

RESEARCH ARTICLE

ASSESSMENT OF INORGANIC NUTRIENTS AND REDFIELD RATIOS IN WATERS ALONG ABOBO-DOUMÉ FISH MARKET, CÔTE D'IVOIRE

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Manuscript Info

Abstract

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Key words:-

Nutrients, Water Quality, Redfield Ratio, Abobo-Doumé Fish Market, Ebrié Lagoon, Côte d'Ivoire Dissolved inorganic nitrogen and phosphorus are among the pollutants that are used worldwide for coastal waters quality assessment due to their ecological and toxicological effects on the aquatic ecosystemsWaters' quality along the Abobo-Doumé Fish Market in Ebrié Lagoon was assessed using five (5) stations by measuring pH, temperature, salinity, Electric conductivity, transparency and Total dissolved solids (TDS) on one hand, and on the other hand, inorganic nutrients concentrations as ammonium (NH_4^+) , nitrite (NO_2^-) , nitrate (NO_3) and phosphates (PO_4^{3}) by colorimetric methods. To quantify the primary production limitation, the N:P ratios were calculated and then compared to the Redfield one (16:1). Temperature, pH, salinity, Electric conductivity, transparency and Total Dissolved Solids (TDS) were found in respective ranges of 27.99-28.71°C; 8.23-8.39; 28.50-30.43%; 44.30-46.7mS/Cm, 0.5-1.0m and 27.48-29.11 mg/L. NH₄⁺, NO_2^- , NO_3^- and PO_4^{3-} were found in the respective ranges of 0.318-0.753, 0.060-0.067, 1.90-5.20 and 0.38-0.55 mg/L. The highest concentrations of nitrogen and phosphorus species were respectively observed in surface and bottom waters. The analyzed waters were of Bad Quality due to high nitrate, nitrite and phosphates concentrations that were more than three times above the Bad Ouality Class defined by the European Environmental Agency's criteria. The N:P ratios ranged from 7.94 to 25.36, and the ratios observed in surface waters were higher than the bottom ones. Waters were generally phosphorus (P)-Limited in surface and nitrogen (N)-Limited in bottom layers. Due to the high nutrients concentrations observed, a long-term assessment is therefore recommended to evaluate the temporal trends of the waters quality along Abobo-Doumé Fish Market.

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Introduction:-

Nitrogen (N) and phosphorus (P) are the major nutrients that cause eutrophication and other adverse impacts associated with nutrient over-enrichment (Howarth et al., 2000; Chen et al., 2020; Tuo et al., 2020a). Nitrogen, the most abundant chemical element of the Earth's atmosphere with almost 80% is also one of the essential component of many key biomolecules such as amino acids, nucleotides, etc. (Camargo and Alonso, 2006). In coastal areas, nutrients of natural origin involves the decomposition of plants and animal materials. The most important of nutrients of natural origins is from anthropogenic activities such as atmospheric, synthetic fertilizer, animals and

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septic wastes, residential development, domestic and agricultural practices, sewage discharges, harbor and industrial activities, etc. These natural inputs of nutrients can increase the nutrients amounts in coastal environments (Camargo and Alonso, 2006; Seitzinger et al., 2010; Kataria et al., 2011; Wise et al., 2011; Tuo et al., 2012; Bhuyan et al., 2017; Tuo et al., 2020a). Ammonium (NH_4^+) , nitrite (NO_2^-) and nitrate (NO_3^-) are widely studied, as they are the most common ionic (reactive) forms of dissolved inorganic nitrogen in aquatic ecosystems (Kinne, 1984; Howarth, 1988; Day et al., 1989; Wetzel, 2001; Rabalais, 2002; Camargo and Alonso, 2006). In oxygenated waters, ammonium is oxidized in nitrite and finally in nitrate by aerobic chemoautotrophic bacteria, primarily Nitrosomonas and Nitrobacter (Sharma and Ahlert, 1977; Wetzel, 2001; Camargo and Alonso, 2006). Dissolved inorganic nitrogen (Howarth, 1988; Harper, 1992; Paerl, 1997; Wetzel, 2001; Dodds et al., 2002; Smith, 2003).

Phosphorus is a vital nutrient for converting sunlight into usable energy, and essential to cellular growth and reproduction. Phosphorus occurs in dissolved organic and inorganic forms or attached to sediments particles. Phosphates, the inorganic form are the preferred forms for plant growth, even if other forms like organics ones are absorbed by plants when phosphates are unavailable. The cultural eutrophication of freshwater, estuarine, and coastal marine ecosystems can cause ecological and toxicological effects that can lead to the proliferation of primary producers. Eutrophication can threaten the ecological equilibrium of the affected water due to hazardous effects like toxic algal blooms, increase growth of nuisance microalgae. An increase in oxygen consumption leading to oxygen depletion in lower water layers, sometimes mortality of marine species such as benthic animals and fish, etc. are often observed in eutrophic areas (Richardson et Jorgensen, 1996; Cloern, 2001; Conley et al., 2002; Tuo et al., 2012). The primary production by phytoplankton is limitation by nitrogen or phosphorus and depends on the relative availability of each of the nutrients in the water. Thus, algal growth will slow when the nutrients concentrations decrease.

A water primary productivity can be assessed through the comparison of N:P ratio observed in the selected water with Redfield ratio which is 16:1 (Redfield, 1958; Howarth, 2000). Indeed, phytoplankton require approximately 16 moles of N for each mole of P they take in. According to the above formulation, if the ratio of available N to available P in an aquatic ecosystem is less than 16:1, algal growth is defined to be N limited. At the opposite, when the ratio is higher, the primary production will tend to be P limited. Generally, nitrogen fixation in marine systems, estuaries, coastal seas and oceanic waters seem regulated by complex interactions of chemical, biological, and physical factors.Using both nutrients and trace metals, several studies have been conducted in the Ebrié Lagoon regarding its waters (Inza et al., 2009; Tuo et al., 2012); sediments (Inza et al., 2009; Inza et al., 2014; Tuo et al., 2013) and marine organisms qualities (Inza et al., 2015; Tuo et al., 2019; Tuo et al., 2020b). The aim of the present work was to assess the waters' quality in the part of the Ebrié Lagoon located along the Abobo-Doumé Fish Market (ADFM) which is submitted to the influence of fisheries, industrial and domestic activities, basing on physicochemical parameters and nutrients data on one hand, and on the over hand, on the N:P ratio. Thus, physicochemical parameters (pH, temperature, salinity, Electric conductivity (E.C), Transparency, Total dissolved solids (TDS)), ammonium, nitrite, nitrate, phosphates and the N:P ratio were studied to provide data regarding the ADFM located in the Ebrié Lagoon (Côte d'Ivoire).

Materials and methods:-

Study area:

The study area is a part of the Ebrié Lagoon which one has an area of 566 km² and stretches on 125 km along the coast of Côte d'Ivoire, between 3°40' and 4°50' West, at latitude 5°50' North (Figure 1) (Tuo et al., 2012). It communicates with the Atlantic Ocean through the Vridi Channel, drilled in 1951, for the building of Abidjan Port, the most important in West Africa. Ebrié Lagoon waters are simultaneously diluted with marine waters during dry seasons and with freshwaters (from coastal rivers, mainly Comoé River) during the rainy and flood seasons.

The names, codes, and principal characteristics of the different sampling stations are presented in Table 1. The sampling area is located along the Abobo-Doumé Fish Market, a well-known market by Abidjan's citizens and still affected by several socio-economic activities such as water travel engines (SOTRA boats, and artisanal boats), sand extraction, sewage, domestic and industrial effluents, fish smokehouses residues, etc. These activities may negatively affect the Ebrié Lagoon waters in the studied area despite its renewal rate (compared to the bays' ones).



Figure 1:- Location of sampling stations (.) along Abobo-Doumé Fish Market.

Sampling:

For the present study, samples were collected in surface and bottom waters in April 2016 after a rain in five selected stations along the Abobo-Doumé Area in the Ebrié Lagoon (Côte d'Ivoire) (Figure 1). Samples were collected according to standards methods (APHA, 2005, Rodier, 2006; Tuo et al., 2012; Tuo et al., 2020).

Analytical techniques:

Dissolved inorganic nutrients (nitrate, nitrite, ammonium and orthophosphate) concentrations were determined by standard colorimetric method using UV–Vis spectrophotometer (Rodier 2006; Tuo et al., 2020).

N:P ratio calculation:

The eutrophication status of surface waters are widely assessed through the determination of N:P ratios (Hodgkiss and Ho, 1997; Havens et al., 2003; They, 2017; Oelsner and Stets, 2019; Tuo et al., 2020a). In the present study, the molar concentrations of nutrients were used to determine the N:P ratio in each of the selected stations (Choudhury and Bhadury, 2015; Tuo et al., 2020a).

Results:-

Physicochemical parameters:

Physicochemical parameters are important for the coastal waters' quality assessment. Table 2 presents the values of Temperature, pH, Salinity, Electric Conductivity, Total Dissolved Solids (TDS) and Transparency.

Temperature values found in surface and bottom layers ranged from 27.99 to 28.71°C and from 24.67 to 28.88°C respectively. Surface waters were slightly hot with a mean value of 28.47±0.29 °C than the bottom ones where a mean temperature of 27.07±1.91°C was recorded(Table 2). Regarding temperature, a stratification was observed between surface and bottom waters at stations S3, S4 and S5 where the depths were above 5m (Figure 2a).

In waters along the ADFM, pH values were found in the ranges of 8.14 to 8.39 and 7.58 to 8.34 respectively in surface and bottom layers (Table 2; Figure 2b). Surface waters, with a mean pH of 8.30±0.07, were more alkaline

than the bottom ones where a mean value of 8.17 ± 0.12 was recorded (Table 2). pH values observed were in the recommended range of 6.0 to 8.5 for coastal waters (Tuo et al., 2012; Tuo et al., 2020a).

Table 2:- Ranges, means and standards deviations (SD) of physicochemical parameters observed in waters along

 Abobo-Doumé Fish Market.

Profile		Temperature	рН	Salinity	E. conductivity	TDS
		(°C)		(‰)	(mS/Cm)	(mg/L)
Surface	Range	27.99-28.71	8.23-8.39	28.50-30.43	44.30-46.7	27.48-29.11
	Mean	28.47	8.30	29.41	45.52	28.25
	SD	0.29	0.07	0.70	0.90	0.59
Bottom	Range	24.67-28.88	8.08-8.34	29.41-39.98	45.6-59.7	28.56-37.00
	Mean	27.07	8.17	33.75	51.38	31.91
	SD	1.91	0.12	5.34	7.10	4.36
Guidelines values		N.A	6.0-8.0*	N.A	N.A	<1500*

E. Conductivity: Electric Conductivity; TDS: Total Dissolved Solids; N.A: Not available.

*: Sargaonkar and Deshpande (2002).



Figure 2:- Physicochemical parameters in waters along Abobo-Doumé Fish Market.

- a) Temperature,
- b) pH,
- c) Salinity,
- d) Electrical conductivity,
- e) Total Dissolved Solids
- f) Transparency.

Waters were saline in the study period with values of salinity that ranged respectively from 28.50 to 30.43‰ and from 29.41 to 39.98‰ in surface and bottom layers (Table 2). Bottom waters were more saline than the surface

layers ones, marked with a stratification at stations S4 and S5. In the first three stations (S1, S2 and S3), no significant differences were observed between the surface and bottom waters (Figure 2c).

The Electrical Conductivity is the ability of waters to conduct electricity and so correlated to both quality and quantity of dissolved ions in the water column.

Along Abobo-Doumé area, values of Electrical conductivity ranged from 27.48 to 29.11 mS/Cm and from 28.56 to 37.00 mS/Cm, respectively in surface and bottom waters (Table 2). Similar to the salinity, highest levels of Electric conductivity were generally recorded in bottom waters and particularly in stations S4 and S5 (Figure 2d).

The Total Dissolved Solids (TDS) concentrations were in the range of 27.48 to 29.11 mg/L in surface waters; and from 28.56 to 37.00 mg/L for the bottom ones (Table 2). The highest concentrations of TDS were observed in bottom waters with a mean of 31.91 ± 4.36 mg/L against 28.25 ± 0.59 mg/L observed in surface waters (Table 2; Figure 2e).

Transparency is also an important parameter for of water body's quality assessment. In the present study, its values ranged from 0.5 to 1.0m (Table 2; Figure 2f). Highest values of transparency were observed at stations S4 and S5, while the lowest were observed at stations S1, S2 and S3 (Figure 2f).

Inorganic nutrients:-

The ranges, means and standard deviations of inorganic nutrients concentrations are shown in table 3.Figure 3 presents the spatial distribution of dissolved inorganic nutrients in surface and bottom waters along the Abobo-Doumé Fish Market. Ammonium concentrations ranged from 0.318 to 0.753 mg/L and from 0.166 to 0.376 mg/L in surface and bottom waters respectively. The mean values were 0.444 ± 0.175 mg/L and 0.310 ± 0.190 mg/L in samples collected from surface and bottom layers. NH₄⁺ amounts found in surface waters were higher than the bottom ones at stations S2 and S4, while the bottom waters were enriched than the surface ones at station S5 (Figure 3a). Regarding ammonium amounts, no significant difference was observed between the surface and bottom waters for stations S1 and S3.

Nutrients		NH4 ⁺	NO ₂ ⁻	NO ₃	PO ₄ ³⁻	
Surface	Range	0.318-0.753	0.060-0.067	1.90-5.20	0.38-0.55	
	Mean	0.444	0.060	3.52	0.44	
	SD	0.175	0.005	1.38	0.07	
Bottom	Range	0.166-0.376	0.030-0.069	1.20-4.50	0.35-0.58	
	Mean	0.310	0.048	2.76	0.50	
	SD	0.190	0.017	1.25	0.10	

Table 3:- Ranges, means and standard deviations (SD) values of nutrients (in mg/L) observed in waters along Abobo-Doumé Fish Market.

Nitrite is an intermediate component between ammonium and nitrate in the nitrification process and generally present in low amounts in coastal waters where there is no source of pollution and when dissolved oxygen is available in acceptable amount. Nitrite concentrations observed in waters for the present study ranged from 0.0060 to 0.067 mg/L and from 0.030 to 0.069 mg/L respectively in surface and bottom layers. Regarding the mean values of 0.060±0.005 mg/L (in surface waters) and 0.048±0.017 mg/L in bottom ones, surface waters recorded the highest concentrations of nitrite (Table 3; Figure 3b). Station S1 recorded the highest concentration in surface and bottom waters with respective concentrations of 0.067 and 0.069 mg/L (Figure 3b). Nitrite levels observed in surface waters at stations S4 and S5 were approximately two times higher than those recorded in bottom waters, while no significant differences were observed in the water column for stations S1, S2 and S3 (Figure 3b).

In oxygenated waters, the nitrate is the most stable component of the nitrification process. For surface waters, its concentrationsalong the Abob-Doumé Fish Market ranged from 1.90 to 5.20 mg/L with an average value of 3.52 ± 1.38 mg/L. In bottom waters, the amounts of nitrate concentrations ranged from 1.20 to 4.50 mg/L with a mean value of 2.76 ± 1.25 mg/L (Table 3).Highest concentrations in nitrate were observed in surface waters at stations S2 and S4, while the bottom layers registered the highest levels in surface waters elsewhere. The highest concentration in nitrate recorded in bottom waters at station S4 (1.2 mg/L), and, in surface waters, the highest one (5.2 mg/L) was observed in station S2 (Figure 3c).



Figure 3:-Nutrients concentrations observed in waters along Abobo-Doumé Fish Market.

- a) Ammmonium,
- b) Nitrite,
- c) Nitrate,
- d) Phosphates.

The phosphorus is among the most important nutrients in coastal waters with nitrogen and silica components. For the present sudy, orthophosphates concentrations were in ranges of 0.38-0.55 mg/L and 0.35-0.58 mg/L, respectively in surface and bottom waters (Table 3; Figure 3d). Respective means of 0.44 0±0.07 mg/L and 0.50 ± 0.10 mg/L were determined in surface and bottom waters respectively, indicating that the bottom waters were the most enriched in phosphates than the surface ones(Table 3). Apart from stations S4 and S5 with high concentrationsof orthophosphates in surface waters, the highest values were observed in bottom waters for waters collected from stations S1, S2 and S3 (Figure 3d).

Nutrient limitation assessment:-

To assess the nutrient which could limit the primary production waters along the Abobo-Doumé Fish Market, the N:P ratio was determined in both surface and bottom waters for each of the five selected stations. The results areshown in Figure 4. The N:P ratios determined ranged from 11.47 to 25.36 and from 7.94 to 17.10, respectively in surface and bottom waters (Figure 4). N:P ratios observed in surface waters were higher than those found in bottom waters in all of the sampling stations. For the studied area, the average value of the N:P ratio was 17.88 \pm 5.59 in surface waters against 11.54 \pm 3.47 in bottom waters. In surface waters, N:P ratios observed at stations S2, S4 and S5 were above the Redfield ratio of 16:1. In bottom waters, only the ratio determined at station S5 was above the Redfield one (Figure 4).



Figure 4:-N:P ratio observed in waters along Abobo-Doumé Fish Market.

Discussions:-

The waters analyzed were found hot with temperature above 25°C in surface waters. Bottom waters recorded the lowest temperature in relation with the depth of each sampling location (Table 2, Figure 2a). Effective thermal gradients were observed at stations S4 and S5 with bottom waters less warm than the surface ones (Figure 2a). The study was made in April, corresponding to the end of the long dry season in Côte d'Ivoire, marked by high air temperatures and also of the waters' ones (Inza et al., 2009; Tuo et al., 2012). In both surface and bottom waters, pH values measured were alkaline with values above 8.0 (Table2, Figure 2b), fairly above the upper value of the threshold range from 6.0 to 8.0 (Sargaonkar and Deshpande, 2003). Apart from Station S1 in which the pH value observed in bottom waters was higher than the surface one, bottom waters were less alkaline than the surface ones elsewhere. This stratification was due to the presence of waters from marine origin that dilute the Ebrié Lagoon, primarily during the dry seasons (Inza et al., 2009; Tuo et al., 2012), through the Vridi Channel (Figures 1 and 2b). The presence of marine waters, more saline than those of continental origins waalso confirmed with the high values in salinity (28.50-39.98‰) and Electric conductivity (44.30-59.70 mS/Cm) (Figure 2c; Figure 2d). Thus, high temperature values, alkaline pH associated with high values of salinity and Electric conductivity have shown that the residence time of marine waters in the Ebrié Lagoon remains after the beginning of the rainy season, particularly in the studied area located in front of the Vridi Channel (Figure 1). Total Dissolved Solids (TDS) in the range of 27.48 to 37.0 mg/L were below 1500mg/L (Table 2, Figure 2e), so in acceptable range (Sargaonkar and Deshpande, 2003).

Ammonium concentrations were found in high amounts compared to the nitrite ones. These highest concentrations in NH_4^+ , particularly in surface waters were of continental origins. However, ammonium concentrations observed in the present study (averages of 0.895 ± 1.095 in surface and 0.592 ± 0.758 mg/L in bottom waters) were less than those reported by Tuo et al., (2012) in several polluted bays in Ebrié Lagoon. In aquatic ecosystems, ammonium tends to be oxidized to nitrate in a two-step process (firstly to NO₂⁻ and finally to NO₃⁻) by aerobic and autotrophic bacteria (Nitrosomonas and Nitrobacter, primarily) (Wetzel, 2001; Camargo and Alonso, 2006). The nitrification process can even occur if levels of dissolved oxygen decline to a value as low as 1.0 mg O_2/L (Stumm and Morgan, 1996; Wetzel, 2001; Camargo and Alonso, 2006). Significant inputs of NH₄⁺ can also contribute to the acidification process since ammonium nitrification produces hydrogen ions (Schuurkes and Mosello, 1988; Vitousek et al., 1997; Wetzel, 2001). The concentration of total ammonia is the sum of NH₄⁺ and NH₃ concentrations, and it is the total ammonia that is commonly measured in water samples. The relative amounts of NH_4^+ and NH_3 of water depend on pH and temperature. Thus, as values of pH and temperature tend to increase, the concentration of NH₃ also increases but the concentration of NH_4^+ decreases (Camargo and Alonso, 2006). Emerson et al. (1975) formula is usually used to estimate the relative concentrations of NH_4^+ and NH_3 from total ammonia amounts (Adams and Bealing, 1994; Richardson, 1997). Unionized ammonia (NH_3) is found toxic to aquatic animals in general and particularly to fish than ammonia (NH_4^+) considered as nontoxic or less toxic (Environment Canada, 2001; Constable et al., 2003).

The nitrite concentrations observed in waters along the Abobo-Doumé Fish Market (0.03-0.069 mg/L) were below those observed in urban bays considered as most polluted in the same Ebrié Lagoon where the range of 0.03 to 0.069 have been reported (Tuo et al., 2012). Nitrite and nitrate concentrations observed along Abobo-Doumé Fish Market were in the respective ranges of 0.65 to 1.50 μ mol/L and 19.35 to 83.87 μ mol/L(Table 4). According to the European Environment Agency (EEA), transitional, coastal and marine waters with nitrate and nitrite concentrations above 16 μ mol/L are of Bad Quality (EEA, 2001). Nitrate and nitrite concentrations observed for the present study were three times higher than the value of Bad Quality for coastal waters such as lagoons (Tables 4 and 5).

Nutrients	N-NH4 ⁺		N-NO ₂		N-NO ₃		P-PO ₄ ³⁻	
Station	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
S1	20.61	20.72	1.46	1.50	37.10	38.71	5.16	5.79
S2	21.56	18.83	1.37	1.24	83.87	54.84	4.21	6.11
S3	21.67	20.89	1.22	1.20	30.65	37.10	4.00	6.00
S4	17.67	9.22	1.26	0.67	67.74	19.35	4.21	3.68
S5	41.83	11.39	1.26	0.65	64.52	72.58	5.79	4.95
Mean	24.67	16.21	1.31	1.05	56. 77	44.52	4.67	5.31
SD	9.73	5.50	0.10	0.37	22.27	20.10	0.77	1.01

Table 4:- Inorganic nutrients concentrations (in µmol/L) observed in the selected stations.

Phosphates concentrations ranged from 3.68 to 6.11 μ mol/L, with respective averages values of 4.67±0.77 and 5.31±1.01 μ mol/L⁻¹ in surface and bottom waters. Regarding phosphates concentrations that were three to six times higher than 1.1 μ mol/L (Tables 4 and 5), the waters analyzed were also of Bad Quality (EEA, 2001). Tuo et al., (2012) have reported respective averagesconcentrations in phosphates of 0.289±0.378 and 0.295±0.393 mg/L for surface and bottom waters in some bays located in Ebrié Lagoon. These values were less than phosphates levels observed in the present study along Abobo-Doumé Fish Market (Tables 3 and 4). Despite a good renewable rateof waters in the studied area in one hand, and on the over hand the low depths (<5m) for S1, S2 and S3 during the sampling period, high amounts of phosphates were observed in relation with phosphorus inputs through waters from continental origins.

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Quality Class	Nitrate and nitrite (µmol/L)	orthophosphate (µmol/L)				
Good	<6.5	<0.5				
Fair	6.5-9.0	0.5-0.7				
Poor	9.0-16.0	0.7-1.1				
Bad	>16.0	> 1.1				

Table 5:- European Environment Agency (EEA) criteria for the assessment of nutrient levels in transitional, coastal and marine waters (EEA, 2001).

According to the Redfield ratio (N:P=16:1), waters were P-Limited in surface at stations S2, S4 and S5, while waters were N-Limited at stations S1 and S3 (Figure 4). In bottom waters, apart from station S5 with the highest N:P ratio of 17.10 so P-Limited, N-Limitationstatus was observed in the other stations where N:P ratios were generally below the Redfied ratio (Figure 4). Finally, during the sampling period, waters were P-Limited in surface waters and N-Limited in bottom layers (Figure 4).

Conclusions:-

Physicochemical parameters, nutrients concentrations and N:P ratios were determined in surface and bottom waters along Abobo-Doumé Fish Market to assess the waters' quality. The dilution of the waters along Abobo-Doumé Fish Market by marine waters from Atlantic Ocean have beenconfirmed by the alkaline pH, high values of salinity and Electric conductivity values. The waters contained high concentrations of Total Dissolved Solids due to the waters of continental origins inputs. Nutrients concentrations were above the recommended limits for coastal waters, sothe studied waters were of Bad Quality Class. Regarding nutrients limitation assessed with N:P ratios, waters were N-Limited in bottom layers and P-Limited in the surface ones. According to our results, there is a need for a long-term assessment to determine the temporal trends of thewaters quality, for a best management of the Ebrié Lagoon, under persistentanthropogenic activities.

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