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Impact of runoffwaters on the nutrients amounts and Redfield ratios in Fresco Lagoon, Côte d'Ivoire

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Abstract: *Phosphorus (P) and nitrogen (N) are known to be the primary nutrients that, in excessive amounts, pollute surface waters such as streams, rivers, lakes and lagoons.pH, temperature, salinity and Electrical Conductivity (EC) were measured in situ. Ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-) and orthophosphate (PO_4^{3-}) concentrations were determined in waters collected from ten (10) selected stationsto assess the water quality in Bolo River, Niouniourou River and Fresco Lagoon. The Redfield (N:P) ratios were also calculated.Average and standard deviation of pH, temperature, salinity, Electrical Conductivity and Total Dissolved Solids (TDS) were in the respective ranges of 5.52±0.01-6.68±0.01; 26.49±0.06-30.61±0.24°C; 0.08±0.02-27.36±0.0; 0.15±0.04-42.70±0.03 mS/C and 78.5±21.9-21350±14.1 mg/L. The average contents in NH_4^+, NO_2^-, NO_3^- andPO_4^{3-} were found in the respective ranges of 0.002±0.000-0.095±0.019, 0.008±0.002-0.034±0.036, 1.00±0.57-14.20±0.00 and 0.17±0.03-1.09±1.22 mg/L. The N:P ratios ranged from to 2.35 to 82.33.Nutrients contents observed in the present work showed high amounts nutrients, particularly in nitrate and orthophosphate which are found of particular concern during the study period. Thus, due to huge concentrations of both TDS and nutrients, the analyzed waters were found to be of "Bad Quality". N:P ratios have revealed that 50% of the sampling stations were under N-limiting and also 50% were under P-limiting, despite the huge contents in nitrogen and orthophosphate. Seasonal assessment is therefore recommended for the understanding of the temporal trend of water quality for long term management of Fresco Lagoon.*

Keywords: *Ammonium, nitrite, nitrate, phosphate, N:P ratio; Fresco Lagoon; Côte d'Ivoire.*

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I. Introduction

Due to its key role for all forms of life, the water quality is of particular importance worldwide, specifically in coastal areas with changes in population, land use, and pollutants inputs from continental sources(Seitzingeret al., 2010; Bhuyanet al., 2017 ; Tuoet al., 2012; Katariaet al., 2011; Wise et al., 2011). Nutrients (phosphorus and nitrogen) are the essential components for marine ecosystem primary production and for biodiversity equilibrium when they occur in acceptable levels. Apart from nitrogen and phosphorus, silicate is also essential for diatom growth, but it is assumed that its input is not significantly influenced by human activity. In coastal areas, a part of nutrient is of natural origin involving the decomposition of plants and animal material, while the most important is from anthropogenic activities (atmospheric, synthetic fertilizer, soil, animals and septic wastes, residential development, domestic and agricultural practices, sewage discharges, harbor and industrial activities, etc.) that can increase nutrients amounts in coastal environments. High amounts of nutrients in surface waters may conduce to several hazardous effects including eutrophication. Thus, concentrations, effects, trends and sources are studied in several coastal areas (Adesuyi et al, 2015; Oelsner and Stets, 2019). The widely documented hazardous effects of eutrophication are toxic algal blooms, increase growth of nuisance microalgae, increase in oxygen consumption leading to oxygen depletion in lower water layers and sometimes mortality of marine species such as benthic animals, fish, etc. (Cloern, 2001; Conley et al., 2002;2004; Tuoet al., 2012). Development in costal watersheds has resulted in significant degradation of estuaries and coastal ecosystems through several interacting factors including habitat loss, nutrient pollution (Carpenter et al., 1998; Foley, 2005; Lotze, 2006; Mallin*et al.*, 2000; Seitzingeret al., 2010; U.S. Environmental Protection Agency, 2016). The geology and land use within lagoon's (also available for a river, a lake, a stream or a bay, etc.) watershed determine the amount of nutrients that can enter the ecosystem via surface water runoff. In general, nitrogen fixation in marine systems, estuaries, coastal seas and oceanic waters seem to be regulated by complex interactions of chemical, biological and physical factors. Recent evidence indicates that cyanobacteria in coastal bays and rivers, for instance are constrained by slow growth rates caused by shortages of trace metals such as iron or molybdenum and by grazing by zooplankton and bottom-dwelling animals. Several anthropogenic activities (farming, fishing, domestic activities wastes, etc.) occurs in the watersheds of

Fresco Lagoon that may modify the chemistry of waters. The aim of the work was to assess the status of the lagoon ecosystem under the influence of freshwaters (from the rivers) during the rainy season, basing on physicochemical parameters and nutrients data on one hand, and on the over hand, on the N:P ratio, to report a useful baseline data in future to measure any anthropogenic contamination level in the studied area for sustainable natural resources management around Fresco City. Thus, hydrological parameters (pH, temperature, salinity, Electrical Conductivity (EC), Total Dissolved Solids (TDS), ammonium, nitrite, nitrate, orthophosphate and the N:P ratio were studied.

II. Material And Methods

Study area and samples collection*:* Fresco Lagoon (5°32'-5°38' W; 5°40'-5°70' N) is located in the Gbôklè Region in Côte d'Ivoire (Table1; Figure 1). The lagoon has an average depth of 4m, with length and width of 6km and 2-4 km respectively. Fresco Lagoon covers an area varying from 17 km^2 (in the dry seasons) to 29 km^2 in the wet ones (Issola et al., 2008).

Table 1: Names and GPS coordinates of the sampling stations in the study area.

Station	Longitude	Latitude
Bolo	5°6'53''N	5°33'47''W
Niouniourou	5°6'29''N	5°33'31''W
Bolo-Niouniourou	5°6'53''N	5°35'46''W
Embouchure	5°4'55''N	5°34'28''W
Dadjidjé	5°5'13''N	5°34'21'W
Falaise	5°6'11''N	5°35'17''W
Vron	5°5'27''N	5°36'46''W
Dabien	5°6'12''N	5°36'35''W
Ex-Zakareko	5°6'12''N	5°35'43''W
Zakareko	5°6'20''N	5°35'9''W

Figure 1: Location of the different sampling stations in Bolo River, Niouniourou River and Fresco Lagoon (●)
Translation of frecnh words in the Legend : Forêt = Forest; Plan d'eau= Water and Ville = City.

The climate is of sub-equatorial with three distinguish seasons including a Dry Season (December-March), a rainy season (April-August) and a flood one (September-November). These three seasons influence the lagoon chemistry due to respective quality and quantity of waters that dilute the lagoon ones.Indeed, in the coastal area in Côte d'Ivoire, dilution waters are from marine origin in the dry seasons, while they are of continental origin in the rainy and flood ones (Issola et al., 2008; Tuoet al., 2012). Fresco lagoon also consists of four feeder rivers, Bolo (84 km), Niouniourou (140 km), Gnou (12 km) and Guitako (5 km) (Issola et al., 2008**)**. For the present study, only Bolo River and Niouniourou River were studied, due to their lengths on one hand, and on the over hand, to the fact that these rivers drain directly into the studied area in Fresco lagoon (Figure 1). Water samples were collected with a Niskin bottle in the rainy season in June 2019 in surface and bottom waters at a total number of 10 stations, with 3 stations outside the lagoon (Bolo, Niouniourou and Bolo-Niouniourou) located in the rivers and the 7 others inside Fresco Lagoon as shown in Figure 1, according to standards methods (APHA,2005; Tuoet al., 2012). The exact position of each sampling station was recorded using Global Positioning System (GPS), while pH, temperature, salinity and Electrical Conductivity (EC) were measured *in situ*, using a multi-parameter (Type HI 9828 pH/ORP/EC/DO). Immediately after collection, water samples were stored in a cooler and transferred to the lab for further analyses.

Nutrients Analysis

Dissolved inorganic nutrients (nitrate, nitrite, ammonium and orthophosphate) were measured by standard Rodier (2006) colorimetric method using UV–Vis spectrophotometer. Ammonium ions (NH_4^+) are treated in an alkaline pH, with sodium hypochlorite and phenol giving indophenol which is of blue coloration. This reaction is catalyzed by nitroprusside. Ammonium was measured colorimetry on 630 nm (Rodier; 2006). Nitrite (NO_2^-) was determined by complexation with the diazotization of sulfanilamide in and with N (1-naphthyl) ethylenediamine in acidic pH, which gave a purple-colored complex. Nitrite was measured colorimetry on 540nm (Rodier, 2006).Nitrate (NO_3^-) was measured colorimetry on 420 nm. Sulfosalicylic acid forms with nitrate in anhydrous environment and releases in basic environment a nitrosalicylate complex which is of yellow color. A colorimetric determination of this ion allows to determine the concentration of nitrate ions in a solution (Rodier, 2006).Orthophosphates react in the presence of antimony molybdate to give phosphomolybdic acid compounds that were reduced by ascorbic acid, giving a blue coloration. Ortho-P was finally measured colorimetry on 885 nm (Rodier, 2006).

N:P ratio determination in waters

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. In the present study, the molar concentrations of the nutrient were used to determine the molar ratio for N:P ratio in each of the selected stations (Redfield-Brzezinski ratio) (Choudhury and Bhadury, 2015).

Statistical analysis

The means, standards deviations and graphs were performed using Microsoft Excel 2007.

III. Results

Physicochemical parameters were measured in surface and bottom waters. The averages and standard deviations of each parameter observed in the selected stations are presented in table 2.

3.1. Physicochemical properties (pH, temperature, salinity, Electrical conductivity and Total dissolved solids)

According to the average values, waters of the study area were found acidic with values less than 7 (Table 2). The lowest value of pH was observed in Niouniourou River (5.52±0.01), while the highest one was recorded in station Dadjidjé (6.68±0.01°C), followed with Embouchure with a value of 6.56. pH values observed in the present work were in the range of ‟ Acceptable Class″ (Tables 2 and 3). A spatial trend was also observed in pH values between fresh waters within rivers (Bolo and Niouniourou) which recorded the low values in pH and the lagoon waters, with highest values regarding pH (Figure 1; Table 2). Levels of pH observed in stations located far from Fresco Lagoon outfall were low than those observed in the stations closed to the outfall area (Table 2).

Waters in the study area were relatively with temperature values found between 26.49±0.06 °C (in station Bolo) and 30.61±0.24 °C observed in station Ex-Zakareko (Figure 1; Table 2). The fresh waters temperature were low than those observed in stations located in the lagoon. An increase in waters temperature were generally observed from the fresh waters (stations Bolo, Niouniourou and Bolo-Niouniourou) to the latest stations located in Fresco Lagoon such as Dabien, Ex-Zakareko and Zakareko with values high than 30°C (Table 2). Average values of salinity ranged from 0.08±0.02 to 27.36±0.03 in the study area (Table 2). The lowest levels (<1.00) of salinity were observed in Bolo River and Niouniourou River, with an increase in their intersection (Bolo-Niouniourou), where an average value of 15.49 was observed. Within the lagoon, the highest levels in salinity were measured in stations (Dadjidjé and Falaise) that are closed to the outfall of Fresco Lagoon with the Atlantic Ocean (Figure1; Table 2).

Average Electrical Conductivity (EC) values observed in the study area were found in the range of 0.15±0.04 to 42.70±0.03 mS/Cm. Similar to the salinity, EC values were low in rivers and high within the lagoon stations (Table 2). During the sampling period (June 2019), considering the values observed for salinity and EC values, waters of the station Bolo-Niouniourou were not fresh. Despite waters dilution with those of continental origin, the lagoon remained of brackish quality, with EC values in the range of 27.86±0.00 to 42.70±0.03 mS/cm.

The Total Dissolved Solids (TDS) values were found in the range of 78.5±21.9 to 21350.0±14.1 mg/L. The lowest TDS values were observed in stations located in the rivers, compared to the lagoon ones that exhibited values high than 13000 mg/L (Figure 1; Table2). According to the classification of water quality Sargaonkar and Deshpande (2002), TDS values observed in Bolo River and Niouniourou River were respectively of Excellent and Acceptable Classes. At the opposite, the other the stations (from Bolo-Niouniourou to Zakareko) recorded TDS values seven to ten times higher than 3000 mg/L, considered to be of ‶ Heavily polluted Class″ (Tables 2 and 3).

Table2: Averages and standard deviations(SD) of physicochemical parameters measured in Bolo River, Niouniourou River and Fresco Lagoon.

Station	pH	Temperature (°C)	Salinity	EC (mS/Cm)	TDS (mg/L)
Bolo	6.04±0.10	26.49±0.06	0.08±0.02	0.15±0.04	78.5±21.9
Niouniourou	5.52±0.01	26.68±1.54	0.50±0.03	1.02±0.06	511.5±28.9
Bolo-Niouniourou	5.71±0.95	27.12±0.07	15.49±21.57	23.0±33.14	11955.5±16566.8
Embouchure	6.56±0.0	28.22±0.00	17.06±0.00	27.86±0.00	13930.0±00
Dadjidjé	6.68±0.01	28.33±0.15	27.36±0.03	42.70±0.03	21350.0±14.1
Falaise	6.32±0.33	28.82±0.72	23.81±6.04	37.63±8.60	18815.0±4292.1
Vron	6.34±0.16	29.55±0.45	18.84±2.92	30.46±4.34	15230.0±2177.8
Dabien	6.14±0.06	30.14±0.78	18.67±0.58	30.31±0.08	15155.0±417.19
Ex-Zakareko	6.24±0.17	30.61±0.24	19.85±3.86	32.02±5.65	16015.0±2821.3
Zakareko	6.24±0.09	30.49±0.78	19.01±4.30	30.77±6.29	15385.0±3146.6
Mean	**6.18**	**28.65**	**16.07**	**25.59**	**12842.55**
SD	**0.35**	**1.54**	**8.97**	**14.20**	**7091.21**

Table3: Classification of water quality proposed by Sargaonkar and Deshpande (2002, modified).

Classification	**Excellent C1**	**Acceptable C2**	**Slightly polluted C3**	**Polluted C4**	**Heavily polluted C5**
Class Index (score)	1	2	4	8	16
Parameters	Concentration limit/ranges				
pH	6.5-7.5	6.0-6.5 & 7.5-8.0	5.0-6.0 & 8.0-9.0	4.5-5 & 9-9.5	<4.5 &>9.5
TDS (mg/L)	500	1500	2100	3000	>3000
NO_3^- (mg/L)	20	45	50	100	200

3.2. Nutrients (Ammonium, nitrite, nitrate and orthophosphate)

In aquatic ecosystems, nitrogen and phosphorus are the most important, as they are most often in short supply relative to the needs of plants, algae and also microbes. These nutrients can be found in both particulate and dissolved phases, and in varying chemical forms in accordance with the waters physicochemical parameters. Due to their high availability than those of particulate forms (living and dead organic matter such as plants, bacterial, animal tissues, etc.), only concentrations of Dissolved Inorganic Nitrogen (DIN) and Dissolved Inorganic Phosphorus (DIP) were determined in the present study. Then, the mean and standard deviation (for surface and bottom waters) of each specie was calculated for each sampling location. The results obtained are presented in Figure 2.

The lowest concentration of ammonium was found in station Dadjidjé with an average value of 0.002 mg/L, followed by station Ex-Zakareko (0.028±0.023 mg/L). The highest content of ammonium was recorded in station Falaise with a mean value of 0.095±0.019 mg/L. Apart from stations Dadjidjé, Vron and Ex-Zakareko, ammonium levels observed in the rivers (0.06±0.02-0.059±0.002 mg/L) were low than the concentrations observed in the stations located in the lagoon waters (Figures 1 and 2a). For nitrite, contents were found in the range of 0.008±0.002 to 0.034±0.036 mg/L. Station Falaise exhibited the highest concentration (0.034 mg/L) of NO_2^-, followed by stations Bolo (0.031 mg/L) and Bolo-Niouniourou (0.021 mg/L). Stations Dabien, Ex-Zakareko and Zakareko exhibited the lowest contents in nitrite (Figures 1 and 2b). A stratification in term of nitrite contents was observed in stations Bolo-Niouniourou and Falaise with high standard deviation observed between the contents of surface and bottom waters (Figure 2b). Nitrate exhibited average concentrations in the range of 1.0 to 14.2 mg/L (Figure 2c). The highest concentrations of nitrate was observed in station Embouchure (the outfall of Fresco Lagoon to the Atlantic Ocean) with a value of 14.2 mg/L, followed with station Bolo-Niouniourou which exhibited an average value of 10.2±7.63 mg/L (Figure 2c). With Niouniourou, stations from Dadjidjé to Zakareko exhibited low concentrations in NO_3^- with values less than 5 mg/L. Thus, according to the water quality classification proposed by Sargaonkar and Deshpande (2002), and regarding the observed levels in NO_3^- (< 20 mg/L), the analyzed waters were within the ‶ C1 Class″, so of ‶ Excellent Quality″ (see Table 3). The spatial distribution of phosphate (PO_4^{3-}) for present study is shown on in figure 2d. The orthophosphate exhibited concentrations ranged from 0.17±0.03 (Zakareko) to 1.09±1.22 mg/L (Falaise). Station Falaise recorded the highest content (1.09 mg/L) in PO_4^{3-}, followed with stations located in Bolo River and Niouniourou River (Figures 1 and 2d). According to the standard deviations, stations Bolo-Niouniourou and Falaise exhibited deference in orthophosphate levels between surface and bottom waters.

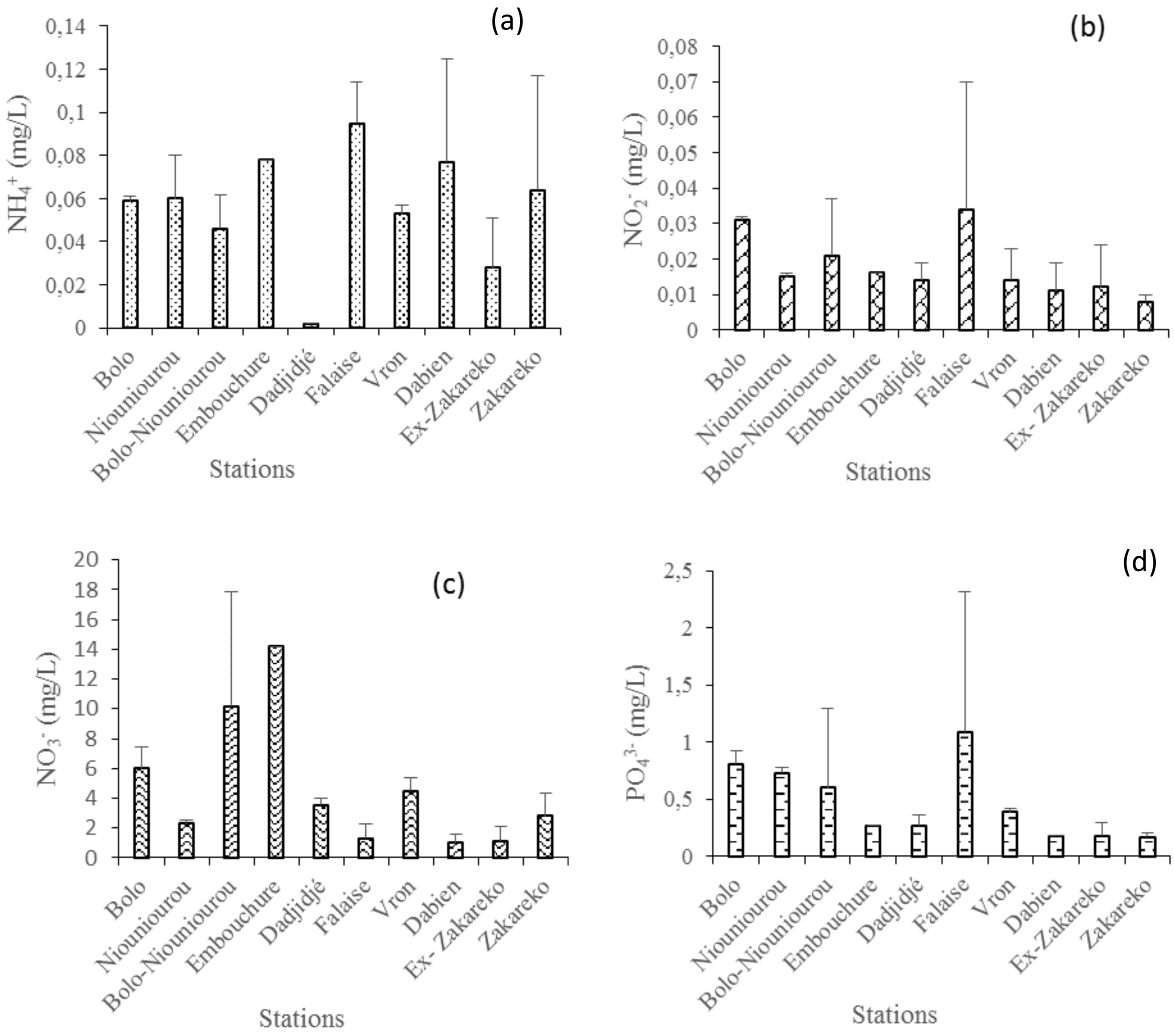

Figure 2: Mean concentrations and standards deviations of nutrients measured in river waters and lagoon waters samples collected in the selected stations. (a): Ammonium, (b); nitrite, (c): nitrate, (d): nitrate.

3.3. N:P ratios observed in the study area

N:P ratio of 16:1 is widely considered as a benchmark to differentiate N-limitation and P-limitation and often considered as a reference point for the upper limit of N:P in oceans (Redfield, 1958; Lenton and watson, 2000). The ratio of nitrogen to phosphorus was calculated for water samples collected for each sampling station (Table 4). The results are presented in Figure 3. N:P ratios observed in the present study were found in the range of 2.35 to 82.23 with an average ratio of 26.60±22.87 (Table 4). According to the N:P ratios, the selected stations could be classified into two distinguish groups. The first group contained stations (Bolo, Niouniourou, Falaise, Dabien and Ex-Zakareko) that exhibited ratios values lower than the threshold ratio (N:P=16:1).The second group include Stations Bolo-Niouniourou, Embouchure, Dadjidjé, Vron and Zakareko with their N:P ratios higher than 16:1 (Table 4, Figure 3).

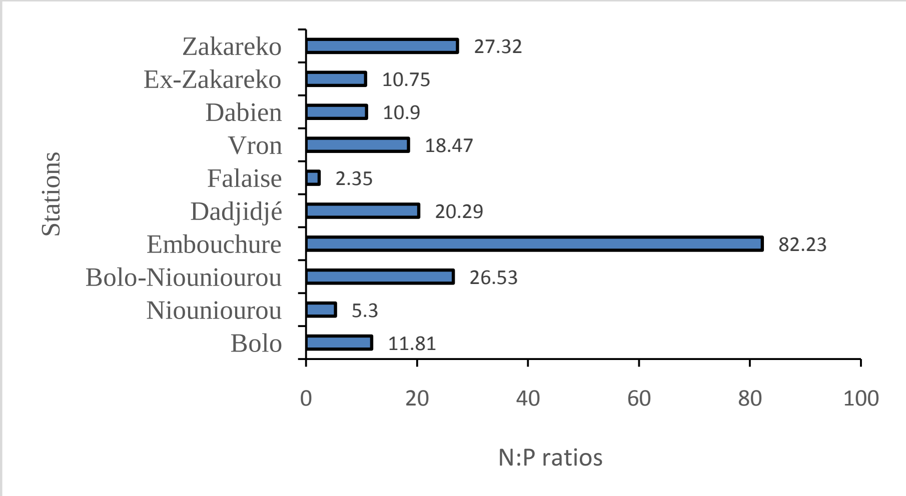

Figure 3: N:P ratios determined in the selected stations.

IV. Discussion

In coastal aquatic systems, pH below 4.5 and above 9.5 are usually lethal to aquatic organisms, and even less extreme pH values can effect reproduction and other biological processes. pH values observed in the present study were generally in the range considered to be safe for marine organisms, apart from fresh waters (Stations Bolo, Niouniourou and Bolo-Niouniourou) where pH values less than 6.0 were recorded (Tables 2 and 3). The lowest levels of pH observed in the rivers are due to their continental origin, so generally acid compared to waters of marine origin (Tuo et al., 2012). According to our data, pH values observed in the present were low in comparison with those (7.42-7.60) reported by Issola et al. (2008) in the same lagoon. Issola et al. (2008) have also reported pH values close to 4.50 during the rainy season, corresponding to the highest dilution rate of the lagoon with fresh waters. A slight acidification of waters observed within Fresco Lagoon was the consequence of the dominance of continental waters that occurred during the rainy season and known to be of low pH, compared to waters of marine origin. The solubility of soil is also known to be influenced with pH (Gasim et al., 2013). pH values observed in the present work were also in the range (5.5-7), considered to be favorable for an increase in phosphatesolubility in soils(Gasim et al., 2013), consequently within the sediments regarding the aquatic ecosystems. In all of the sampling stations, the waters analyzed recorded temperature values above 26°C (Table 2). Temperature values observed within the rivers were less than those of the lagoon ones, where temperature exhibited values above 28°C (Table 2). Levels of temperature observed in the present study were also found to be above 25 °C considered to be the maximum value tolerated by several marine organisms (WHO, 2011).The spatial variation in temperature was influenced by the depth of each sampling station during the study period.Indeed, stations located in the rivers were deeper than those located in Fresco lagoon which exhibited several depths less than one meter. Thus, any increase of sunshine will lead to a rapid increase in lagoon waters temperature than those within the rivers. An over parameter link to the low temperature observed in rivers is the presence of vegetation, mainly mangroves trees, around the rivers and that form a natural barrier to the sunlight impact on waters. Unfortunately, more than 80% of the vegetation has been destroyed around the lagoon for agricultural activities, mainly of Rubber, Cocoa, Casanova, Maize and sometimes Rice. The increase of temperature in Fresco Lagoon will be harmful for many marine organisms such as crustaceans and oysters (already disappeared in several areas within the lagoon). Rivers naturally recorded lowest values of salinity and Electrical conductivity (EC), while the highest values of both salinity and EC were recorded inside the lagoon (Table 2; Figure 1). Regarding salinity and EC values, waters from stations located outside the lagoon (Bolo and Niouniourou) were fresh, while those of Bolo-Niouniourou and Fresco Lagoon were brackish, confirming the presence of waters of marine origin, despite the dilution with continental waters that occurred in the rainy season. The brackish status observed in Bolo-Niouniourou, located at the intersection of the two rivers (Bolo and Niouniourou) has confirmed its dilution with waters from the Atlantic Ocean (Figure 1, Table 2). High concentrations in Total Dissolved Solids (TDS) were observed at all of the stations located in Fresco Lagoon, compared to the amounts recorded in rivers (Table 2). According to the classification of water quality (Sargaonkar and Deshpande (2002) regarding TDS amounts, waters from Bolo River and Niouniourou River were of 〝Excellent Class〞, while those of Bolo-Niouniourou and Fresco Lagoon were found to be of 〝Heavily polluted class〞 (Tables 2 and 3). High loads of TDS observed in the present work were linked to the increase in erosion due to forest clearing for agricultural activities (Rubber, Cocoa, Cassava, Rice, maize, etc.) all around the study area.Oelsner and Stets (2019)reported that sediment loading to estuaries is complicated and possible negative consequences can result from either too much or too little. Indeed, land clearing and disturbance increases erosion and can lead to enhanced coastal loading (Dauer et al., 2000; Thrush et al., 2004; Syvitski, 2005) while hydrologic modification from the development of dam and reservoir systems can decrease sediment loads (Meade and Moody, 2009). A reduce in water clarity associated with a loss of submerged aquatic vegetation associated to an increase in sediment loads were also reported (Bricker et al., 2007; Orth et al., 2006; Waycott et al., 2009). However, sufficient sediment loading is necessary to sustain coastal wetlands as well as estuaries which provide critical habitat for wildlife and fisheries and serve as buffers against storms and sea-level rise (Bricker et al., 2007; National Research Council, 2000; U.S. environmental Protection Agency, 2016).In Fresco Lagoon, a continuous increase in sediments loads in relation with land clearing will, at long term, lead to a decrease in its depth and an increase in water temperature.It's therefore important to act for the conservation of vegetation around the lagoon for the preservation of its biodiversity. According to our data, nitrogen species were found in the following descending rank: NO_2^-> NH_4^+> NO_3^-(Figure 2; Table 4). For the four nutrients assessed and with average loads consideration, the following ascending rank was observed: NO_2^- < NH_4^+< PO_4^{3-}< NO_3^- (Table 4).

Table 4: Meanof nutrients concentrations in (µmol/L), dissolved inorganic nitrogen and phosphorus and N/P ratios observed in the selected stations in Bolo River, Niouniourou River and Fresco Lagoon in the rainy season.

Station	NH_4^+	NO_2^-	NO_3^-	PO_4^{3}=DIP$^-$	DIN=∑N	N:P*
Bolo	3.28	0.67	96.77	8.53	100.73	11.81
Niouniourou	3.33	0.33	37.10	7.68	40.76	5.30
Bolo-Niouniourou	2.56	0.46	164.52	6.32	167.53	26.53
Embouchure	4.33	0.35	229.03	2.84	233.71	82.23
Dadjidjé	0.11	0.30	57.26	2.84	57.67	20.29
Falaise	5.28	0.74	20.97	11.47	26.98	2.35
Vron	2.94	0.30	72.58	4.11	75.83	18.47
Dabien	4.28	0.24	16.13	1.89	20.65	10.90
Ex-Zakareko	1.56	0.26	18.55	1.89	20.36	10.75
Zakareko	3.56	0.17	45.16	1.79	48.89	27.32
Mean	**3,12**	**0,38**	**75,81**	**4,94**	**79,31**	**21,60**
SD	**1,47**	**0,19**	**70,26**	**3,38**	**70,42**	**22,87**

*N:P is calculated as DIN/DIP with DIN=∑N=NH_4^++NO_2^-+NO_3^- and DIP= PO_4^{3-}

In oxygenated conditions, ammonia is oxidized into nitrite, which nitrite is finally oxidized into nitrate, the last state of inorganic nitrogen compounds in surface waters. These different steps are known as nitrification. Nitrate, the most abundant nitrogen specie in both Bolo River, Niouniourou River and Fresco Lagoon waters. Nitrate, take alone, recorded levels that exceeded more than twenty-times the 〝Bad class〞 nitrate value of 16.0 µmol/L (Tables 4 and 5). However, according to the classification of water quality proposed by Sargaonkar and Deshpande (2002), nitrate concentrations were less than 20 mg/L (Figure 2c) and the waters could be considered to be of 〝Excellent quality〞(Figure 2, Table 3). Nitrite and nitrate contents observed in the studied stations were higher than 16 µmol/L, indicating that the waters analyzed were of 〝Bad Quality〞 according to the European Environment Agency's classification of waters (EEA, 2001) (Tables 4 and 5).

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

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

Regarding phosphorus, phytoplankton and most plants assimilate orthophosphate, although some can directly access dissolved organic phosphorus using phosphatase enzymes. However, particular organic forms of phosphorus and nitrogen are slowly converted back into soluble forms. Phosphorus is a vital nutrient in sunlight conversion into usable energy and is therefore essential to cellular growth and reproduction. Unfortunately, in high amounts in surface waters, it can be responsible of excessive algae growth, leading to the degradation of water quality. In the present study, Falaise recorded highest level (11.47 µmol/L) of orthophosphate, and Nouveau Zakareko exhibited the lowest one of 1.79 µmol/L. Orthophosphate contents observed in all of the stations were higher than 1.1 µmol/L, considered to be of 〝Bad Quality Class〞 (Tables 4 and 5). Thus, regarding contents of orthophosphate and the European Environmental Agency classification (EEA, 2001), waters of the study area were generally of 〝Bad Quality〞. Finally, regarding nutrients contents, the waters analyzed were of bad quality. Population growth and the increase in human activities in coastal areas can increase nutrient inputs to coastal waters through higher volumes of agricultural and urban nonpoint-pollution, higher demand for wastewater treatment, and consumption of fossil fuels (Bricker et al., 2007; U.S. Environmental Protection Agency, 2016).

According to the Redfield (1958) ratio interpretation, waters with N:P ratio lower than 16:1 are considered to be of N-limiting, while those with high ratios (>16:1) are P-limiting. Thus, for the present study, waters from Bolo, Niouniourou, Falaise, Dabien and Ex-Zakareko were N-limiting. At the opposite, a P-limiting status occurred in stationsBolo-Niouniourou, Embouchure, Dadjidjé, Vron and Zakareko with N:P ratios higher than 16:1 (Figure 3, Table 4). The mean Redfield value observed for all of the studied area was 21.60 (> 16:1), that indicates a general phosphate limitation for of primary production. Station Falaise, which recorded the highest amount in phosphate (11.47 µmol/L), exhibited the lowest N:P ratio (2.35). At the opposite, station Embouchure where the highest concentration in total nitrogen (233.71 µmol/L) was observed, has recorded the highest Redfield ratio of 82.23 (Table 4). According to its formula, Redfield ratio is depend on both nitrogen and phosphorus species concentrations that occurred in the waters bodies. Thus, a low N:P ratio can be observed where nutrients occurred in high amounts compared to their respective threshold values. As example, for 50% of the ten studied stations, N:P ratios were below 16:1, so of N-limiting despite the highest levels in dissolved nitrogen observed (Table 4). The previous observation is also valid for several high N:P ratios observed in several stations which exhibited high concentrations in orthophosphate.Thus, the interpretation of the N:P ratio must consider the individual concentrations of both nutrients (nitrogen and phosphorus) species to understand nutrient limitation in the studied area.

V. Conclusion

pH, temperature, salinity, Electrical conductivity (EC), Total Dissolved Solids (TDS), NH_4^+, NO_2^-, NO_3^-, PO_4^{3-} were measured outside the lagoon (Bolo and Niouniourou) and within Fresco Lagoon. According to the data, a slight acidification of waters occurred during the studied rainy season, marked with a decrease in salinity, Electrical Conductivity and high loads in Total Dissolved Solids (TDS). Regarding nitrogen species, nitrite was the less abundant component, while nitrate was found in hugeamounts. Orthophosphate was also found in high amounts compared with Environmental Protection Agencies. According to the European Environment Agency (EEA) criteria for the assessment of nutrient levels in transitional, coastal, and marine waters,en enrichments of the studied waters occurred during the rainfall leading their ‶ Bad Quality Class″. The N:P ratio values showed either nitrogen or phosphorus limitation in the sampling stations.The waters analyzed were of bad quality due to the high inflow in dissolved solids, nitrate and orthophosphate from continental waters that occurred in the rainy season.In conclusion, a particular attention is needed in the uses of fertilizers around Fresco lagoon, in order to avoid increasing the nutrients inflows for an ecological management.

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