Original Research Article

EUTROPHICATION OF A RIVER IMPACTED BY AGRICULTURAL ACTIVITIES (N'ZI RIVER, CÔTE D'IVOIRE)

ABSTRACT

Water eutrophication is a global environmental problem. In Côte d'Ivoire, no data is available to predict this phenomenon in rivers. The purpose of this study is to evaluate the impact of agricultural activities on the eutrophication phenomenon of the N'zi River in Côte d'Ivoire. The approach used focused on two points. The first one was to determine the different dissolved forms of phosphorus and nitrogen in the water of the N'zi River using AFNOR methods. The second focused on the mobility of phosphorus in sediments using the sequential extraction procedure of Williams. Results show that the inorganic phosphorus concentrations (IP) in sediments decrease in favor of contents in the water. Moreover, nitrate ions (NO_3^-) quantitatively dominates the nitrogenous forms in water. These results are attributable to the intensive use of fertilizers in agriculture, the leaching of cropland and/or contamination by human or animal waste. The phosphorus sequential extraction shows that 29 to 72% of the iron-bound bioavailable P (Fe-P) in sediments is likely to be mobilized into the water column and contributes to N'zi River eutrophication. Therefore, an awareness and monitoring program must be put in place to reduce the nutrients inputs in the N'zi River upstream.

Keywords: Phosphorus, nitrogen, river, sediments, fertilizer, agriculture.

INTRODUCTION

Nutrients availability in water, such as nitrogen and phosphorus most often contributes to the limiting factor effect of the plants development, which form the basis of the food chain [1,2]. Although they are essential elements for crops, phosphorus and nitrogen cause water eutrophication when they are in excess in the aquatic environment [3,4]. This phenomenon is generally manifested by abnormal proliferation of microalgae, aquatic plants or both simultaneously. Water eutrophication is recognized as a global environmental problem with variable and numerous consequences: modification of the water physico-chemical characteristics, disappearance or sharp reduction of number of animals and certain aquatic plants, and reduction of aquatic oxygen level [5].

Phosphorus is generally considered to be the main cause of water eutrophication [6,7]. Once in the aquatic environment, phosphorus can accumulate in sediments [8-10]. However, not all forms of phosphorus in sediment participate in eutrophication [11-13]. Indeed, depending on the physico-chemical conditions of the environment (pH, temperature, dissolved oxygen, salinity, etc.), certain phosphorus forms are likely to be released from the sediment to the water column [14-16]. The phosphorus speciation in sediments is therefore necessary to understand and predict eutrophication. The inputs that contribute to the continental and marine waters eutrophication are shared between natural and anthropogenic sources. This ecological evil is experiencing particular development due to the increase in anthropogenic activities (domestic and industrial effluent discharges, intensive agriculture) in the rivers watersheds concerned. Human activities such as the fertilizers and pesticides use in agriculture excessively enrich soils with nutrients and pollutants [17]. Erosion and soils leaching due to heavy rainfall as well as exchanges between water and sediments significantly increase the phosphorus and nitrogen amount in rivers waters [18-20].

In recent decades in Côte d'Ivoire, agriculture has intensified with the increasing of fertilizers use to improve yields. This can alter the nutrient cycle and help to accelerate waters eutrophication [21]. The N'zi River waters could be threatened by eutrophication given the strong agricultural potential of its watershed. Since few studies have been carried out on eutrophication of this river, this work aims to fill this gap. Thus, the study of the impact of agricultural activities on the N'zi River eutrophication was envisaged. To this end, the spatial distribution of the different dissolved forms of phosphorus and nitrogen in the N'zi River waters was studied; then the potential phosphorus mobility from surface sediments to the water column was assessed; and finally a database for future studies on the eutrophication of this river in Côte d'Ivoire was created.

MATERIALS AND METHODS

Study area

The study area is located in the south of the N'zi River watershed, between the Mohofouê upstream and N'zianoua downstream villages. Figure 1 shows the geographical location of the five stations (Mohofouê, Apiamôh, Dibi, N'zianoua, SCB) which were studied in this work. These choices were made taking into account the intense agricultural activity (rubber, coffee, cocoa, sweet bananas) in this part of the N'zi River basin.

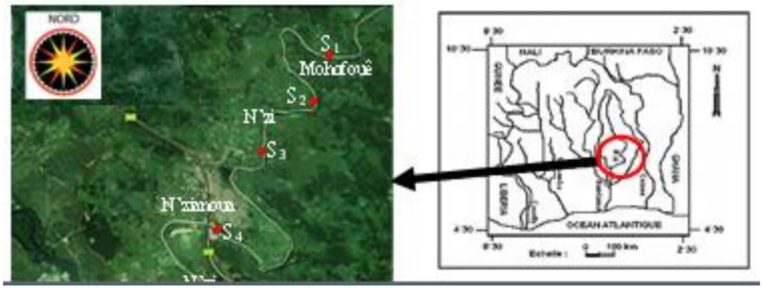

Figure 1. Sampling stations in the N'zi River

Sample collection and preservation techniques

Water samples were collected with a 2.5 L Niskin bottle at 0.3 m below the surface of the stream. A multiparameter Meter with GPS - HANNA HI 9828 was used to measure *in situ* parameters including pH, conductivity, temperature, total dissolved solids. Water samples were then filtered through a 0.45 µm Whatman GF/C filter and stored in polyethylene flasks of 1 L volume (previously rinse twice with the sample water). Subsequently, these vials were acidified with hydrochloric acid, stored in a cooler at 4 °C. Surface sediment sampling was carried out using a steel Van Veen grab type with a surface area of 250 cm^2. Only surface sediments (0 - 2 cm) were retained, because they represent the area likely to be released from in the water column during floods. The sediments were collected and stored in polyethylene bottles in the dark in a cooler (4 °C).

Measurement protocols

The chemical parameters concentrations such as: orthophosphates (PO_4^{3-}), total phosphorus (TP), nitrate ions (NO_3^-), nitrite ions (NO_2^-), ammonium ions (NH_4^+) and chlorophyll *a* (Chl *a*) were measured in water samples according to the AFNOR methods [22,23].

Phosphorus fractions in sediments were determined using the sequential extraction procedure of Williams (Figure 2): *i.e.* iron-bound P (Fe-P) bioavailable, calcium-bound P (Ca-P) non available, total P (TP), organic P (Org-P) partly available and inorganic P (IP).

The Murphy and Riley colorimetric method is used for phosphate determination in the supernatant [23,24].

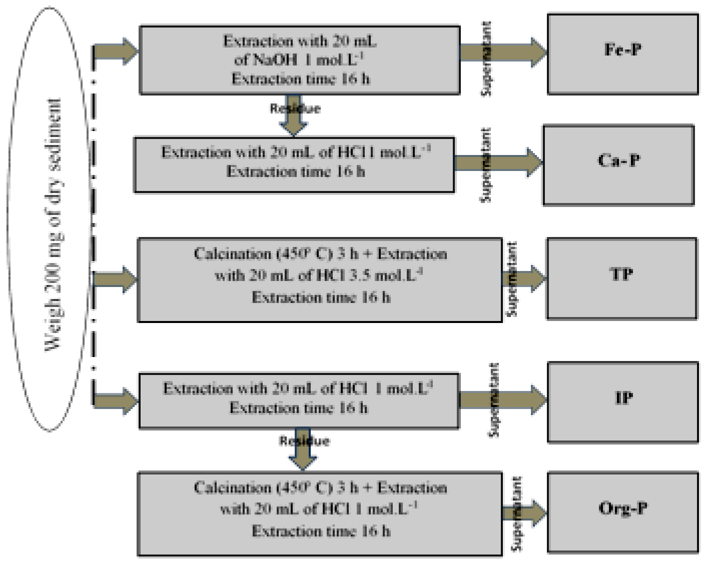

Figure 2. Phosphorus fractions in sediments according to the Williams sequential extraction procedure (1976)

The concentration in the supernatant for HCl-P extraction (Ca-P, IP, Org-P, TP):

C = **Error!** (mg/g of P dry weight) (Eq.1)

The concentration in the supernatant for NaOH-P extraction (Fe-P):

C = **Error!** (mg/g of P dry weight) (Eq.2)

with S: P concentration in the extract in mg/L of P; V: volume of reagent used for extraction (20 mL); m: mass of the test sample (200 mg dry weight) and 14: correction factor.

Statistical analyzes

Graphs, descriptive statistics and correlation matrix were produced using Microsoft Office Excel 2013 software.

RESULTS

Physicochemical parameters

Table 1 shows the results of the physicochemical properties of water samples taken from the N’zi River, in Côte d'Ivoire.

Table 1. Parameters determined *in situ*

Stations	pH	EC (mS/cm)	TDS (mg/L)	T (°C)
Mohofouê	6.10	0.09	0.05	25.6

Apiamôh	6.48	0.09	0.04	27.44
Dibi	6.41	0.1	0.05	26.8
N'zianoua	6.36	0.1	0.05	27.2
SCB	6.94	1.5	0.76	26.3
Mean	6.46±0.31	0.38±0.63	0.19±0.32	26.67±0.74

T: temperature, EC: electrical conductivity, TDS: total dissolved solids

The river water temperature values oscillated between 25.6 °C (Mohofouê) and 27.44 °C (Apiamôh). These values were within the limit of 27 °C recommended by the World Health Organization (WHO). The N'zi River water was slightly acidic with pH values ranging from 6.1 to 6.9 from upstream to downstream. These values remained below the limits of 6.5 - 8.0 recommended by the World Health Organization (WHO). Electrical conductivity (EC) ranged from 0.09 to 1.5 mS/cm, increasing upstream to downstream. The samples water conductivity was due to the dissolved ions. The range for total dissolved solids (TDS) was 0.04 to 0.76 mg/L, which was well below the limit of 1000 mg/L recommended by the WHO.

Spatial distribution of nutrients and chlorophyll *a* in the water column

The spatial distributions of the dissolved phosphorus forms in the water column are given in Figure 3.

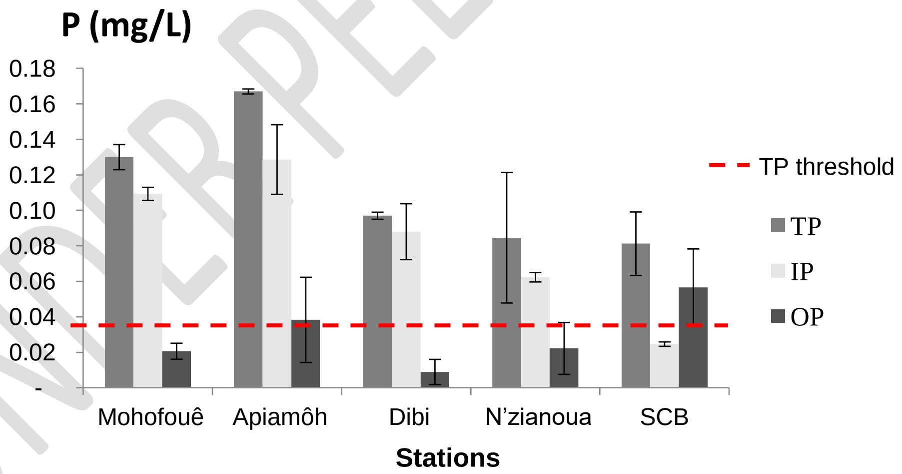

Figure 3. Variations of the dissolved phosphorus forms concentrations in the N'zi River

Total phosphorus (TP) concentrations in water ranged from 0.08 mg/L (downstream) to 0.17 mg/L (upstream), with an average value of 0.11 ± 0.03 mg/L. The N'zi River water was more loaded with phosphorus upstream also evidenced by inorganic phosphorus (IP) concentrations, which ranged from 0.02 mg/L downstream to 0.11 mg/L upstream. Organic phosphorus (OP) concentrations were in the range of 0.02 mg/L (upstream) to 0.06 mg/L (downstream).

The spatial distributions of the dissolved nitrogen forms in the water column are given in Figure 4.

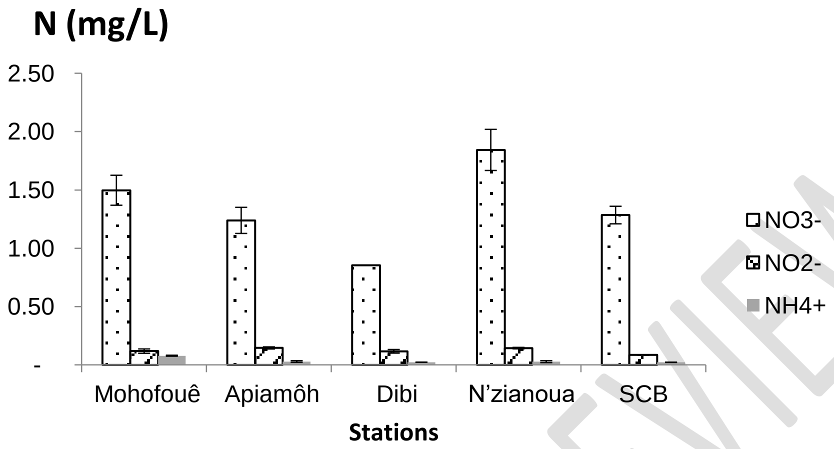

Figure 4. Variations of the dissolved nitrogen forms concentrations in the N'zi River

The nitrate ions (NO_3^-) concentrations in the water fluctuated between 0.85 mg/L (Dibi) and 1.84 mg/L (N'zianoua), with an average value of 1.34 ± 0.36 mg/L. The N'zi River was more loaded with nitrate ions, followed by nitrite ions (NO_2^-) 0.09 - 0.15 mg/L, and finally ammonium ions (NH_4^+) 0.02 - 0.08 mg /L. Chlorophyll *a* (Chl *a*) concentrations ranged from 21.30 µg/L (Dibi) to 31.60 µg/L (Mohofouê) (Figure 5), with an average value of 25.96 ± 0.01µg/L.

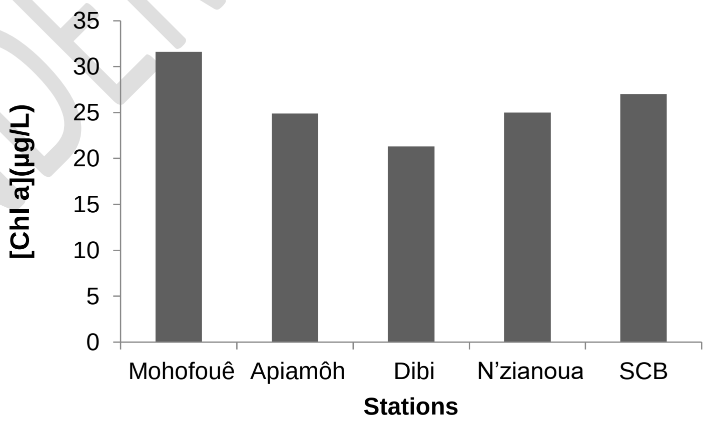

Figure 5. Variations of chlorophyll *a* concentrations in the N'zi River

Phosphorus distribution in sediments

The spatial distributions of phosphorus fractions in the sediments of the N'zi River are given in Figure 6.

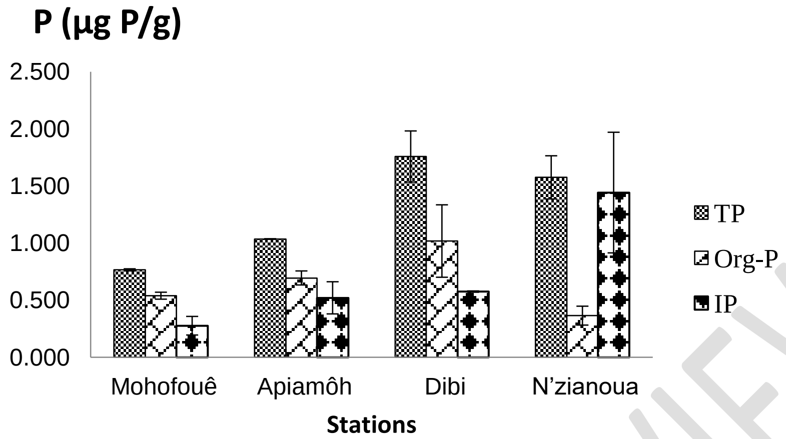

Figure 6. Phosphorus fractions concentrations in the N'zi River sediments

Total phosphorus (TP) concentrations in the sediments varied between 0.765 µg P/g dry weight (Mohofouê) and 1.758 µg P/g dry weight (Dibi), with an average value of 1.283 ± 0.400 µg P/g dry weight. In the N'zi River sediments, the inorganic phosphorus (IP) concentrations ranges were 0.277 to 1.442 µg P/g dry weight, and 0.365 to 1.018 µg P/g dry weight for the organic fraction (Org-P). With an average value of 0.704 ± 0.510 µg P/g dry weight, the inorganic phosphorus fraction (IP) in the sediments was higher than the organic one (Org-P).

DISCUSSION

Relationship between the water parameters and the N'zi River eutrophication

The water pH mean value was 6.46 $\pm$ 0.31; which reflects the slightly acidic character of the N'zi River compared to the limits (6.5 - 8.0) recommended by the World Health Organization (WHO). This result was due to the decomposition of the organic matter resulting from the proliferation of algae, by bacteria which produce acid by-products as shown by Pazou et al. 2018 [25] in their work. High correlations were obtained between the water pH values and the water temperature (r = 0.95), ammonium ions (r = - 0.95) and chlorophyll *a* (r = - 0.87) respectively (Table 2). It appears that the water pH (6.1 - 6.94) and water temperature (25.6 °C - 27.44 °C) ranges of the N'zi river were ideal for the existence of the non-toxic dissolved form of ammonium ions (NH_4^+), favorable to the development of algae. This is corroborated by the Ouffoué et al. 2014 [26] work carried out in the Boubo River in Côte d'Ivoire.

An average electrical conductivity (EC) of less than 0.2 mS/cm was obtained in the first four stations, reflecting a low water mineralization in this part of the N'zi basin. According to the WHO, waters with conductivity values between 0.1 and 0.2 mS/cm are weakly mineralized and therefore are fresh water. The average conductivity value of the first four stations is also similar to the Boubo River one in Côte d'Ivoire (0.1 mS/cm) obtained by Ouffoué et al. 2014 [26]. However, a conductivity peak was observed at the SCB station (1.5 mS/cm), indicating excessive mineralization and high salt dissolving capacity. This value was three times higher than the average of 0.5 mS/cm obtained by Adeosun 2019 [27] in the Ogun River in Nigeria. This reflects the nutrient enrichment in the N'zi River water, linked to the agricultural inputs used in the large farms adjoining the SCB station. Moreover, high negative correlations were obtained between electrical conductivity and inorganic phosphorus values (r = - 0.89), then ammonium (r = - 0.62) respectively (Table 2). Therefore, conductivity variations at different stations could be due to nutrient inputs mainly from agricultural activities in the watershed and reduced water volume (low water period), as shown in Adeosun 2019 [27] work.

Average concentration of the total dissolved solids (TDS) was 0.047 mg/L at the first four stations while it was 0.76 mg/L at the last SCB station. There were high negative correlations between TDS concentrations and dissolved phosphorus forms (r = - 0.85 for TP, r = - 0.74 for IP and r = - 0.87 for OP). Consequently, discharges from industrial farms near the SCB station would increase the dissolved salts load in this part of the N'zi River water [28].

Table 2. Correlation matrix of water parameters in the N'zi River

	pH	EC	TDS	T	TP	IP	OP	NO_3^-	NO_2^-	NH_4^+	Chl *a*	TP(S)	Org-P(S)	IP(S)	Ca-P	Fe-P
pH	1															
EC		1														
TDS			1													
T	0.95*			1												
TP		-0.90*	-0.85*		1											
IP		-0.89*	-0.74*		0.96*	1										
OP		-0.66*	-0.87*	0.41*	0.78*		1									
NO_3^-								1								
NO_2^-			-0.61*	0.77*			0.78*		1							
NH_4^+	-0.95*	-0.62*		-0.91*						1						
Chl *a*	-0.87*	-0.69*		-0.75*						0.95*	1					
TP(S)		0.96*			-0.74*	-0.72*				-0.79*	-0.87*	1				
Org-P(S)								-0.99*					1			
IP(S)		0.69*			-0.64*	-0.82*		0.60*				0.60*		1		
Ca-P	-0.71*							0.91*			0.81*		-0.92*		1	
Fe-P		0.92*			-0.84*	-0.93*				-0.61*		0.84*		0.92*		1

*Significant correlation ($P < 0.05$)

T: temperature, EC: electrical conductivity, TDS: total dissolved solids, TP: total phosphorus, IP: inorganic phosphorus, OP: organic phosphorus, NO_3^-: nitrate ions, NO_2^-: nitrite ions, NH_4^+: ammonium ions, Chl *a*: chlorophyll *a*, Fe-P: iron-bound P, Ca-P: calcium-bound P, TP (S): total phosphorus in sediments, Org-P (S): organic phosphorus and IP (S): inorganic phosphorus in sediments

Spatial distribution of nutrients in the water column

All sampling stations waters are eutrophic (TP > 0.035 mg/L - Figure 3) according to the classification of Yang et al. 2008 [29]. These high TP values obtained reveal that anthropogenic activities are the key factors in the phosphorus dynamics cycle [30]. Table 3 presents a comparison of the N'zi River TP concentrations, with those of other rivers in the world.

Table 3. Comparison of TP concentrations of the N'zi River with other rivers in the world

River	TP (mg/L)
N'zi River (Côte d'Ivoire)	**0.110**
San Francisco (Brazil)	0.090
Tocantins (Brazil)	0.076
Klamath (USA)	0.130
Jiaxing (China)	0.760

TP average concentration in the N'zi River were higher than those of the San Francisco (0.09 mg/L) and Tocantins (0.076 mg/L) Rivers in Brazil, obtained by Fonseca et al. 2011 [31]. However, they remain close to the mean value obtained by Oliver et al. 2014 [32] in the Klamath River (0.13 mg/L) in the United States. Moreover, TP concentration (0.760 mg/L) obtained by Liang et al. 2014 [33] in the Jiaxing River in China, was higher than our study value. The N'zi River is therefore one of the most eutrophic rivers. Indeed, this area is subject to intensive export agriculture (rubber, cocoa, coffee, sweet bananas) which uses frequently fertilizers and infiltrate soil. Agricultural runoff as well as soil leaching during rainfall are strongly linked to the eutrophication of the N'zi River water [34].

Additionally, dissolved inorganic phosphorus (IP) shows the same spatial variations as TP, except at the SCB station. This form of P is directly available for uptake by aquatic plants and therefore has a direct impact on eutrophication. As for the SCB station, the low dissolved PI content could be due to the rapid assimilation of this element by bacteria and algae [35].

Generally, nitrate ions (NO_3^-) quantitatively dominates all nitrogenous forms in the water column (Figure 4). In the Mohofouê, Apiamôh, N'zianoua and SCB stations, the nitrate ions contents are well above the eutrophication threshold value (1 mg/L) for the rivers. These nitrate ions concentrations would be the result of the fertilizers use in agriculture, leaching of cultivated land and/or contamination by waste of human or animal origin (artisanal manufacture of alcohol, livestock farms) [36]. The low nitrate ions content at the Dibi station is probably linked to assimilation by algae, very present during our campaign. More, there was a high positive correlation (r = 0.95) between ammonium ions and chlorophyll *a* (Chl *a*) values. Ammonium ions (NH_4^+) was de facto the nitrogen form most assimilated by algae, as evidenced by the very low levels in the water column (0.02 - 0.08 mg/L). Nitrites ions did not have a direct influence on chlorophyll *a* as no correlation was found between these two parameters. However, the weak correlation between nitrites and nitrates ions (r = 0.51), shows that the nitrite contents in the water column are linked to the nitrification activity of bacteria. This result is in the same vein as the conclusions of Gboko et al. 2019 [37] in the Ono Lagoon.

The nitrogen and phosphate N/P ratio ([N = NO_2^- + NO_3^- + NH_4^+]/[P = PO_4^{3-}]) of Ryding and Rast 1994 [38] is greater than 7 in all stations (Figure 7). Consequently, algal bloom was limited by phosphorus.

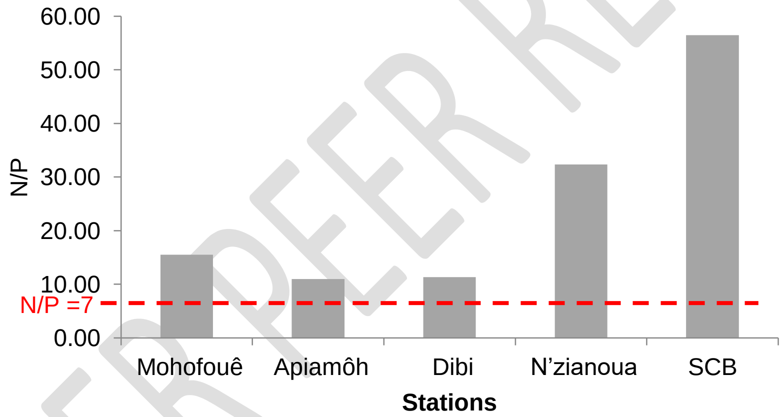

Figure 7. Spatial variations of the N/P ratio in the water column

The N'zi River waters are eutrophic (Chl *a* > 10 µg/L at all sampling stations) according to the classification proposed by Huo et al. 2013 [39]. These high Chl *a* contents reflect high algal productivity, linked to the high availability of nutrients (phosphates and nitrogen) as well as the proximity of stations to areas of intense agricultural activities.

Phosphorus speciation in the sediments

An increasing gradient of concentrations was observed as one approached the mouth of the N'zi River (Station SCB). This reflects a phosphorus flux in a north-south direction, following the river current and thus confirming the leaching of agricultural soils along the watershed of the N'zi River. There appears to be a marked adsorption of phosphorus in the sediments at the Dibi and N'zianoua stations supported by a TP drop in the water column at these stations.

This adsorption could result from the bathymetry and the particle size distribution of the sediments [40]. A high negative correlation existed between sedimentary total phosphorus (TP) and chlorophyll *a* (r = - 0.87), indicating that sediments phosphorus was readily mobilized for algal growth.

Moreover, the inorganic phosphorus (IP) concentrations (range: 0.277 - 1.442 µg P/g of dry sediment) were low compared to the organic fraction (Org-P) one at the Mohofouê, Apiamôh and Dibi stations except at the N'zianoua station. The inorganic phosphorus (IP) is called weakly bound phosphorus or labile phosphorus which can easily desorb from sediments. It becomes available for the algae growth as a high correlation between the sediments IP and the dissolved IP (r = - 0.82) has been observed. These algae trap the phosphorus bioavailable fraction and help to reduce the IP fraction in the sediment [41]. A high average dissolved IP concentration (0.11 mg/L) was obtained in the water column at Mohofouê, Apiamôh and Dibi stations (Figure 8). As a result, much of the inorganic phosphorus (IP) in the sediment is mobilized in the water column and promotes the algae growth. More, the iron-bound P (Fe-P) which forms weak bonds with the sediment varied from 28.35% to 71.91% (Figure 8).

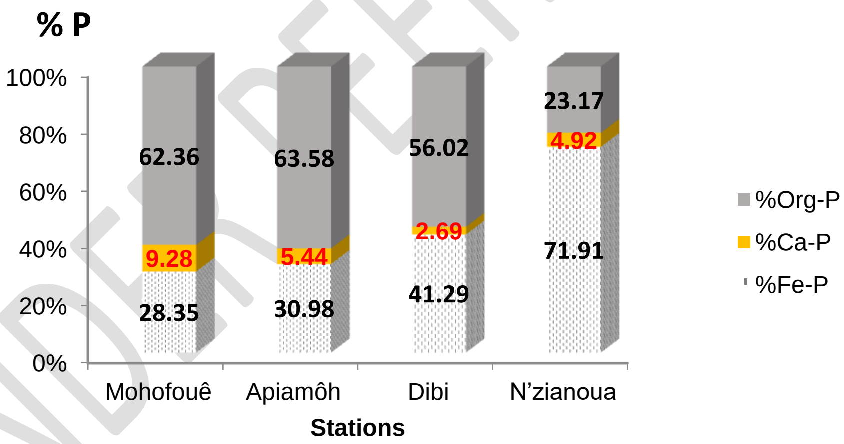

Figure 8. Spatial distributions of the iron-bound P (Fe-P), Calcium-bound P (Ca-P) and organic

matter P (Org-P) proportions in the N'zi River sediments

That linked to organic matter (Org-P) was found to be the most important at the three stations Mohofouê, Apiamôh and Dibi. Calcium-bound P (Ca-P) forms strong bounds with the sediment, therefore unavailable, showed the lowest proportion, *i.e.* 5.59% on average. Moreover, a high negative correlation existed between the iron-bound P (Fe-P) and the dissolved IP (r = - 0.93). These results suggest that the iron-bound P fraction (Fe-P) would be largely released into the water column at the Mohofouê, Apiamôh, Dibi stations and would participate in maintaining algal activity. Similar results were obtained by N'goran et al. 2019 [17] in the M'badon bay in Côte d'Ivoire. The high organic fraction proportions (Org-P) at these stations would be the result of the strong organic decomposition (zooplankton, phytoplankton, decomposing algae) in the water column. Furthermore, the high proportion of Fe-P at the N'zianoua station would probably be attributable to the numerous plantations and domestic waste (washing liquids, wastewater, and livestock) which saturate the water column and promote phosphorus precipitation in sediments. However, this fraction can still potentially be used to contribute to eutrophication [42].

CONCLUSION

This study is the first to assess the agricultural activities impact on the N'zi River eutrophication, tributary of Bandama River. It provides evidence that the nutrients flux such as phosphorus and nitrogen from anthropogenic inputs increases algal growth in the water column. More, the sediments sequential phosphorus extraction showed that exchanges at the water-sediment interface can lead to ecological imbalances allowing an anarchic development of algae. Although it is too early to deduce with certainty these trends on the basis of a measurement campaign, it is evident that the use of agricultural fertilizers is intensifying in the N'zi-Bandama watershed with the consequence of an increase in nitrogen and phosphate concentrations in this area. The populations should be sensitized to the moderate use of agricultural inputs in order to reduce the eutrophication of the N'zi River.

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