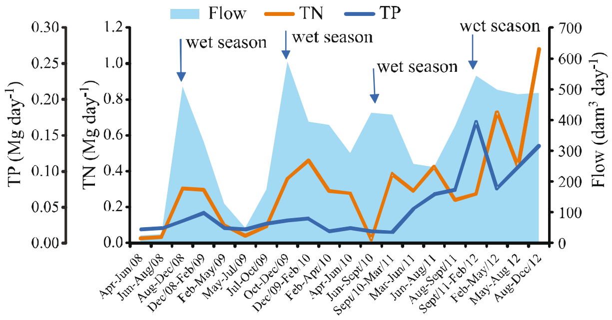
Removal of the natural cover with the introduction of farming breaks the internal nutrient cycle, and it becomes necessary to adopt fertilisers to maintain or increase agricultural productivity. In general, more nutrients are applied than the crops can absorb, leaving them available for transport by surface runoff (KAMPF *et al*., 2016; MOLISANI *et al.*, 2013) and deposition in the waterbodies (BECKER *et al*., 2010). The replacement of the natural vegetation by agriculture results in lower rates of infiltration and greater surface runoff. This fact, together with the rainfall regime (ANDRADE *et al*., 2016) and shallow soils of the tributary basin of the reservoir, determine a low rate of infiltration and high runoff depths, thereby favouring greater transport of nutrients to the waterbodies.

Figure 5 - Input flow of Total nitrogen (TN) and Total phosphorus (TP) in the Orós reservoir, during the monitoring period (April 2008 to December 2012)



Although the outputs of TN and TP from the reservoir do not show similar behaviour (Figure 6), as was seen for input (Figure 5), the delivery rate of the TN, as for the input, was always higher than that of the TP. Such a fact is to be expected, since nitrogen is the most abundant chemical element in the atmosphere and the fifth in nature (GIESE *et al.*, 2011), and a great part of the nitrogen present in the waterbodies is added by the rains, originating in the atmosphere (GIESE *et al*., 2011).

Figure 6 - Output flow of Total nitrogen (TN) and Total phosphorus (TP) in the Orós reservoir, during the monitoring period (April 2008 to December 2012)



However, an increase in concentration over the period of study can be seen for both nitrogen and phosphorus, although it is less pronounced in the latter. This difference in accumulation is a function of the total input of each nutrient, and of the way they are retained as bed material and in the water column (LI *et al.*, 2015). The TN and TP input average rates were 18 Mg day^{-1} and 3.82 Mg day^{-1}, respectively. The maximum discharges of TN and TP coinciding with the maximum discharges from the reservoir, express the action of the wet season on nutrient delivery from the reservoir to the lower parts of the basin (BECKER *et al*., 2010; MOLISANI *et al.*, 2013). The TN and TP output average rates were 2.28 Mg day^{-1} and 0.34 Mg day^{-1}, respectively. Although, the TN input and output rates are almost 5 times higher than the TP rates; both have similar relative delivery rates: 12% for TN and 9% for TP.

During the study period, there was a progressive accumulation of nitrogen (Figure 7), totalling 176 Mg of TN, expressing the enrichment of the waters of the Orós reservoir. Output of the nutrient in the last campaign (shown by the slight fall in the value of the accumulated balance) can be explained by the flow rate released by the reservoir being greater than the input flow rate (VIDAL; CAPELO NETO, 2014). It can be seen that the largest increases in nitrogen input flow occurred during the rainy seasons of 2009 and 2011. Rainfall for the two years was 1,007 mm in 2009 and 1,229 in 2011, which was higher than the annual average (823 mm).

The phosphorus (Figure 8) showed the same trend as the nitrogen (Figure 7), i.e. a higher input rate over time, and a higher accumulation of the nutrient in the waters of the reservoir. This expresses the availability of nutrients in the water, favouring the process of eutrophication (JORDAN *et al*., 2012; LI *et al.*, 2015). The low rate of nutrient output over time compared to input resulted in an accumulation of 230 Mg of TP in 4 years, with the reservoir becoming a nutrient sink in relation to the Jaguaribe river basin.

Figure 7 - Nitrogen flow and balance in the Orós reservoir, Iguatu, Ceará

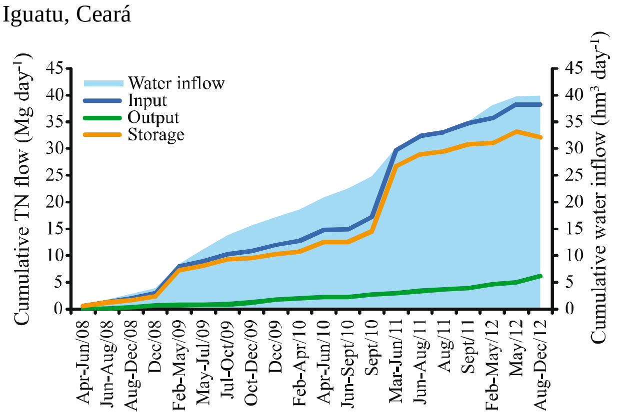
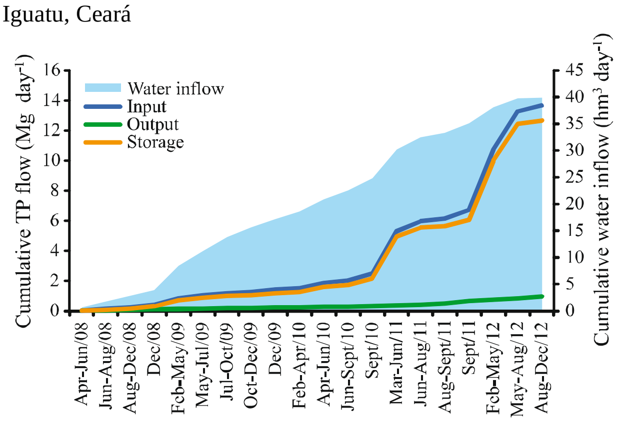


Figure 8 - Phosphorus flow and balance in the Orós reservoir, Iguatu, Ceará



The increase in phosphorus input to the reservoir during the periods considered as rainy is characteristic of an input due to surface runoff from areas of agricultural activity (GIESE *et al.*, 2011; LI *et al.*, 2015). Similar results were found by Molisani *et al.* (2013) in the Castanhão reservoir. According to Maia, Lopes and Andrade (2018), more than 15% of the permanent protection area around the Orós reservoir is occupied by rice crops; this type of land use results in the release of nutrients such as phosphorus and nitrogen into the reservoir (WU *et al*., 2016).

Furthermore, the high increase in accumulated flow during 2011 was similar to that of the nitrogen and was also associated with the intense rainfall that occurred that year (FUNDAÇÃO CEARENSE DE METEOROLOGIA E RECURSOS HÍDRICOS, 2014). In addition to the increase in affluent load, there was phosphorus retention, which can be caused by the concentration of various ions in the reservoir, such as iron, aluminium and sulphide, in addition to conditions of pH and redox, factors which together can cause the precipitation and storage of phosphorus in the reservoir (MOLISANI *et al*., 2013; SANTOS *et al*., 2016b; VIDAL; CAPELO NETO, 2014).

The increasing accumulation of the two nutrients by the end of the study period underlines the eutrophic potential of the reservoir, since they are regulators of the process. It is also worth noting that nitrogen is considered the mainly limiting element in triggering the process of eutrophication, as some species of algae show the ability to fix nitrogen from the atmosphere (VAROL, 2013). This N limitation is verified by the concentrations observed in Tables 3 and 4 which reinforce the evidence for a low N/P ratio, confirmed by the dominance of cyanobacteria (ROCHA *et al*., 2016).

CONCLUSIONS

The results point out that the highest concentrations of TN and TP during the rainy season are due to diffuse pollution sources. The main source for Nitrogen enrichment of the water is related to fish farming. The low average rate of TN (2.28 Mg day^{-1}) and TP (0.34 Mg day^{-1}) output over time when compared to intake (18 Mg day^{-1} and 3.82 Mg day^{-1} to TN and TP, respectively), characterizes the reservoir as a nutrient sink in relation to the Jaguaribe river basin. The TN and TP retained in the reservoir can lead to the water being compromised by eutrophication, increasing the financial cost of water treatment and compromising water availability for human, agricultural and livestock consumption. During the 56 months of study, the Orós reservoir showed a positive balance accumulating 176 Mg of nitrogen and 230 Mg of phosphorus. Increased nutrient input to the reservoir over time was detected as well as a similar input trend, since they share the same origin: agricultural areas and livestock. As the areas of fish farming are included in the reservoir, they already show a stocked load.

ACKNOWLEDGEMENTS

The authors wish to thank Brazilian National Council for Scientific and Technological Development (CNPq) and Coordination for the Improvement of Higher Education Personnel (CAPES) for their financial support of this research and scholarships.

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