



## Characterization and phosphorus fractionation of the surface sediment of Nokoué Lake (Benin)

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Original Submitted In 5<sup>th</sup> June 2011. Published online at [www.biosciences.elewa.org](http://www.biosciences.elewa.org) on September 29, 2011.

### ABSTRACT

*Objectives:* Lake Nokoué in South of Benin (West Africa) is a eutrophic lake with great area covered by hyacinth during the rainy season (July to October). pH-water and pH-KCl values show short variations and sediment re-suspension. The aim of this study was to estimate the eutrophication status of Nokoué based on nutrients in the sediment and to estimate the amounts and forms of potentially mobile P in surface sediments using sequential P extraction (P-fractionation).

*Methodology and results:* Different forms of P in sediment samples were determined by extracting P according to the scheme proposed by Rydin and Welch (1998) modified based on Hieltjes and Lijklema (1980) and Psenner (1984) protocol. The application of eutrophication risk framework to sediment nutrient content showed that 75% of the samples were “very bad.” (that indicates a most high eutrophication risk). According to phosphorus fractionation. Fe-bound-P. Al-bound-P and Organic-bound-P comprised the largest phosphorus pool (50% of Total Phosphorus). Phosphorus release was from the Fe-P. Al-P and organic fractions. The organic matter mineralization occurring at the end of summer can also influence P release as illustrated by the difference in total phosphorus content between sediment samples of June (beginning of rainy season) and of September and October. This type of P release was observed in the Lake. High soluble reactive phosphorus content was measured in the water column; however. this part of phosphorus was in particulate form and can release and contribute to macrophyte or algae growth

*Conclusion and application:* The results showed that it is necessary to reduce P content in the water column in order to decrease primary productivity and subsequent organic matter sedimentation. Sediment is a main internal source of eutrophication in L. Nokoué. The results could serve as a basis for formulating national policies and other environmental policies designed to protect the coastal lagoons and living organisms.

**Key words:** Eutrophication. surface sediment. phosphorus fractionation. Nokoué lake

## INTRODUCTION

Phosphate is the primary cause of eutrophication of numerous water bodies. Its presence in natural aquatic ecosystems is due to human activity (Correll. 1998; Parinet. 2000; Van Hullebusch. 2002; Mama,. 2010). The endogenous sources show two types of inputs into the lakes via groundwater infiltration or through leaching from the sediments. Efforts to restore surface water quality in eutrophied systems have typically focused on reduction of P loadings. particularly from external sources (e.g. wastewater treatment plant effluent or agricultural runoff). However. lake sediments generally act as net sinks of phosphorus (P). although a large part of the inorganic P in surface sediments is in equilibrium with the water above (Golterman. 1995). P release from sediments can contribute up to 99% of the total P input into some shallow lakes. even under toxic conditions at the sediment surface (Boström *et al.*. 1988; Jensen and Andersen. 1992; Rydin and Brunberg. 1998; Penn. 2000; Van Hullebusch. 2002). This phosphorus release is generally called internal loading to distinguish it from external loading. This internal loading can determine the eutrophication status of the lake and the time lag for ecosystem rehabilitation (Bootsma *et al.*. 1999;

Ifremer. 2000). Internal loading is greatest in summer. when phosphorus concentration in the water of eutrophic lakes can be several times higher than in the inflowing waters (Pettersson. 1998) particularly in shallow polymictic lakes. P load via wind causes re-suspension of particles (Kristensen *et al.*. 1992; Sondergaard *et al.*. 1992; Van Hullebusch. 2002). Inactivation of phosphorus from sediments is usually employed following controls on excessive external loads.

Total phosphorus content in the sediment can be a good predictor of potential eutrophication in a lake (Trinquier. 2009; Mama. 2010). However. characterization of sediment phosphorus. usually based on sequential chemical extractions. is also necessary. P can be exchangeable. bound to iron. aluminium and manganese hydroxides. organic matter and calcium (Rydin and Welch. 1998). This fractionation allows the potential mobile P fraction under oxic and anoxic conditions to be estimated (Rydin. 2000). The aim of this study was to estimate the eutrophication status of Nokoué based on nutrients in the sediment and to estimate the amounts and forms of potentially mobile P in surface sediments by using sequential P extraction (P-fractionation).

## MATERIALS AND METHODS

**Study site:** Lake Nokoué is a shallow estuary lake (surface area = 150 km<sup>2</sup>. mean depth = 1.5 m during the dry season and 2.5 m during the rainy season) located to the North of Cotonou in Benin (West Africa). This lake is classified as being eutrophic according to the OECD (Organization for Economic Cooperation and Development) classification (Mama 2010). Hydraulic residence time was estimated to be approximately one year. The catchment constituted by Ouémé delta area (46500 km<sup>2</sup>) is occupied by rural activities while the south of the lake is occupied by an urbanized sector (Cotonou city); 40% of the lake is occupied by traditional fisheries framework called "acadja".

Lake Nokoué bathymetry is characterized by a depth of 2.8m over an area of 28. 5 km<sup>2</sup>: 1 to 2m for 104

km<sup>2</sup> and under 1m for 30 km<sup>2</sup>. An average reduction of 0.6m has been recorded during 20 years (0.03 m/year approximately). "Acadja" and sediment load caused by lake hydrodynamics are the main source of this reduction in lake depth.

**Sample collection and preparation:** A hand scoop was used to sample surface sediment (5 cm depth). this corresponds to the sediment accumulated over several years and to the sediment generally prone to re-suspension in shallow lakes (Reddy *et al.*. 1996). Sampling was carried out at four stations (map of figure 1): Ganvié (S1); Sô-Ava (S2); Center of lake (S5) and Calavi (S7).



**Figure 1:** Sediment sampling stations map

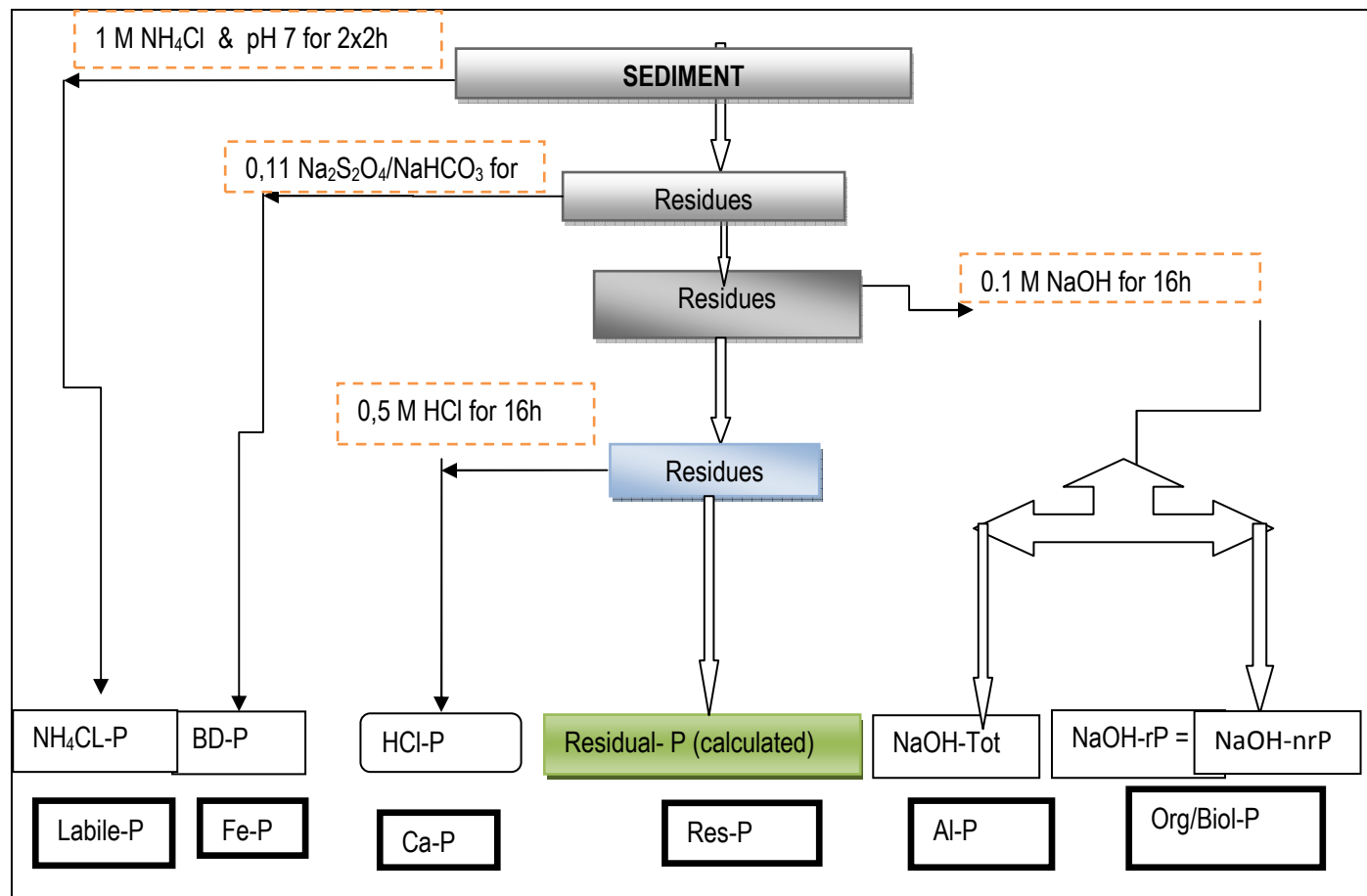
The collected samples were stocked in polyethylene containers previously decontaminated with  $\text{HNO}_3$  (10%) and rinsed with ultra pure water (Milli Q system) (Rubio and Ure. 1993; Van Hullebusch. 2002).

The duration of sampling was approximately 6 months: from June to November 2007. Oxidic conditions are sustained at the water/sediment interface throughout the year (Van Hullebusch *et al.* 2002a. b). Thus, the sample could be dried in the open air with no modification of phosphorus speciation (Bordas and Bourg. 1998). In this study, after drying, samples were sieved using a nylon sieve mesh (2 mm) according to the AFNOR standard X31-101 (AFNOR. 1994).

**Sediment mineralization:** The reagents used for 0.5 g dried sediment were 3 mls HCl (37%) + 1 mls  $\text{HNO}_3$

(69%) + 3 mls HF (48%). The digestion procedure was carried out in three steps. 15 min at 100°C. 15 min at 150 °C and 60 min at 200 °C. At the end of the procedure 3 mls of saturated boric acid solution was added to neutralize fluoride ions (Quevauviller *et al.* 1993; Van Hullebusch. 2002).

**Study of phosphorus fractionation:** Different forms of P in sediment samples were determined by extracting P according to the scheme proposed by Rydin and Welch (1998) modified based on Hieltjes and Lijklema (1980) and Psenner (1984) protocol. This protocol was chosen because it allows easy evaluation of phosphorus and hydroxide bonded to aluminium metal compared to other recent protocols (Van Hullebusch. 2002).



**Figure 2:** Phosphorus fractionation scheme used from Rydin and Welch (1998).

Different forms of P in sediment samples were determined by extracting P according to the scheme proposed by Rydin and Welch, 1998 (Figure 2). P fractions listed here were (i) loosely bound or labile-P (including SRP) in pore water (NH<sub>4</sub>Cl-P); (ii) Fe-adsorbed P, obtained by anoxic treatment with bicarbonate dithionite (BD-P); (iii) Al-adsorbed P (NaOH-rP) and organic P (NaOH-nrP) detected after persulfate mineralization of the extract. Including bacteria incorporated P; (iv) Ca-bound P (HCl-P) and (v) residual P consisting mainly of refractory organic P as well as the inert P fraction (Res). Residual P was determined as total phosphorus (TP) minus total extract P.

**Analytical methods:** The methods selected for characterization of sediments were as follows: Organic

## RESULTS

**Sediment characteristic:** *Granulometric sediments*  
Sediments consisted of a soft, Blackish, fine grained material (<2 mm) rich in organic substances carbonate

matter was estimated by Walkley-Black method (Jackson *et al.*, 1984) and dry weight (DW) was determined by drying to constant weight at 105 °C X31-505 (AFNOR, 1994). Organic matter loss on ignition was determined by mineralization to constant weight at 550 °C (AFNOR, 1994); carbonate content was determined according to the Rauret protocol (Rauret *et al.*, 1988) and total phosphorus content (TP) in the sediment was determined after persulfate mineralization at 120 °C for 2 hours (Gächter *et al.*, 1992). Soluble Reactive Phosphorus (SRP) was measured using the molybdate-method (AFNOR, 1998) and Ca-Mg-Na-K was measured by Flame AAS NFT 90-005 (AFNOR, 1998).

content in the samples was too low to have an impact on the sediment chemistry (Table 1).

**Table 1:** Physical characterization of sediments in Lake Nokoue. Benin.

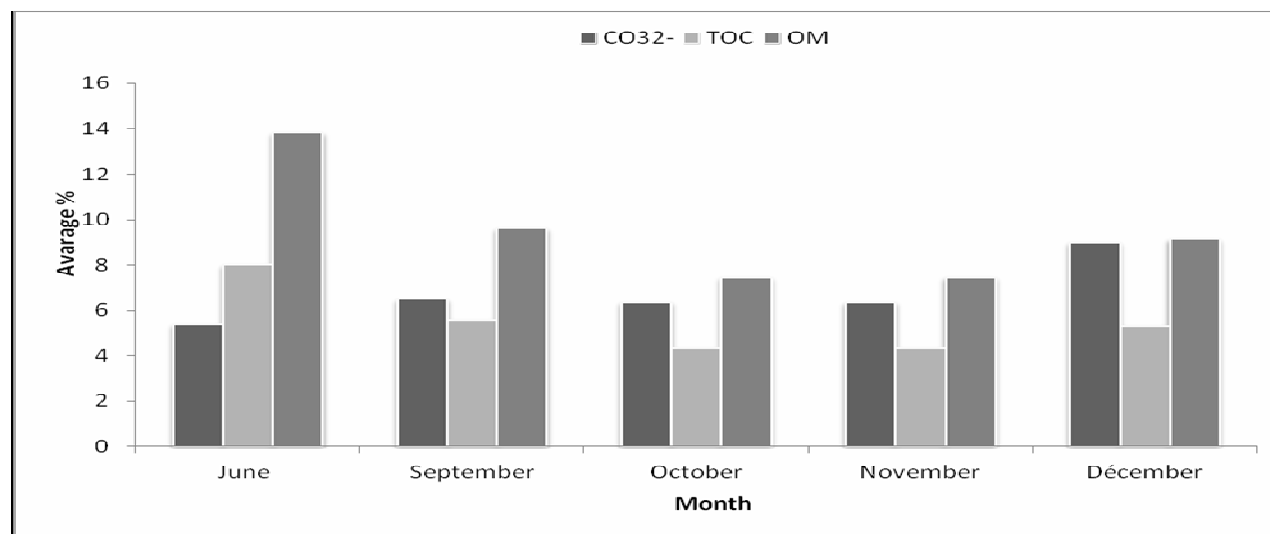
Sample	Fraction > 50 $\mu$ m	Fraction < 50 $\mu$ m
S <sub>1</sub> (Ganvié)	37.5	62.5
S <sub>2</sub> (Sô – Ava)	36.1	63.9
S <sub>5</sub> (center of Lake)	15.1	84.9
S <sub>7</sub> (Calavi)	73.0	27.0

**Alkalinity and organic matter** Carbonate, organic matter and total organic carbonate values at stations S1 (Ganvié), S2 (So -Ava), S5 (center of lake), S7 (Calavi) in 2007 are shown in figures 3 and 4.

Carbonate Content at Ganvié (figure 4) shows minor temporal variability. However; the highest value was observed in December (when there is high discharge into the lake). This content ranged from 4.3 to 9%

(mass percent). Carbonate value reduction was observed from 6+

June to October, the minimal value observed was 7.4% and the maximal value was 13.8% in June, which can be associated with accumulated organic waste load in the lake, mainly near Ganvié village where uncontrolled deposit occur from the neighboring village.



**Figure 3:** Organic matter in sediment in lake Noukoue. Content of carbonate, total organic carbon and organic matter variability in sediment (S1)

At Sô – Ava (figure 5), the highest content of carbonate and organic matter was observed in September and the low content of TOC in October. In November, organic

matter, total organic carbon and carbonates had same values which can be explained by the fact that they are mainly in carbonate form.

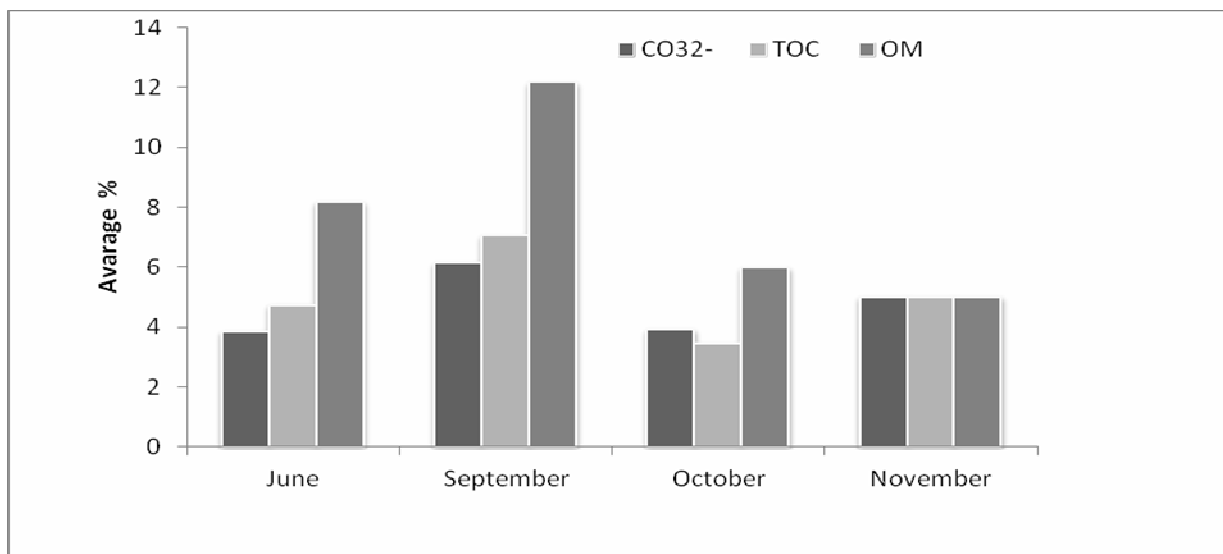


Figure 4: Content of carbonate and organic matter for sediment from location S2, (Sô - Ava).

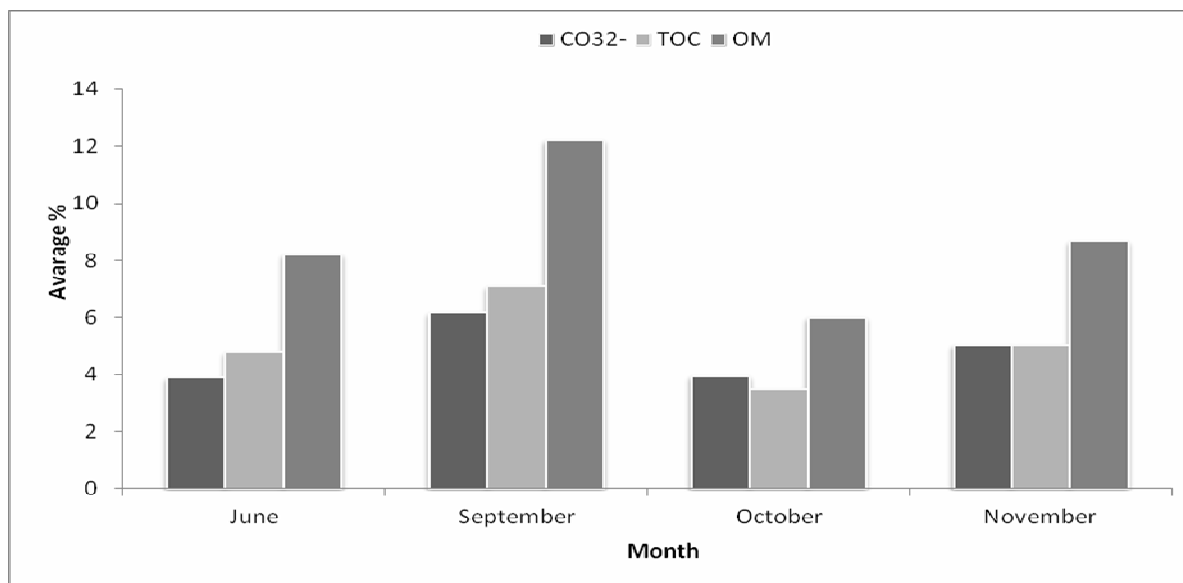


Figure 5: Content of carbonate and organic matter for sediments from location S5, (Center of lake).

Organic matter content was low with minimal value in October (0.63%) and maximal value in September (12.2%), which is the flood month in the lake region. Sand content at this station was high with significant load of suspended matter brought in by River Ouémé.

**pH<sub>(water)</sub> and pH<sub>(KCl)</sub>:** Figure 6 shows that pH - (H<sub>2</sub>O) and pH - KCl of sediments were lowest for anthropogenic site: S1 (Ganvié); S2 (Sô – Ava) and S7 (Calavi). The months of June and December had the least values (3.18 to 4) while September, October and November had the highest values (between 4 and 6).

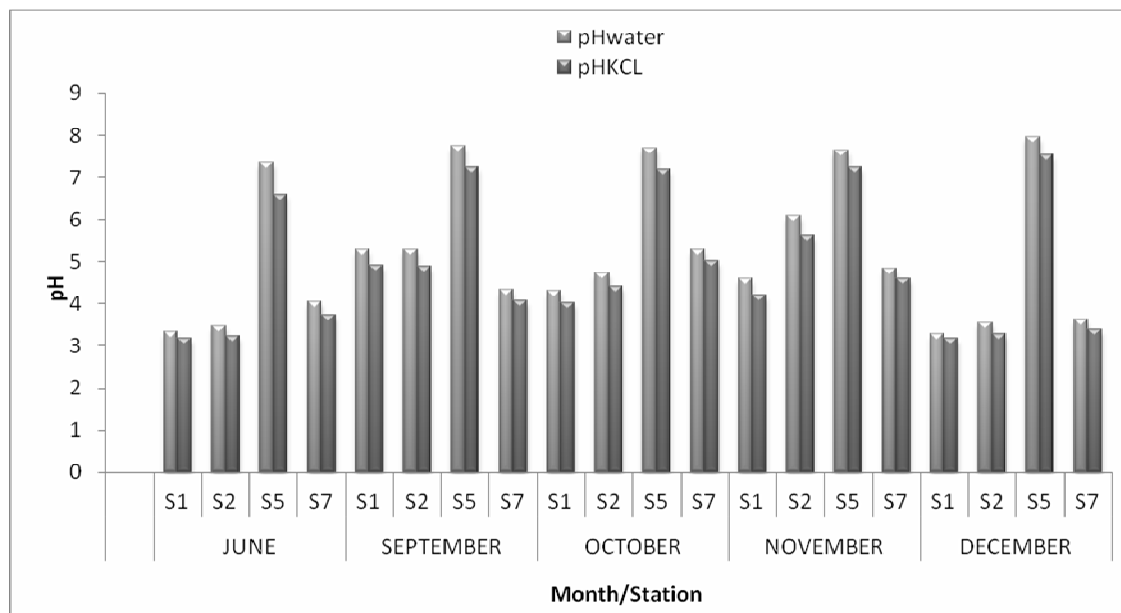


Figure 6: pH<sub>water</sub> and pH<sub>KCl</sub> variability of sediments in Lake Nokoue, Benin.

### Total Nitrogen and Phosphorous

Table 2: Organic mater. total nitrogen and total phosphorus variability

Months	Parameters	OM	TN	TP
	Stations	(%)	(g/kg)	(µg/g)
June	S <sub>1</sub> (Ganvie)	8.2	4.1	1414.65
	S <sub>2</sub> (Sô – Ava)	13.8	6.9	4508.26
	S <sub>5</sub> (Lake center)	4.4	2.2	496.37
	S <sub>7</sub> (Emb- Calavi)	10	5	881.05
September	S <sub>1</sub> (Ganvie)	12.2	6.1	1005.15
	S <sub>2</sub> (Sô – Ava)	9.6	4.8	819.01
	S <sub>5</sub> (Lake center)	2.12	1.06	546
	S <sub>7</sub> (Calavi)	16.6	8.3	1092.01
October	S <sub>1</sub> (Ganvie)	6	3	819.01
	S <sub>2</sub> (Sô – Ava)	7.44	3.7	1240.92
	S <sub>5</sub> (Lake center)	2.66	1.3	595.64
	S <sub>7</sub> (Calavi)	8.88	4.4	2109.56
November	S <sub>1</sub> (Ganvie)	8.66	4.3	620.46
	S <sub>2</sub> (Sô – Ava)	8.32	4.2	1141.65
	S <sub>5</sub> (Lake center)	2.18	1.1	794.2
	S <sub>7</sub> (Calavi)	38.22	19.1	1985.5
December	S <sub>1</sub> (Ganvie)	9.982	5	1501.51
	S <sub>2</sub> (Sô – Ava)	9.137	4.6	1116.83
	S <sub>5</sub> (Lake center)	0.634	0.3	670.1
	S <sub>7</sub> (Calavi)	21.77	10.9	1886.2

Table 2 show nitrogen mass fraction and phosphorous in samples from several stations from May to

December 2007. Sediment point S<sub>7</sub> (Calavi) had the highest rate of nitrogen especially in November while

the lowest values were observed in location S5 (Central Zone of the lake).

Content of phosphorus was significantly high in June (rainy season) for station S2 and from October to December for station S7. Station S5 at the center of the

lake showed little variation of phosphorus content in sediment except in September (flood period). This tendency of nutrients increasing during the rainy season was observed in water column.

**Diagnostic of Nokoué lake sediment eutrophication status**

**Table 3:** Eutrophication risk diagnostic framework used for sediment which was applied on Nokoué Lake (Ifremer. 2000).

Variable	Very good (None eutrophication risk)	Good (low risk)	Middle (50% risk) I	Bad (high risk)	Very bad (very high eutrophication risk)
MO (%)	3.5	5	7.5	10	
NT (g/kg)	1	2	3	4	
PT(mg/kg)	400	500	600	700	

OM=Organic Matter; TN=Total Nitrogen; TP=Total Phosphorus

**Table 4:** Framework apply results on Nokoué lake for Station S1: Ganvié village

		Bad (high risk)	Very Bad (very high eutrophication risk)
Organique mater (OM)	%	9.5±0.25	
Total Nitrogen (TN)	g/kg DM		4.5±0.25
Total Phosphorus (TP)	mg/kg DM		1072±0.35SD=±0.35

**Table 5:** Framework apply results on Nokoué lake for Station S2 (Sô-Ava)

		Bad	Very Bad
Organique mater (OM)	%	9.1±0.26	
Total Nitrogen (TN)	g/kg		4.8 ±0.570.56
Total Phosphorus (TP)	mg/kg		1965±1 (SD= 1987)
		Bad	Very Bad
Organique mater (OM)	%	9.1±0.26	
Total Nitrogen (TN)	g/kg		4.8 ±0.570.56
Total Phosphorus (TP)	mg/kg		1965±1 (SD= 1987)



**Table 6:** Framework apply results on Nokoué lake for Station S5 (Center of lake)

		Very Good (None eutrophication risk)	Good (Low eutrophication risk)	Bad (high eutrophication risk)
Organique mater (OM)	%	2.4 ±0.58		
Total Nitrogen (TN)	g/kg		1.2±0.57	
Total Phosphorus (TP)	mg/kg			620 ±0.19

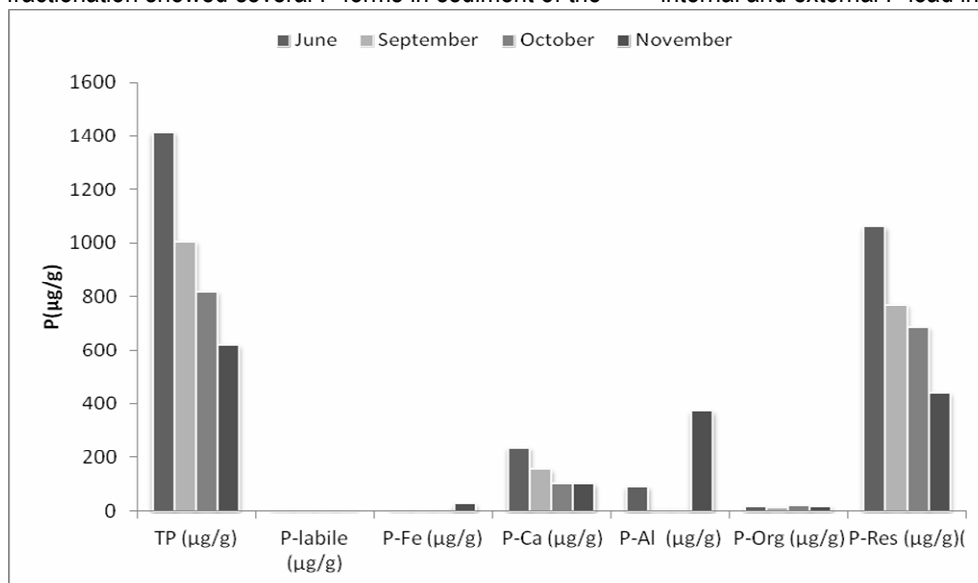
**Table 7:** Framework apply results on Nokoué lake for Station S7 (Calavi)

		Very Bad (very high eutrophication risk)
Organique mater (OM)	%	19 ± 0.62
Total Nitrogen (TN)	g/kg	9.5 ± 0.62
Total Phosphorus (TP)	mg/kg	1591 ± 0.35(SD=562)

75% of stations (S1; S2 and S7) presented very bad quality according to eutrophication risk based on total nitrogen (TN) and total phosphorus (TP).

**Phosphorus sediment fractionation:** Phosphorus fractionation showed several P forms in sediment of the

sampled stations. this gives opportunity to establish internal and external P load in Nokoué lake.



**Figure 7:** Phosphorus Fractions over time at station S1 (Garvié) in lake Nokoue. Benin.

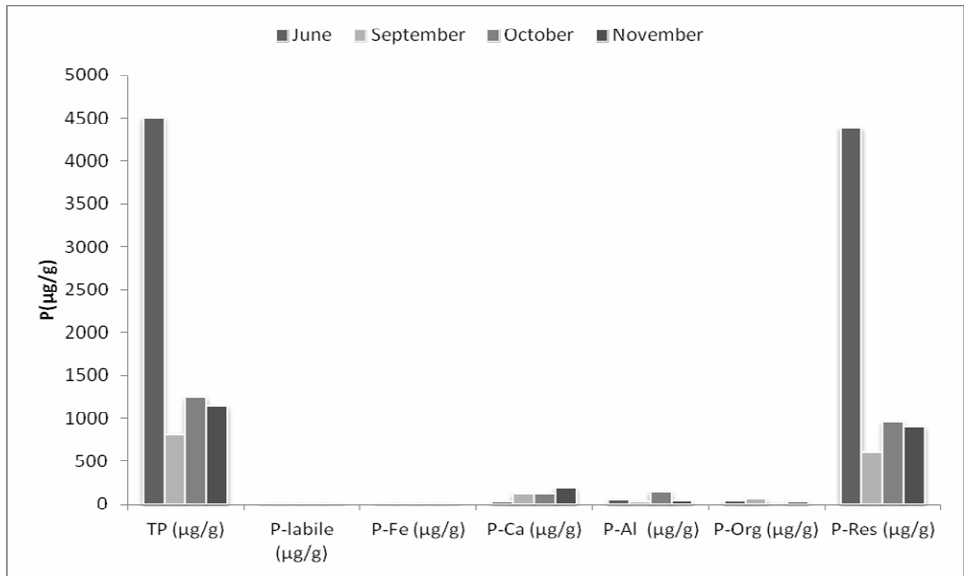


Figure 8: Phosphorus fraction over time at station S2 (Sô - Ava)

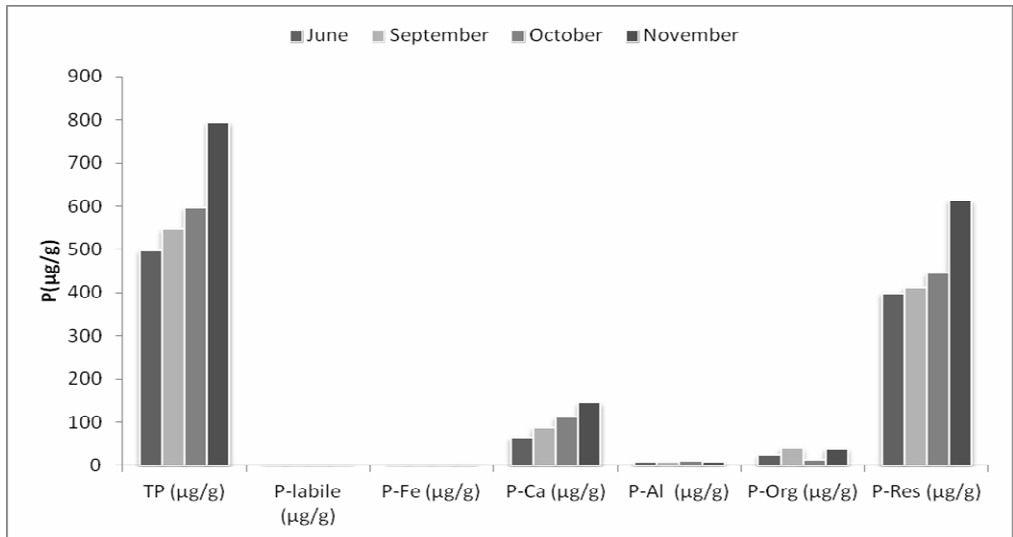


Figure 9: Phosphorus fractions over time in sediments at station S5 (Center of lake)

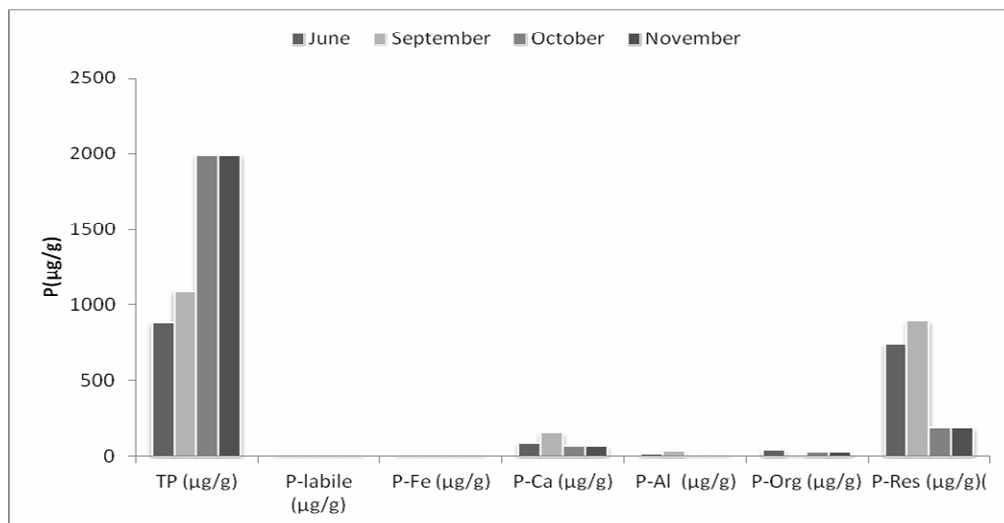


Figure 10: Phosphorus Fraction in sediments at station S7 (Calavi).

Phosphorus fractionation contributes to the evaluation of potential mobile phosphorus in the sediment under environmental conditions (Rydin, 2000). Labile forms, one bound to organic matter and that accounted for by iron are negligible. For the S1 site, the form linked to

calcium and aluminum is relatively high. This relatively high rate is linked to high levels of calcium obtained from this station as shown by the result in table 7 below.

Table 8: variability of Calcium (mg/L) content in the water body of lake Nokoué.

Station Month	S1	S2	S3	S4	S5	S6	S7
December 2006	-	7.2	7.4	7.2	214	460	260
February 2007	306	245	116	232	772	1182	862
March 2007	658	508	312	510	922	1238	940
Average	482	253	145	250	636	960	687
Standard deviation	0	250	154	251	333	434	372

Calcium content increases in the dry season due to increased load of salinity brought by sea water. Stations S5 and S7 had the highest value of calcium linked to tide variability in the Cotonou Chanel. As

calcium had marine source according to calcium monitoring results which is observed from June to September (rainy season).

## DISCUSSIONS

The organic matter content (OM) ranged from 7.4 to 13.8% dry weight (DW) using the Walkley-Black determination and was similar to loss on ignition determination (13.8–23.9% DW). OM content was significantly higher for samples collected in June (beginning of running season at Cotonou) than in October (end of running season). These OM contents were low compared to the results obtained by Rydin (2000) in a slightly eutrophic lake (Lake Erken, in Sweden) and Van Hullebusch (2002) in the shallow lake Cortille in France. The station at the center of the lake (S5) had the highest value of pH 7 during the

period of this study. Growth of algae (case of this station), increased pH value, because of photosynthetic activities in diurnal period. In a general case, pH-water and pH-KCl gives similar values. Water pH does not represent totality of acid ions (proton and aluminum ion) because some are integrated in humic argillite complexes. It was also observed that pH-KCl < pH-water. The variation between pH-KCl and pH-water is comprised between 0.5 and 1.5 pH unity.

Nitrogen rates changed over time in much the same way with low amplitude for all points except in S7. The station (S7) is the area where there are many sewage

discharge points and accumulation of nitrogen in sediment corroborates the results obtained on the water mass.

Total Phosphorus (TP) content in trap sediment was significantly higher in sample S2 (June). We have not significantly difference content of total phosphorus for September and October (high flow observed period in Nokoue lake).

Seventy five percent of the sampling stations (S1; S2 and S7) presented bad quality according to eutrophication risk based on organic matter. Results confirm higher eutrophication risk with internal source of nutrient (nitrogen and phosphorus mainly) (Mama. 2010).

For station S5. calcium and organic matter are relatively important and the fraction bound to MO increase from June to October. This result is linked the

importance of currents hydro - sedimentology which is under the influence of high loads of mineral and organic Ouémé made by the river and passing through the mouth of the river Sô at Totchè. The bound form of organic matter and that related to aluminum are negligible. For this site. the calcium-bound form is relatively high from June to October (heavy rain period in Cotonou and increased water supply from the central and northern countries). Over the area. in terms of hydrodynamics. undergoes a more pronounced influence of sea water which provides more calcium in the water body (Negusse. 2009).

Thus. phosphorus from sewage plants is readily bioavailable (75 to 90%). while for other sources. it is less so (P eroded from 30 to 40%. and P from atmospheric deposition: 25 to 50%) (Ryding and Wast. 1994).

## CONCLUSION

The oxic sediment of Lake Nokoué had a high retention capacity. Fe-P, Al-P and Organic-bound-P (Org/Bact-P) comprised the largest P pool. Due to high organic matter content in the sediments and could have an impact on water chemical characteristic and the trophic state of lake following sediment resuspension. According to Ifremer framework, Nokoué lake sediment was very bad and showed a high eutrophication risk. Phosphorus fractionation showed low value of labile P. More of phosphorus in the sediment was bonded and could be released at different pH levels (5 to 10). As a

common characteristic in eutrophic lakes during summer and in temperate climate or tropical site, the link with intensive re-suspension may increase of internal P loading in Nokoue lake risk. Phosphorus release was from the Fe-P bound, the Al- P bound fraction and the organic fraction. It represents on average 50% of total phosphorus released. Organic matter mineralization can also influence long term P release (38.2% for S7: Calavi).

## ACKNOWLEDGMENT

This Study was supported by "Agence Universitaire de la Francophonie"

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