

Original Research Article

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## Fractionation of Sediment Phosphorus in Lagoon Porto-Novo (Benin Republic) Revisited: Changes in Phosphorus Fractions and Release as Affected by Seasons and Sampling Sites

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### ABSTRACT

P is a key factor responsible of continental water eutrophication. In lagoon Porto-Novo sediments, it arises from slope basin supplies and biological activity. The present study has the main objective to evaluate phosphorus release rate coming from lagoon sediment, and to analyse the availability of these nutrient fractions. Four sampling point served to take up waters and sediments destined to analyses. The first five centimetres of sediments and waters were used and analyses (sequential extraction method) carried out on fraction 250  $\mu\text{m}$ , lyophilized for phosphorus fractionation. Phosphorus release rate was calculated applying Nürnberg regression equations which have been built from PT concentrations measured in seven Ontario and Connecticut Lake sediments. One-way variance analysis (ANOVA 1) using Dunnett method and Pearson (r) correlation implemented in MINITAB and JMP were applied. Results showed different phosphorus forms inside sediment. These forms were: P-labile, P-Fe, P-Ca, P-Al and P-Org accompanied by P-reside with a rate in mobilizable phosphorus reaching 66.39% PT. P-Org was the most abundant, attaining proportion between  $452.6 \pm 53.50 \mu\text{gP/g}$  -  $2035.4 \pm 311.2 \mu\text{gP/g}$  of dry sediment, consequence of organic matter accumulation from slope basin due to diverse human activities, and animal and plant organic matters present on the watershed. P-Ca is relatively more found in station S1 and S4 in contrast to S2 and S3. Release rate (TL) registered ( $11,05 \text{ mg} \cdot \text{m}^{-2} \cdot \text{j}^{-1}$ ) indicates then that lagoon Porto-Novo is in a more or less advanced degradation state with an internal load estimated by  $156,03 \text{ mg} \cdot \text{m}^{-2} \cdot \text{saïson}^{-1}$ . These results should be helpful for local and national authorities and stakeholders in setting environmental policies regarding phosphorus reduction, particularly that flowing from slope basin.

### Keywords

Sequential extraction, Phosphorus, Release, Fractionation, Release rate.

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### Introduction

Continental waters as receptor environments of slope basin accumulate nutrients from

natural as well as anthropoid origins (Oraison *et al.*, 2011). These facts lead to not only an

eutrophication of the surface waters, but also to that of environments located more downstream. Under temperate zones, the main cause of this increased eutrophication also called cultural eutrophication remains an increment in phosphorus supplies (Pienitz and Vincent, 2003). Similar observation is made in tropical areas with consequence corresponding to the proliferation of macrophytes. According to Gerdes and Kunst (1998), phosphorus is identified as a key nutrient causing eutrophication in continental aquatic areas. It is known as plant growth limiting factor in surface water (Smith *et al.*, 1999) and interrestrial ecosystems (Craaq, 2008). Lagoon phosphorus essentially came from slope basin, and then has terrestrial origin (Hou *et al.*, 2013) on Daihai Lake in Northwest China.

Sediment role in phosphorus cycle and their impact upon lake eutrophication process may be considerable (Golterman, 2004a, 2004b). Hence, comparatively to phosphorus from slope basin which is under dissolved and particle form, released phosphorus from sediment appears exclusively under dissolved form (Nürnberg, 2009). It is therefore totally equitable by living organisms such as phytoplankton, and can stimulate highly lake primary productivity. According to Oraison *et al.*, (2011), nutrients can be immobilized more or less temporally whenever touching sediments. They can be stored perennially whenever combined with other ions present within soil particles (iron, aluminium). Thus, human slope basin exploitation provokes an accumulation of phosphorus in sediments (Labrecque *et al.*, 2012). Actual phosphorus in sediments hinges also upon biological activity running in the lake (Stenzel *et al.*, 2017). It drifts across years and is freed by release phenomenon once some conditions admit it. Water swellings which mobilize sediments may move in suspension nutrients previously fixed in. According to Nürnberg

and Lazerte (2004), phosphorus release rate (TL) between 2 and 7  $\text{mg}\cdot\text{m}^{-2}\cdot\text{jour}^{-1}$  characterize mesotrophic lakes. Evaluation of an area trophic potential depends then on phosphorus concentration in water, and on its sedimentary countenance (Bootsma *et al.*, 1999; Kaiserli *et al.*, 2002).

Although soils contain a high amount of phosphorus reaching over 15 to 150 times the needs of plants (Craaq, 2008), only bioavailable phosphorus is awardable to them and other living organisms. Measuring uniquely total phosphorus stock may not be therefore sufficient to evaluate the rate of phosphorus potentially releasable from sediments. All phosphorus forms are not able to be subjected to releasing (Ruban *et al.*, 1996), and it appears important to know which part of the stock may be remobilizable. The measure of different phosphorus fractions in sediment allows to understanding better the mobilizable phosphates, and then those equitable by algae (Rydin, 2000). An exceeded amount of bioavailable phosphorus in surface waters favors growth of aquatic vegetation such as phytoplankton and algae (Achat, 2009). This fact is bound to an increased alteration of watershed quality as well as a rapid modification in the fauna habitat.

Preliminary studies on the lagoon Porto-Novo, notably those conducted by Chitou *et al.*, (2011), revealed that this lagoon stirs a high amount of phosphorus. Akogbéto (2012) evaluated up to 3536 mg/L PT the phosphorus average rate present in the sediments and water column respectively, rendering the environment eutrophic. But those investigations lacked in identifying the different phosphorus fractions responsible of that augmentation as well as their bioavailability and on the other hand, the phosphorus release capacity in the water column which knowledge should ease establishment of any prevention actions.

Well, in these kinds of hydrosystems, important interactions between sediments and water column exist and lead to a phosphorus release. These interactions are influenced by many factors such as water pH, organic matter mineralization, etc. Oxygen presence and anoxia at the interface water-sediment for example modifies this release unidirectional water-sediment or sediment-water (Wetzel, 2001, Mortimer, 1941, Böstrom *et al.*, 1988). That phosphorus release can be sometimes largely over external supplies (Sondergaard *et al.*, 2003, Ryding and Burnberg, 1998) and cause a sudden increase of phosphorus rate, and as consequence the fish death.

This study enters the same logics insight to evaluate the release rate of phosphorus arising from lagoon sediments, and further to investigate this nutrient faction availability taking into account spatial and temporal variations in order to allow local authorities towards their consideration during any setting of eventual strategies on eutrophication reduction and on that lagoon restoration. Moreover, results from these studies shall broaden our knowledge with relevance to other or similar hydrosystems more or less connected with one another both at the national and sub-regional scales regarding the environmental phenomenon of interest.

## **Materials and Methods**

### **Study Sites**

With an area of 35 km<sup>2</sup>, Porto-Novo lagoon is located in South-eastern Benin between 6° 25 and 6°30 N, and the meridians 2°30 and 2°38 E. On the one hand it is joined in the Northern part to the Ouémé river via a multitude of branches, from where it receives suit water and alleviated supplies in swelling water period, and on the other hand, the lagoon is connected to lake Nokoué in South-western through Totché channel and in the far Eastern

via Atlantic ocean in Lagos where it receives saline water in dry season (Figure 1). Porto-Novo lagoon undergoes influence of subequatorial climate with warm and wet characteristics of Southern Benin, with rainfall following two rainy seasons, a long (April-July) and a short (October-November) separated by two dry seasons from December-March and August-September (Adam and Boko, 1993). The lagoon investigated possesses a low depth preventing an installation of a veritable thermal stratification. Sediment and nutrient supply arises from the slope basin erosion and many anthropoid activities which elucidate the choice of the station S1 situated on the link rive at the village Djassin and more influenced by the above mentioned factors. In contrast, station S2 is located on the right rive in the village Wedji and less affected by watershed erosion. S2 was chosen for comparisons. Two other stations were also retained, Donoukpa (S3) on the right rive, and Tchakou (S4) on the link one to analyze the effects of Ouémé River (tributary of the lagoon) and the parameter behavior at the outflow to Nigeria. Table 1 shows characteristics of this studying and survey points.

The sampling survey was carried out in two steps; the first following the four seasons in the year (GSP=long rainy season; PSS=short dry season; PSP= short rainy season; GSS=long dry season) and at 10 cm depth to assess phosphorus release rate; and the second step consisted in taking probes at 5 cm depth to estimate the nutrient bioavailability.

### **Probe Sampling and analysis methods**

#### **Water column**

pH, potential redox (rH), temperature, Electrical conductivity (EC), Dissolved Oxygen (DO), organic and mineral matter in

suspension (MES), transparency, TDS, depth and PT are physicochemical parameters associated to water column. Measurements of these parameters (rH, temperature, EC, pH, DO, TDS, etc.) were carried out in situ in the morning between 8 am and 10 am. A WTW 3110 SET 1 portable pH-meter was used to measure pH and rH with an accuracy of  $\pm 0.01$ . A Hach DR 800 colorimeter was used to measure turbidity and MES. Dissolved oxygen concentration was recorded with WTW TetraCon 325 Oximeter. WTW Cond 3210 was useful for measuring EC, TDS and temperature with accuracy of  $\pm 0.1$ . A Secchi disc was necessary to measure the transparency and depth of the water.

Water chemical parameters such as PT were determined in the Laboratory and assayed by a Hach 2800 spectrophotometer according to AFNOR NFT 90-023. Chlorophyll a content was measured according to AFNOR NFT 90-117 norm (1984).

Water taken at a depth of about 20 cm was stored in a 1.5L bottle after carefully washing and rinsing it many times and washing it by the end with the water to be collected. These bottles were stored in a cooler and immediately conveyed to laboratory for chemical analysis. Two bottles were filled by station; the second being packed in black bag for determination of chlorophyll a content.

### **Sediments**

Sediments were sampled in the same stations as previously for the physico-chemical profiles. A graduated cylindrical dispositive of 6 cm diameter, opened at the base and finely perforated at the second base, installed at mid-height of the cylinder, was plunged into the lagoon depths for a sequential probing. Sediment was registered in a black bag and maintained fresh in a cooler until expedition to laboratory where chemical

parameters were determined. Analyses were performed on sieved sediments at 250  $\mu\text{m}$ . Sediments were lyophilized using apparatus EYELA FDU-2110 at 3.5 Pa pressure and 25.5°C for 28 hours.

The first five cm layer stratum was used to fulfill phosphorus fractionation. This depth was chosen after preliminary analysis on three successive strata of five cm layer which informed that the phosphorus concentration drops according to depth. However, a stratum consisting in the 10 first cm was retained to estimate phosphorus release rate.

pH (KCl), organic matter content, alkalinity, exchangeable bases, cation exchange capacity (CEC), total phosphorus (PT) and its fractionation (labile P, Fe-P, Ca-P, Al-P, Org-P) were physico-chemical parameters analyzed in investigated sediments :

NF X31-103 norm was used for sediment pH determination;

Organic matter content was obtained by calcinations at 550°C following AFNOR X31-102 (AFNOR, 1994) norm. Total organic carbon (COT) was then determines applying this norm.

Alkalinity was determined as carbonate percent reported to the sediment weight using the followed formula:

$$\%CO_3^{2-} = \frac{(20 - X) \times 0.001 \times 60 \times 100}{100 \times 2 \times m}$$

With m=sediment weight, and X=NaOH volume by equivalence (mL).

PT content estimation and its fractionation were achieved following similar methodology as in the water column using a spectrophotometer model Hach 2800 according to AFNOR NFT 90 – 023 norms.

Different forms of phosphorus were extracted using 5 g dry sediment according to the protocol proposed by Hieltjes and Lijklema (1980) and Psenner (1984), modified by Rydin and Welch (1998). This methodology allowed the separation of labile phosphorus with  $\text{NH}_4\text{Cl}$  at pH 7, Fe-P using  $\text{Na}_2\text{S}_2\text{O}_4/\text{NaHCO}_3$ , while Ca-P was extracted in HCl. Al-P and Org-P were separated in basic (NaOH) medium for 16 hours extract digestion in the presence of potassium persulfate in acid solution, following the protocol of Gachter and Meyer (1992).

This extraction methodology is summarized in Figure 2 as presented below:

To study the short term scavenged phosphorus mobility in sediments, pH effect on phosphorus remobilization in oxic conditions was retained as criteria. To that end, bioavailable phosphorus will be determined after pH variation of the sediment percolation solution around the average pH, e.g. at pH 5.7 and 9. This study was conducted on another probe.

Other sequenced sediment probes were used for particle size analysis undertaken at the Laboratory of Geology, Mines and Environment (GME), University Abomey-Calavi.

Isovalue map was established using 3D Analyst of the ArcGIS (version 10.2) software allowing extrapolation of depth between points of given and known depth.

Determination of isovalue curves was possible through small equidistance (scale of 1 m). Using the module ARCPY of the Spatial Analyst package of ArcToolbox, MNT file corrected by grid executable extension was applied to generate curves (isobaths) at different equidistance. Algorithm

functioning under PYTHON language served as fundament for experimentations.

### **Estimation of phosphorus release rate**

Release rate ( $\text{mg}\times\text{m}^{-2}\times\text{jour}^{-1}$ ) was calculated by the means of regression equations established on the basis of Nürnberg regression equations (Nürnberg, 1988, 1996).

### **Limiting conditions for the application of Nürnberg methodology**

Morphological characteristics: low mean depth proving the non-taking into account of oxygen profiles,

Oxycycline and thermocline are by the same depth,

Anoxic duration corresponds to the night duration [12 h in tropical areas according to Tailling (1957)],

Epilimnetic summery PT corresponds to that at the long dry season.

### **Statistical analysis**

Data collected in the four stations retained for phosphorus load evaluation were compared among them and between the four annual seasons applying a one-way variance analysis (ANOVA1) for each parameter. Dunnett multiple range method applied to that one-way ANOVA permitted comparing pH means. All those analyses were achieved by MINITAB (2014) and JMP (SAS Institute, 2007) software.

Pearson correlation coefficient (r) and its significance were also estimated to verify existing relationship among parameters investigated, and to conclude on their interrelationships with respect to the environmental state of the lagoon.

## Results and Discussion

### Water column physico-chemical parameters

Results on physico-chemical parameters of the water column are represented in Table 2.

Waters of the lagoon Porto-Novo are relatively less oxygenized. Water OD concentration shows a variation with relevance to season and station considered.

Site S1 registers highest average value ( $2.00\pm 0.53$  mg/L), while S4 presents the lower value ( $1.24\pm 0.38$  mg/L).

GSS shows the most oxygenized waters with a mean corresponding to  $2.30\pm 0.43$  mg/L followed by GSP, PSS and with  $2.28\pm 0.5$  mg/L,  $1.20\pm 0.26$  mg/L and finally  $0.90\pm 0.20$  mg/L, respectively.

TDSs present the most elevated values for GSS and GSP with  $2580.00\pm 711.00$  mg/L and  $1444.8\pm 355.75$  mg/L, respectively for a value around 120 mg/L in PSS and PSP. Site S3 registers the highest value ( $1389\pm 845$  mg/L) and S4 the lowest ( $773\pm 529$  mg/L).

Chlorophyll a has a relatively high mean value ( $4.99\pm 0.83$ ). It stands at  $5.54\pm 1.76$  and  $5.15\pm 1.98$ , respectively in PSS and PSP, whereas a value of  $4.40\pm 1.78$ , the lowest during GSS. Site S2 shows the highest chlorophyll a content being  $6.06\pm 1.53$ . The lowest rate ( $3.70\pm 1.65$ ) is measured in Site S3.

Turbidity shows the highest value ( $61.25\pm 9.68$  mg/L) in PSP, and the lowest ( $4.50\pm 0.95$  mg/L) in GSS whereas PSS and GSP register  $10.75\pm 2.32$  mg/L and  $15.75\pm 1.97$  mg/L, respectively. S3 offers the highest mean value ( $30.25\pm 19.12$  mg/L) followed by sites S2, S4 and S5 with mean

values corresponding to  $21.75\pm 14.63$  mg/L,  $20.75\pm 9.68$  mg/L and  $19.50\pm 8.72$  mg/L, respectively.

Waters of lagoon Porto-Novo are more transparent in PSP and GSS with average values of  $128.50\pm 35.06$  cm and  $127.25\pm 33.80$  cm, respectively. PSS is the less transparent with a mean transparency equalling to  $72.25\pm 12.96$  cm. In S2 and S3, the highest transparencies were recorded with values corresponding to  $126.75\pm 33.75$  cm and  $112.50\pm 42.78$  cm. S1 presents the lowest transparency ( $80.75\pm 5.50$  cm).

Values recorded for temperature show certain homogeneity from a season to another. Highest values are registered during GSS and PSP, with respectively  $32.82\pm 0.20^\circ\text{C}$  and  $30.60\pm 0.48^\circ\text{C}$ . Lowest values are obtained in GSP and PSS oscillating around  $27^\circ\text{C}$ . No significant variation is observed from a site to another.

rH is highest ( $24.78\pm 5.38$  mV) in PSS, and lowest ( $0.58\pm 4.77$  mV) in PSP. These values are indicating oxic conditions at the sediment surface in the whole sites by these periods. During GSS and GSP, anoxic conditions are observed with values of  $15.78\pm 4.80$  mV and  $-11.95\pm 6.06$  mV, respectively. Station S3 registers the highest mean value ( $-11.78\pm 10.50$  mV), while S4 delivers the lowest ( $0.33\pm 6.90$  mV).

GSS registers highest average value for water PT ( $5.03\pm 0.40$  mg/L) followed in PSS and PSP with average mean of  $2.14\pm 0.44$  and  $1.86\pm 0.48$  mg/L. The lowest concentration ( $0.97\pm 0.34$ ) is dosed in GSP, and seems corresponding to dilution effect due to rainy water. The highest value ( $3.01\pm 0.48$  mg/L) has been recorded in site S1 witnessing a continental origin for this nutrient. All other stations present PT content comprised between  $2.77\pm 1.00$  and  $2.07\pm 0.84$  mg/L.

## **Sediment physico-chemical characteristics**

### **Sediments**

Hydromorphic soils mildly organic, humic with gley, not or little saline and undifferentiated, located on lagoon alluvial and alluvio-colluvial fluvial material, are observed in lagoon Porto-Novo (Alassane, 2004). These are extremely heterogenic soils having as common character the presence of a permanent water sheet at low depth which provokes the formation of an organic matter horizon badly or very little decomposed.

In average, soil texture is organic more or less rich in silt by their surface, and sandy-loam at depth. In some stations, texture is clearly loamy. Results out of particle size surveys are presented in Table 3.

### **pH (KCl) and pH (eau)**

Figure 3 is showing that water pH and sediment pH (KCl) are acid and relatively low from a season to another. From  $6.41 \pm 0.07$  in PSS, pH increases to  $6.96 \pm 0.08$  and  $6.91 \pm 0.10$ , respectively in GSS and GSP. Station S3 presents the highest pH ( $6.91 \pm 0.17$ ) and the lowest is observed in S1 ( $6.63 \pm 0.14$ ). pH (KCl) mean value is  $6.61 \pm 0.24$ . S3 and S4 present respectively  $7.09 \pm 0.51$  and  $6.92 \pm 0.58$  as pH (KCl). The lowest value is registered at site S2 ( $5.57 \pm 0.25$ ). pH(water) and sediment pH(KCl) mean value comparison by Dunnett method applied to one-way ANOVA (factor station) showed that mean values considered by pair are not significantly different from pH(water) and pH(KCl)=7 (water pH in S3=7.21 during GSS, and sediment pH(KCl) in S3 equals 8.10 at GSP) by 95% confidence, given that variance comparisons revealed always negative values (absolute value of variance difference-LSD) whatever the station of interest ( $p > 0.05$ ).

## **Alkalinity and organic matters**

Figure 4 is presenting temporal variation of carbonates, organic matter and total carbon content from a season to another.

Carbonates rate at S1 is the lowest ( $1.02 \pm 0.11\%$ ) while S4 shows the highest value ( $11.90 \pm 1.60\%$ ). PSP registers the lowest content in all seasons ( $2.98 \pm 1.42\%$ ). It varies between ( $4.80 \pm 3.26$ ) and ( $4.48 \pm 2.92\%$ ) for GSP, GSS and PSS. MO shows a mean value of  $8.56 \pm 2.33$ . S4 is the site with highest MO concentration ( $23.83 \pm 1.46\%$ ). Low values ( $2.98 \pm 0.51$  and  $2.19 \pm 0.45$ ) are recorded respectively in S3 and S1. GSP and PSP indicate highest MO showing a variation ranging from  $9.18 \pm 4.74$  to  $9.22 \pm 6.27$ . GSS and PSS register  $7.83 \pm 5.03$  and  $7.67 \pm 5.05\%$  MO, respectively.

COT content ranges from  $3.80 \pm 1.54\%$  to  $3.06 \pm 1.53$  in different seasons. It varies from  $9.52 \pm 0.63\%$  (maximal concentration) in S4 in contrast to S1 with the lowest COT ( $0.87 \pm 0.18$ )

### **Phosphorus composition and its fractionation**

According to Figure 5, dry sediment PT launches a mean value of  $1561 \pm 261 \mu\text{g/g}$ . It corresponds to  $1983 \pm 973 \mu\text{g/g}$  (S4) and  $1264 \pm 466 \mu\text{g/g}$  (S3). PT oscillates between  $1659 \pm 614 \mu\text{g/g}$  and  $1337 \pm 307 \mu\text{g/g}$  in S1 and S2. Mean PT concentration registers the highest value during GSS with  $2783.3 \pm 742.7 \mu\text{g/g}$  followed by values in PSP ( $1970.3 \pm 241.05 \mu\text{g/g}$ ). Lowest PT concentrations ( $445.3 \pm 12.05 \mu\text{g/g}$ ) are noted during PSS.

Total phosphorus stock evaluation remains a very good approach for a better understanding of sediment contamination degree and extent. But generally, such evaluation opens doors to

little information on mobility of the concerned element in the sediments. Fractioning allows then to highlight the different forms presented by phosphorus in sediments arisen from the sampling points. Among those forms, dissolved labile mineral phosphorus ( $\text{PO}_4^{3-}$ ) in interstitial waters is directly equitable by algae. Fraction bound to iron (P-Fe) represents the most available fraction.

Figures 6-9 illustrate spatial repartition of the different phosphorus forms observed: labile form, P-Fe, P-Ca, P-Al and P-Org accompanied by P-resid.

At S1, P-Org and P-Ca represent the main fractions with  $810.80 \pm 151.25 \mu\text{g/g}$  and  $103.15 \pm 42.77$  equalling to 54.41% and 6.92% PT, respectively. This rate is 55.62% and 1.63% in S2, 66.36% and 1.83% at S3, and 55.13%, 5.90% at S4.

P-labile is the less represented fraction ranging from  $14.75 \pm 2.70 \mu\text{g/g}$  (corresponding to 0.98% PT) at S1 to 0.75%, 0.44% and 2.07% for S2, S3 and S4, respectively. Remaining fractions, P-Al and P-Fe are 3.44 and 1.44% in S1, while they are represented by 1.43, 0.68, 0.88, 0.36, 2.24 and 0.72% at S2, S3 and S4, respectively.

Highest P-Org concentration is observed in GSS across February, and corresponds to  $2035.40 \pm 311.20 \mu\text{g/g}$ , whereas the lowest is noted for PSS in September. In the later season, P-Al is rather more concentrated in sediments ( $48.73 \pm 10.95 \mu\text{g/g}$ ). P-Al is lower during GSS ( $17.95 \pm 9.24 \mu\text{g/g}$ ). Similar variations are observed for all other phosphorus fractions. Thus, P-Fe and P-labile represent  $17.23 \pm 10.45 \mu\text{g/g}$  and  $40.89 \pm 2.50 \mu\text{g/g}$  in GSS, respectively. Their lower values are  $11.41 \pm 1.02 \mu\text{g/g}$  and  $8.92 \pm 0.69 \mu\text{g/g}$ , respectively during PSS and GSP. Sediment P-Ca maximal content is around

$132.55 \pm 40.60 \mu\text{g/g}$  in PSP and  $2.56 \pm 1.30 \mu\text{g/g}$  - the lowest value - during GSS.

Residual organic phosphate (P-resid) in the lagoon Porto-Novo is higher during GSS ( $1299.20 \pm 275.20 \mu\text{g/g}$ ) and lower ( $274.4 \pm 274.4 \mu\text{g/g}$ ) in PSS. The highest P-resid mean is recorded in S3 ( $758.10 \pm 273.25 \mu\text{g/g}$ ), while its value is the lowest in S1 ( $489.70 \pm 145.10 \mu\text{g/g}$ ). S2 and S4 show  $603.9 \pm 442.20 \mu\text{g/g}$  and  $625.00 \pm 306.80 \mu\text{g/g}$  P-resid, respectively.

$\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  concentrations as well as cationic exchange capacity are obtained at GSS (February) and within the four sampling sites under investigation (Table 4).

Highest values for those ions are noted from sediments of S1 followed by S3 and S4. The lowest values are observed at site S2. That increase of ion concentration at S1 can be explained by the high pollution recorded at this station. Hence, S1 is where many economical activities run, but also it receives waters arising from Zounvi, the main channel to drain off wastewaters from the town Porto-Novo (Table 4).

Cationic exchange capacity (CEC) represents the maximal amount of ions able to be exchanged on a solid in presence of an ion excess in solution. It varies among 14 meq/100g (S3) during PSP and 32 meq/100g (S1) at the same season with a mean value corresponding to 24.25 meq/100g the most elevated at site S1 (Table 4).

### **Short-term mobility of phosphorus in sediments**

Phosphorus release by sediments is affected by external factors such as dissolved oxygen content, pH in water column as well as climatic factors including water column stirring through the wind (Reddy *et al.*, 2008).



**Table.1** Survey site geographical coordinates

Sites	Codes	Coordinates	Reasons on the Choice
Djassin	S1	06° 28' 14.2'' 002°36'0.16''	Household muck discharge, mechanically water hyacinth destruction, good and sand traffics by humans.
Wedji	S2	06° 27' 42.6'' 002°34'39.0''	concentration zone of 'acadjas' (Fishing technique)
Donoukpa	S3	06° 28' 15.3'' 002°35'02.0''	Entry of Ouémé river, tributary of that lagoon
Tchakou	S4	06° 27' 34.6'' 002°42'62.9''	Exit of the lagoon.

**Table.2** Mean and standard deviation of physico-chemical parameters in relation to seasons

Parameters	GSP	PSS	PSP	GSS	Min	max	Moy
Temp	27.10±0.16	27.62 ±0.07	30.60±0.48	32.82±0.20	33.10	26.90	29.53±0.61
OD	2.28±0.5	1.20±0.26	0.90±0.20	2.30±0.43	3.54	0.53	1.67±0.23
TDS	1444.8±355.75	120.7±14.05	120.00±10.00	2580.00±711.00	3660	93.5	1066.00±319.00
Turb	15.75±1.97	10.75±2.32	61.25±9.68	4.50±0.95	87.00	2.00	23.06±6.22
Predox	-11.95±6.06	24.78±5.38	0.58±4.77	-15.78±4.80	39.80	-30.10	-0.59±4.72
Transp	78.00±5.83	72.25±12.96	128.50±35.06	127.25±33.80	230.00	38.00	101.5±13.2
Chl a	4.88±1.84	5.54±1.76	5.15±1.98	4.40±1.78	9.52	1.22	4.99±0.83

**Table.3** Particle size composition and substratum nature at different sites in lagoon Porto-Novo

STATIONS	CODES	COULOUR	PARTICLE SIZE		CLASSIFICATION (according to Intès et Loeuff-1986)
			(%) S	(%) A+L	
Djassin	S <sub>1</sub> A	Black	63.18	35.68	Sandy-loamy
	S <sub>1</sub> B	Greyish	73.94	25.16	Sandy-loamy
	S <sub>1</sub> C	Greyish	74.00	25.24	Sandy-loamy
Wedji	S <sub>2</sub> A	Greyish	21.37	78.29	Loamy-sandy
	S <sub>2</sub> B	Greyish	46.95	52.29	Loamy-sandy
	S <sub>2</sub> C	Grey	45.43	64.18	Loamy-sandy
Donoukpa	S <sub>3</sub> A	Black	30.66	69.10	Loamy-sandy
	S <sub>3</sub> B	Grey	23.83	75.15	Loamy-sandy
	S <sub>3</sub> C	Grey	50.29	48.53	Sandy-loamy
Tchakou	S <sub>4</sub> A	Greyish	18.84	80.62	Silty
	S <sub>4</sub> B	Greyish	25.17	74.22	Loamy-sandy
	S <sub>4</sub> C	Greyish	47.71	51.26	Loamy-sandy

Legend: S = sand: elements with diameter among 63 µm and 02 mm; A = loam: elements with diameter inferior to 4 µm ; L = silt: elements with diameter among 63µm and 4µm.

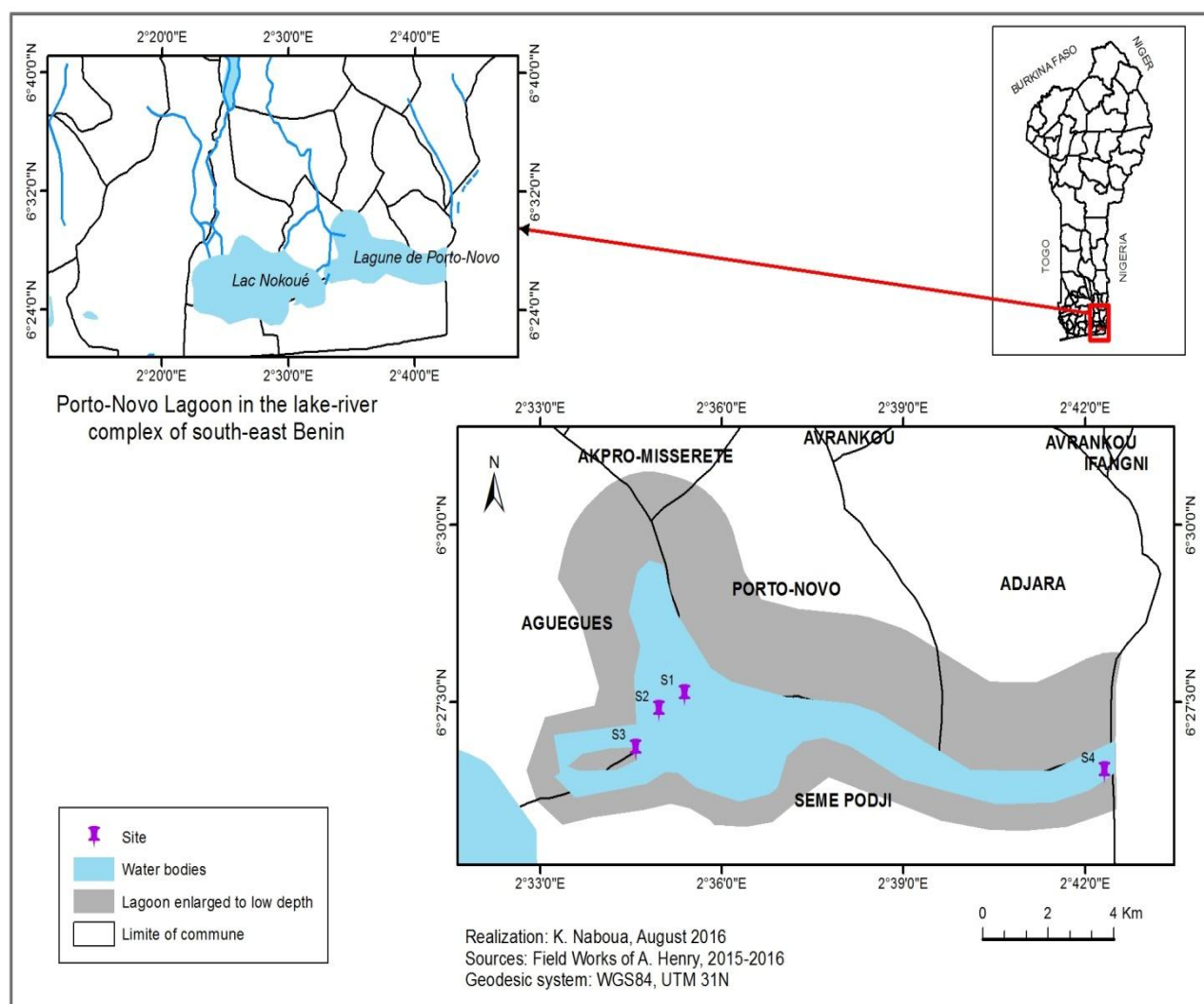
**Table.4** Evolution of exchangeable cations and CEC means at four sites investigated in the lagoon Porto-Novo

SITES	Ca <sup>2+</sup> (meq/100g)	K <sup>+</sup> (meq/100g)	Mg <sup>2+</sup> (meq/100g)	Na <sup>+</sup> (meq/100g)	CEC (meq/100g)
S1	6.85	0.32	6.95	1.95	24.25
S2	2.7	0.13	2.47	0.45	20.25
S3	3.32	0.19	3.65	0.75	19.5
S4	3.72	0.21	4.92	1.8	16.5

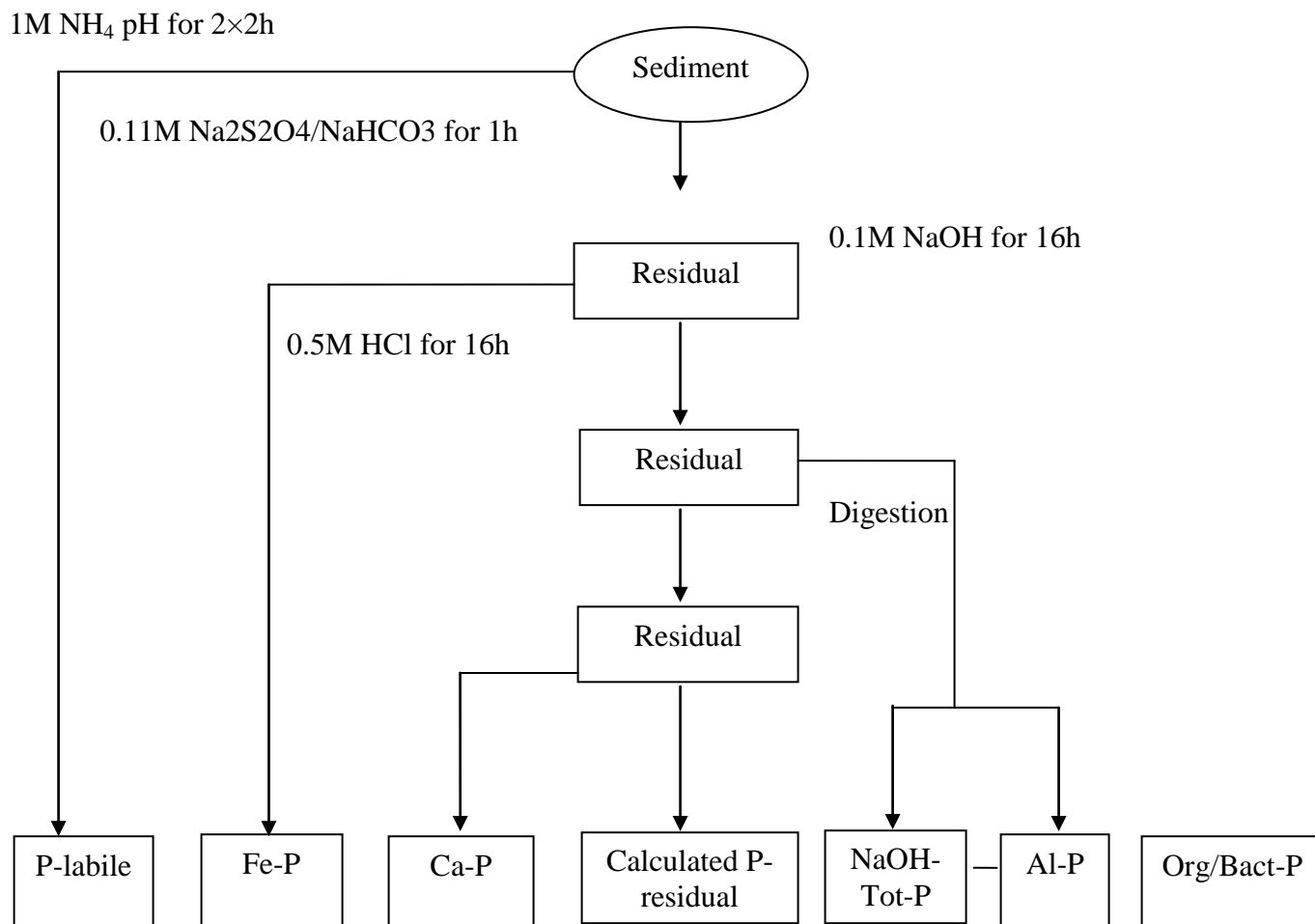
**Table.5** Correlation coefficients between some parameters with p-values

	P- Org	PTSed	MO	Chl a	Transp		P- Org	PTSed	MO	Chl a	Transp
<b>During GSS</b>	P- Org	1				<b>During PSS</b>	P- Org	1			
	PTSed	-	1				PTSed	0.845	1		
		0.068						0.155			
		0.932									
	MO	0.414	0.855	1			MO	-	-0.489	1	
		0.586	0.145					0.731	0.511		
								0.269			
	Chl a	0.089	0.380	0.574	1		Chl a	-	-0.090	0.725	1
		0.911	0.620	0.426				0.603	0.910	0.275	
								0.397			
Transp	-	-0.578	-	0.522	1	Transp	-	0.145	0.779	0.853	1
	0.015	0.422	0.346	0.478			0.299	0.855	0.221	0.147	
	0.985		0.654				0.701				

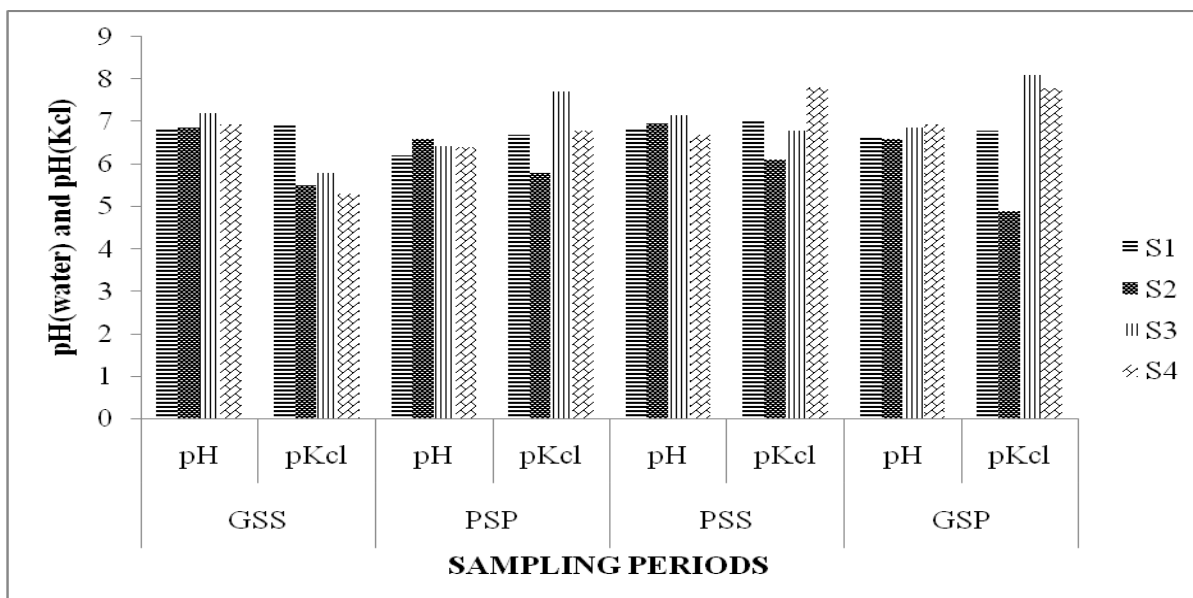
**Fig.1** Localization of lagoon Porto-Novo in the lagoon complex of South-eastern Benin



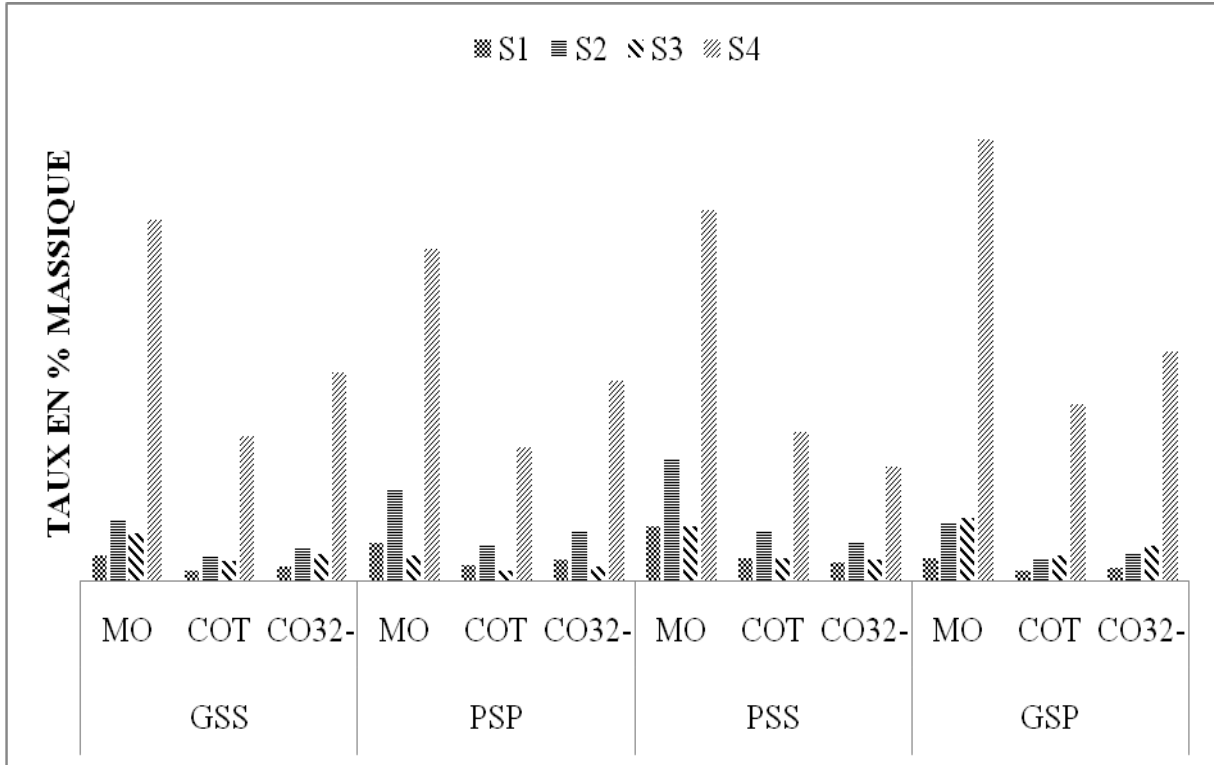
**Fig.2** Sequential extraction scheme of phosphorus according to Rydin and Welch (1998)



**Fig.3** Variation of sediment pH (water) and pH (KCl) reported to seasons and sampling sites



**Fig.4** Evolution of carbonate and organic matter rate in all seasons in the year



**Fig.5** Evolution of sediment PT at 10 cm depth at the four sites studied in the lagoon Porto-Novo

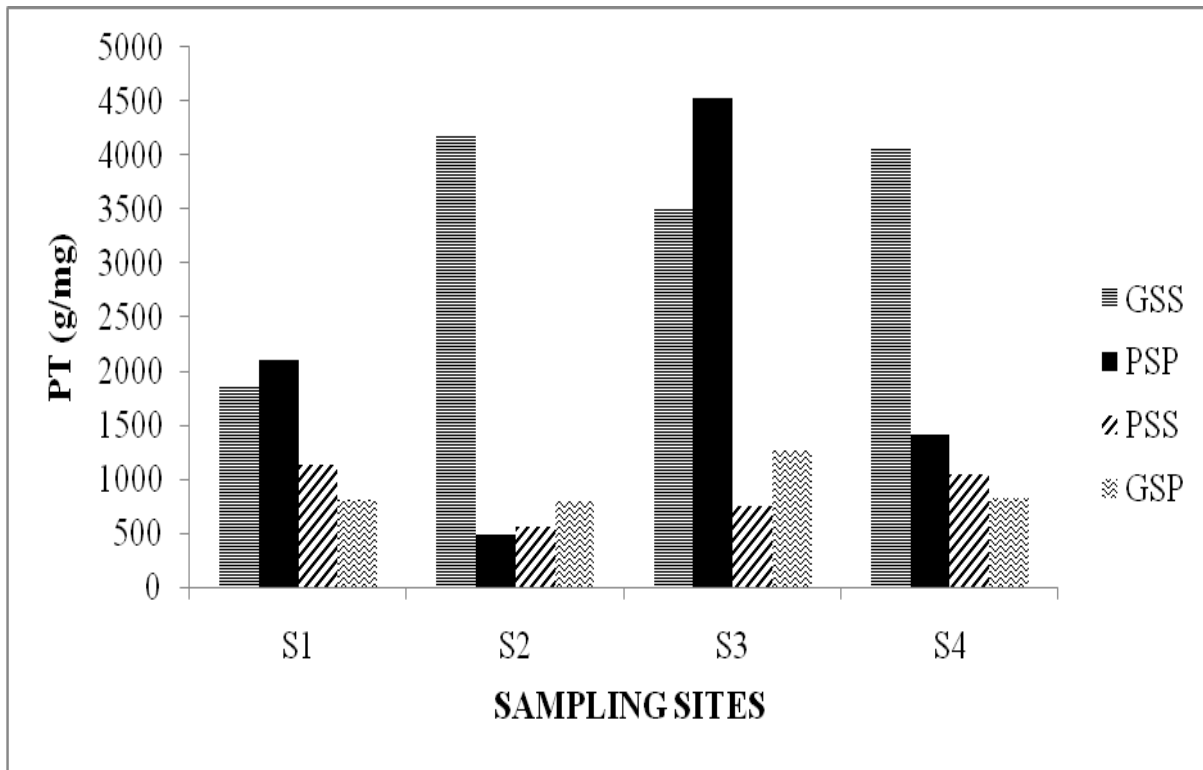


Fig.6 Phosphorus fractionation at site S1

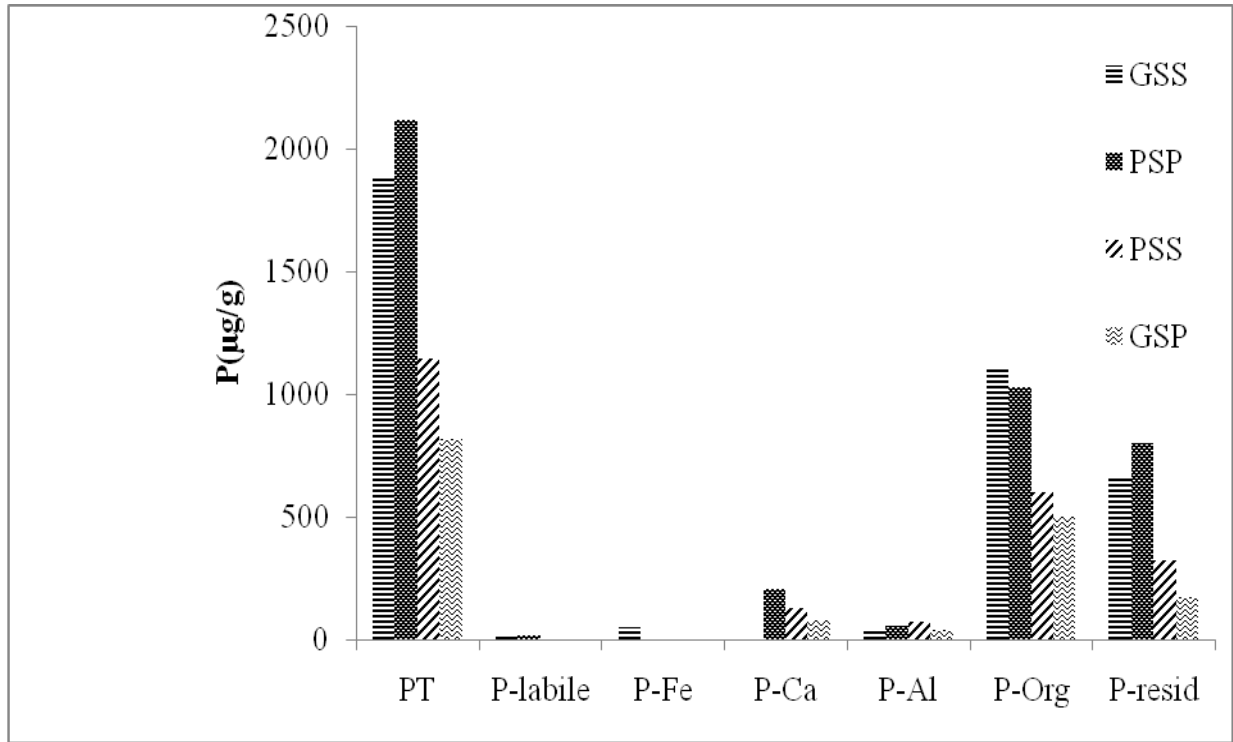


Fig.7 Phosphorus fractionation at site S2

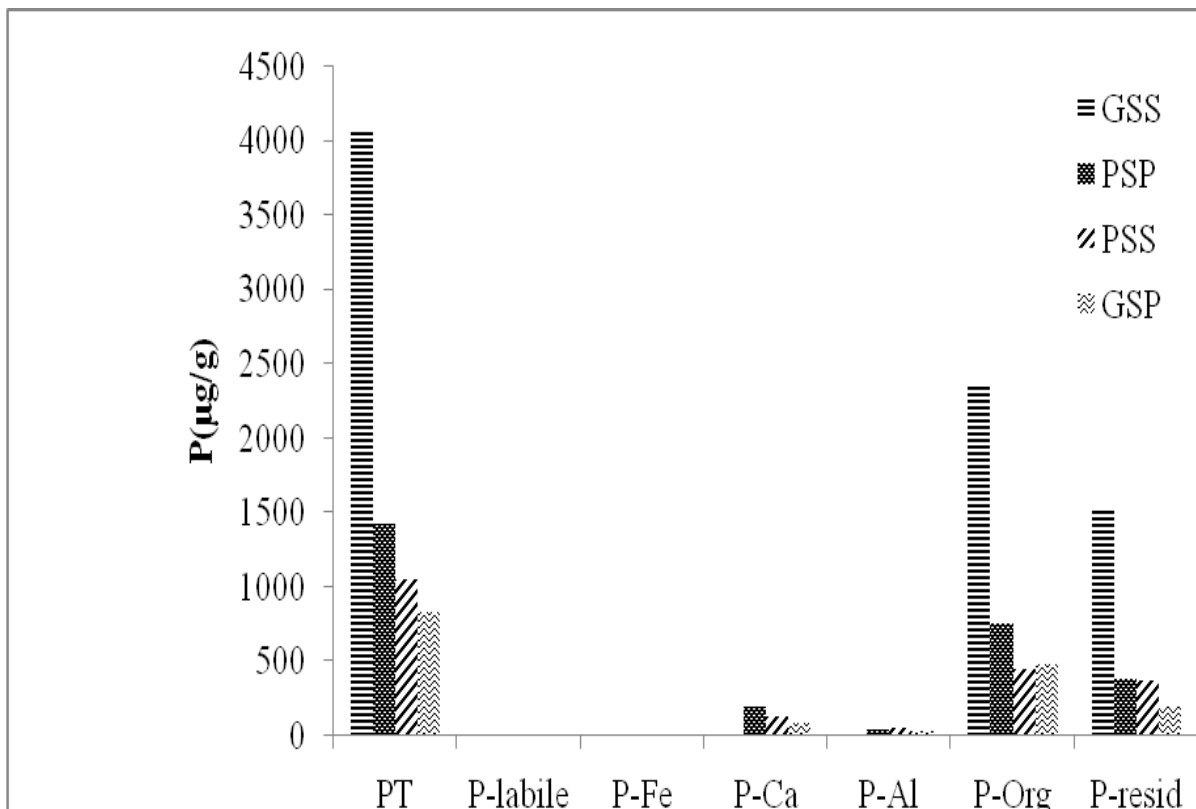


Fig.8 Phosphorus fractionation at site S3

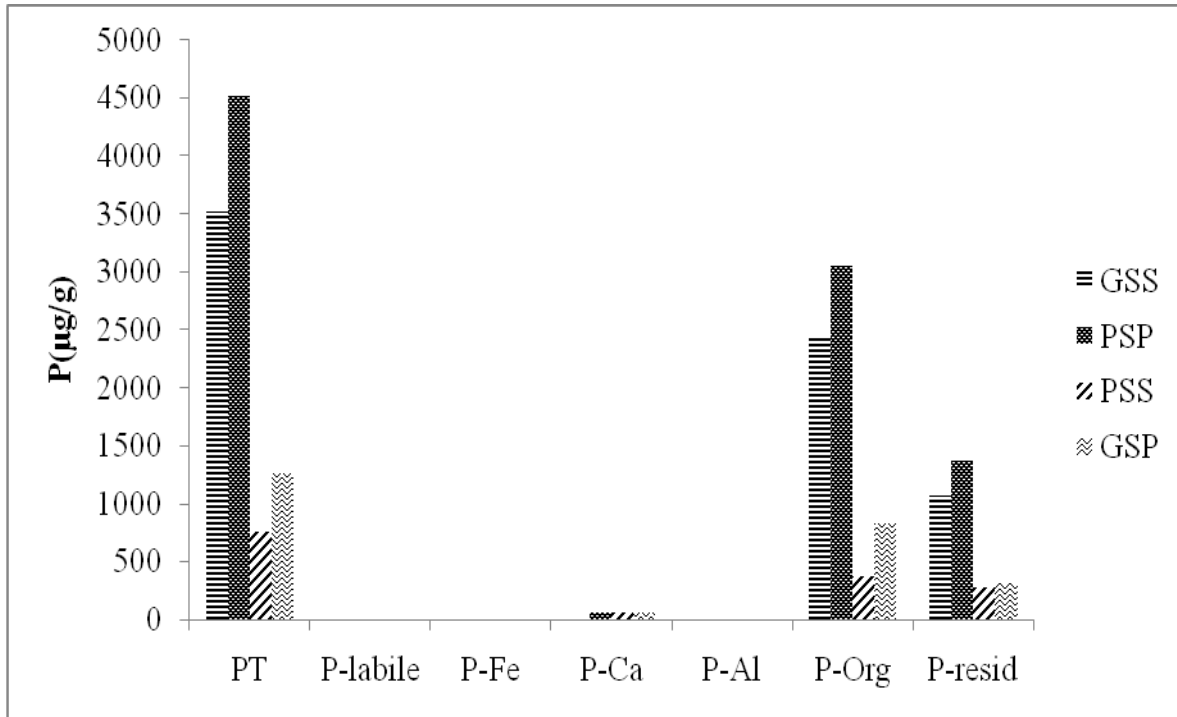
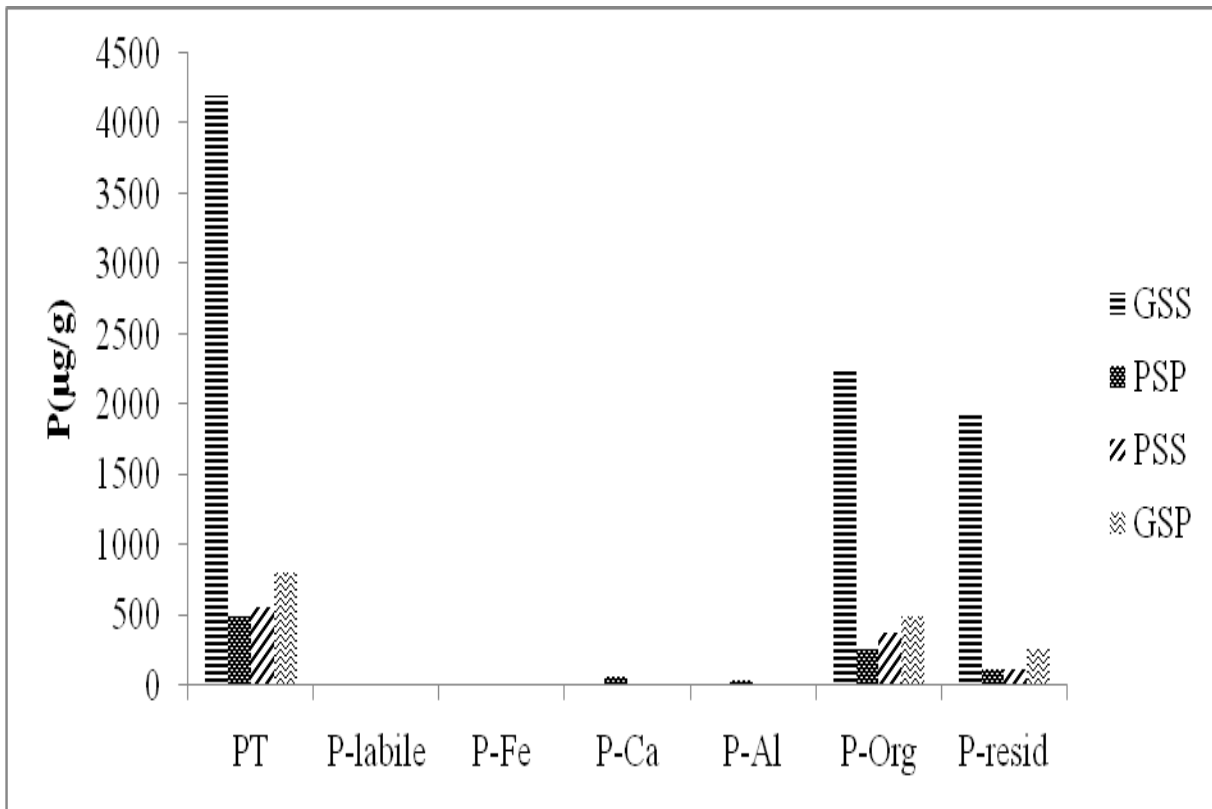
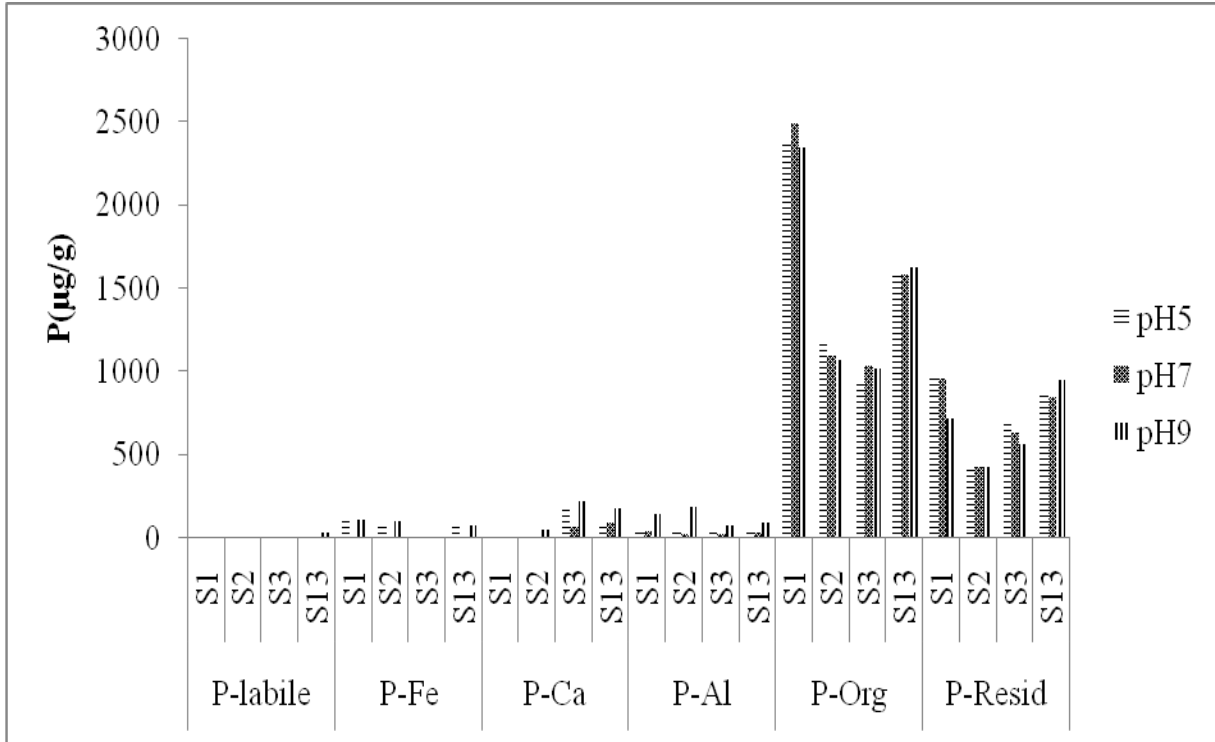


Fig.9 Phosphorus fractionation at site S4



**Fig.10** Variation of phosphorus fraction content at different pH



**Fig.11** PT variation according to TL

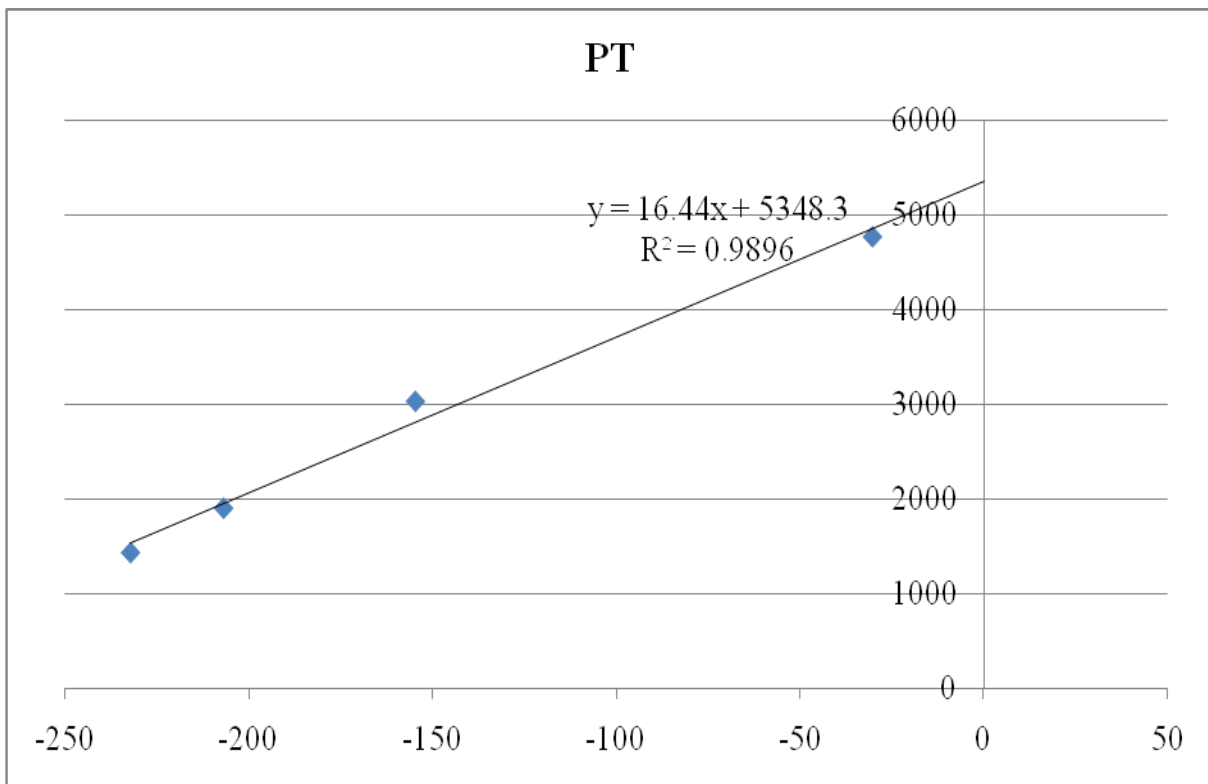
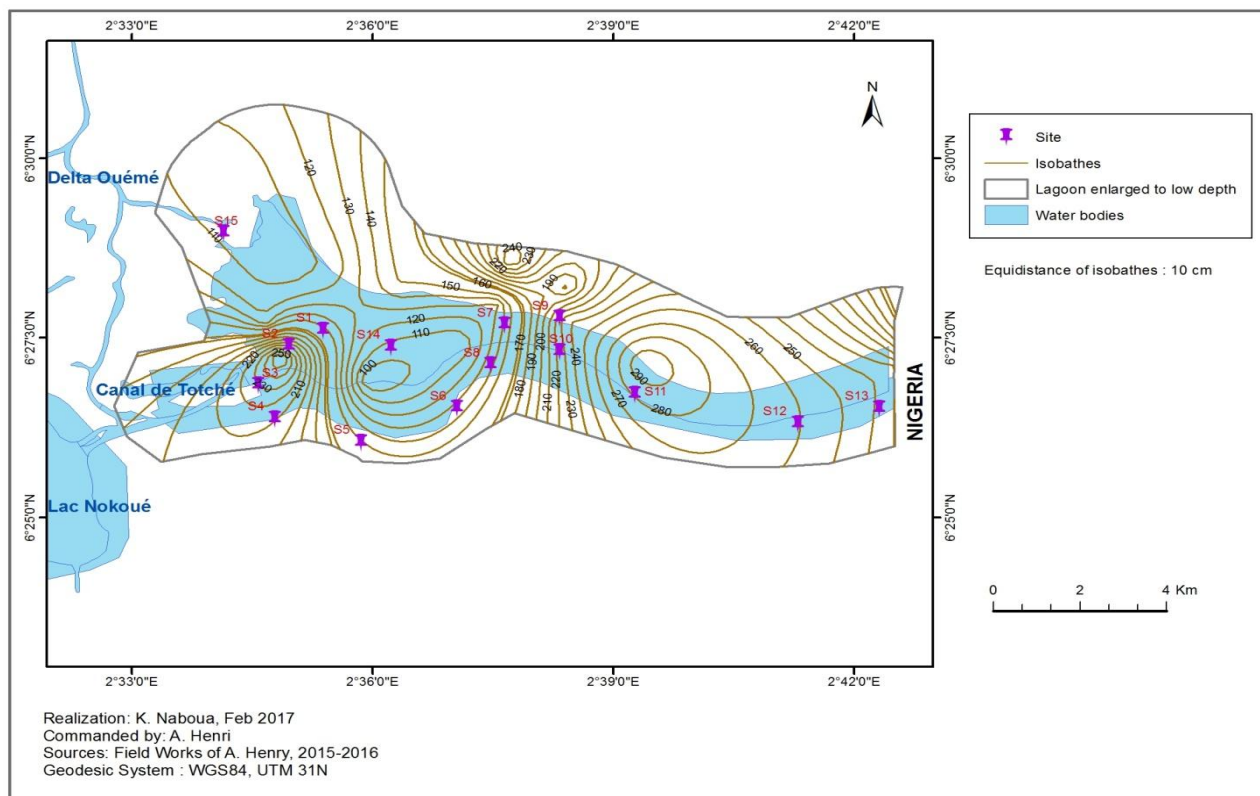


Fig.12 ISO value curves



Water column pH and sediment pH (KCl) in all sampling sites and the whole experimental period present no significant mean compared to 7. pH 7 is used as reference one. pH variation around 5 and 9 under oxic conditions gives some results on phosphorus fractions as shown in Figure 10.

P-labile, P-Fe and P-Al contents at pH 5 and 9 are higher in all sites if compared to the registered values at pH 7 considered as environmental pH by the time of experimentation. P-Ca indicates the same trends apart from site S1 where its concentration at pH 5 and 9 is inferior to that observed at pH 7. With respect to P-Org, concentration at pH 5 and 9 is inferior to that observed at pH 7 at S1 and S3. It is rather higher at S4. P-Org at S2 is higher at pH 5 compared to pH 7 and lower at pH 9 than at pH 7 being the reference.

PH decrease or increase favours so the phosphorus fractionation release.

This is confirmed to the observation of Böstrom *et al.*, (1988) on lake sediment, and these variations of pH should emphasize eutrophication phenomenon.

### Phosphorus release rate

Nürnberg regression equations (Nürnberg, 1988, 1996) are shown as below:

$$TL = 4.78 + 2.75[PT] - 0.177[LOI]$$

At 10 cm depth with TL=Release rate [PT] = sediment PT concentration and LOI=% of organic matter in sediment.

$$FA_{estimated} = -36.2 + 50.1 \times \text{Log} [PT_{epi}] + 0.762 \times Z/Ao^{0.5}, \text{ with } AF = \text{Anoxic Factor.}$$



Z=Mean depth, A<sub>o</sub>=Surface of lagoon, [PT<sub>epi</sub>] = epilimnetic PT concentration.

This equation applied to the lagoon Porto-Novo during GSS produce the graph of Figure 11. Means depths allowed establishment of isobaths curves as presented in Figure 12. Correlation coefficients between sediment organic phosphorus, total phosphorus, organic matter content, water chlorophyll a and transparency allowed us validating the above mentioned Nürnberg equations (Table 5).

Graph presented on Figure 11 shows PT variation according to TL, where AF represents an estimated factor. The regression equation of this variation is the following:

$$Y = 16.44X + 5348.3 \text{ with correlation coefficient } R^2=0.98 \text{ (1)}$$

Y = sediment PT concentration and x= Phosphorus internal load (TLxFA).

This equation becomes:

$$PT=16.44(FA \times TL) + 5348.3 \text{ (2)}$$

$$TL = \frac{-5348.3 + PT}{16.44FA} \text{ ou } TL = \frac{-5348.3}{16.44FA} + \frac{PT}{16.44FA} \text{ (3)}$$

The following estimations derive from those equations:

Release rate (TL): 11.05 mg\*m<sup>-2</sup>\*j<sup>-1</sup>

Phosphorus internal load: 156.03 mg\*m<sup>-2</sup>\*season<sup>-1</sup>

The low average depth of the lagoon Porto-Novo (166 cm) prevents establishment of any thermal stratification as well as conditions for a veritable anoxia. Water residence time (18.04 minutes) is not of nature to present repercussions on its quality. Conversely, PT average mean over the whole study period

and all the sites investigated taken together is showing that PT is highly concentrated in sediments. Apart from GSP, PT concentration in sediments decreases from site S1 to S2 suggesting that external supplies in phosphorus should be linked to soil leaching from slope basin, e.g. from continental origin. Hou *et al.*, (2013) achieved with the same conclusion on Dailai Lakein Northwest China. This observation is justified also by the very high water PT concentration at S1 when compared with all other sites excepted during the GSS (Figure 4). Sediment PT concentration in S4 is relatively high due to hydrodynamic conditions reigning at this level of the lagoon. Hence, S4 is located in an area which profile shows decreasing depth into the exit of the lagoon (Figure 11). High depth allows waters to be more calm increasing thus sedimentation, productivity and organic matter mineralization phenomenon, and sets then a control upon chemical element repartition including phosphorus (Taoufik *et al.*, 2005). Detrital sedimentation takes place upstream S4 in relatively deep zones from alluvial sediments arising from Western sides of the lagoon, notably from Ouémé River. Those sediments are contemporary, well known by sand handlers, who are able to discriminate them from older depots. This detrital sedimentation may be accompanied by that of phosphorus removed in suspension, trained by water flow into new depot downstream. All happen regarding phosphorus as a series of sedimentations and restorations in suspension, provoking nutrient accumulation towards exiting part at S4, witnessed by sediment phosphorus concentration increment in S4 reported to S3.

P-labile fraction is considered as the unique form preferentially and directly equitable by algae (Reynolds, 1984). More than its assimilation by those organisms, P-labile can also be retained by adsorption, complexation

and precipitations reducing its presence in waters (Ormaza Gonzales and Statham, 1991; Stumm and Morgan, 1996). In lagoon Porto-Novo, its rate ranges from 0.44 to 14.75% PT in sediments, very low compared to other phosphorus fractions. Similar observations have been made by Pourriot and Meybeck (1995) stating that such rate is inferior to 1% in sediments. It is lower than 0.005% in lake Naine (Labrecque, 2012).

Phosphorus fraction bound to iron (P-Fe) results from phosphate anion fixation on iron oxides. Adsorption mechanisms and their incidence on surface properties of oxides are well known (Barrow, 1970; Hingston *et al.*, 1974; Parfitt *et al.*, 1975; Wann and Uehara, 1978). Fortin *et al.*, (1993) demonstrated that ferridhydrite and lepidocrocite are the most important iron oxihydroxides in many lakes that make easier phosphate ion adsorption. Goethites are other iron oxihydroxides which adsorption on phosphate ions has raised much attention (Sigg and Stumm, 1980; Stumm *et al.*, 1980; Goldberg and Sposito, 1984; Hawke *et al.*, 1989; Nilsson *et al.*, 1992; Lumsdon and Evans, 1994). These elements arise from ferralitic soils also called 'Terre de barre' of the slope under-basin on which the town Porto-Novo is built (Alassane, 2004). Phosphate adsorption thanks surface properties induced by oxides needs compensating ions such as  $\text{Na}^+$ . According to Hawke *et al.*, (1989), humic substances ( $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ) reduce phosphate ion adsorption on goethite. Sediment richness in silt and its relatively high  $\text{Mg}^{2+}$  concentration (Table 2) may result in the low P-Fe form observed in sediments at stations S2 and S4 rich in silt and loam. P-Fe is the most available phosphorus fraction, sensitive to pH and rH variations (Böstrom, 1984; Skovgaard and Thamdrup, 1993; Kuma *et al.*, 1996). Christophoridis and Fytianos (2006) observed that P-Fe is sensitive to redox potential reduction, and can be released after susjacent

water anoxia. pH variation to 5 and 9 shows that P-Fe is more released at pH 9 than 5 on sediments of the lagoon Porto-Novo. This result can be elucidated by the phosphate ion adsorption capacity on iron oxihydroxide surface. Hence, according to Stumm (1992), stressed by Gomez 1999, whenever iron oxihydroxide surface is exposed to aqueous environment, it is covered by hydroxyl groupings. Fe (III) ions at the surface bind water molecules which dissociate in  $-\text{OH}$  groups amphoters. From there, they can either capture a proton and acquire a positive charge, or lose a proton and become negatively charged. Global charge of iron hydroxide results mainly from proton transfer on the surface, and depends upon therefore pH. Iron atom bound to hydroxyl group can exchange its  $-\text{OH}$  group against  $\text{PO}_4^{3-}$  (Martin and Smart, 1987). pH variations facilitate P-Fe complex release. Basic pH by stabilizing proton transfer may facilitate this release moreover.

Phosphorus fraction bound to Calcium (P-Ca) is the main path of phosphorus storage in sediments (Golterman *et al.*, 1998; Kozerski and Kleeberg, 1998). This fraction has been considered for a long time as non mobilizable. Nowadays, P-Ca, P-Fe as well as P-labile are known as also mobilizable (Taoufik *et al.*, 2005). In sediments of the lagoon Porto-Novo, it may arise from phosphorus atom fixation on  $\text{CaCO}_3$  issued from shell sedimentation of chalk organisms after their death, given that many chalk shell mollusk and crustaceans constitute the main invertebrate fauna in the lagoon Porto-Novo (Adandédjan, 2011). Reports from particle size analysis revealed in the first two stratums an existence of many gastropod and lamellibranches shells. P-Ca is evaluated as 1.63% PT. pH variation on sediments under study shows that the pH drop (around pH 5) leads to the decrease in P-Ca rate in accordance with previous observations made

by Boers (1991), Böstrom *et al.*, (1988), Eckert *et al.*, (1997). Furthermore, pH increase has favorite P-Ca precipitation leading to its augmentation in sediments sampled in the area of study as earlier observed by Dittrich *et al.*, (2000) and Lopez and Morgui (1992) in artificial experiments and a coastal lagoon, respectively.

Phosphorus fraction bound to Aluminium (P-Al) in the lagoon Porto-Novo ranges from  $17.95 \pm 8.24$   $\mu\text{g/g}$  to  $48.73 \pm 10.95$   $\mu\text{g/g}$ . Such low rate (2.19% PT) in sediments is comparable to earlier reports made by Mama in Lake Nokoué (Mama, 2010). P-Al fraction sources from ion phosphate ( $\text{PO}_4^{3-}$ ) fixation on aluminium particles. PH diminution reported to average experimental one or in contrast its augmentation provokes P-Al release in accordance with the work of Tometin (2008).

Phosphorus fixed in organic matter (P-Org) out of the survey in lagoon Porto-Novo reaches proportions ranging from  $452.6 \pm 53.50$   $\mu\text{g/g}$  to  $2035.4 \pm 311.2$   $\mu\text{g/g}$ . P-Org content in organic matter variation from a season to another seems to be related to the complexation of phosphate ions on organic matter and to a hydro-sedimentological phenomenon. Hence, correlation between P-Org and organic matter loaded in sediments contents (Table 3) during dry periods (GSS and PSS) shows relatively high coefficients,  $R=0.414$  ( $p=0$ ) and  $R=0.731$  ( $p=0.269$ ), witnessing certain relationship among P-Org formation and organic matter sedimentation. The high content in this phosphorus fraction compared to others is the consequence on the one hand of organic matter accumulation arising from the slope bowl through diverse anthropoid activities such as agriculture, animal husbanding, etc., and on the other hand the effects of plant and animal organic matters present on the lagoon. Plant biomass contains indeed organic phosphorus essential for their metabolism. Algal cell content in

phosphorus is largely variable while that of bacteria in similar conditions is any case five to ten times richer (Brussaard and Riegman, 1998; Stenzel *et al.*, 2017). According to Lukkari *et al.*, (2007), P-Org availability from its builders hinges upon the size and stability of molecules in opposition to hydrolysis, and besides to degradation processes linked to microbial activities and environmental conditions such as pH. Sediment organic phosphorus is mainly under monoester and di-ester orthophosphate form (Ingall *et al.*, 1990). It is also well known that lake sediments are rich in polyphosphates synthesized and stored as inorganic granules in microbial cells (Hupfer *et al.*, 1995). After cell death, phosphorus is rapidly released by autolysis. Brock and Schulz-Vogt (2011) testing phosphate release to anoxia and high concentration of acetate found out that increasing anoxia resulted in a decomposition of polyphosphate. These authors concluded that such physiological reaction provides a new explanation for high phosphate concentration in marine sediment. These results are enough similar to our observations in Porto-Novo lagoon.

P-resid is considered as very difficult mobilizable from sediments owing to the fact that its extraction needs very energetic treatments (Taoufik *et al.*, 2004), and after Mesnage (1994) and Golterman *et al.*, (1998), this fraction can be mineralized only by intense bacterial activity. Its relatively high rate in sediments meet in the lagoon Porto-Novo is indicating the weakness of bacterial activities inside.

Phosphorus release rate (TL) recorded ( $11,05$   $\text{mg} \cdot \text{m}^{-2} \cdot \text{j}^{-1}$ ) is over the value indicated by Labrecque *et al.*, (2012) in lake Naime ( $4$   $\text{mg} \cdot \text{m}^{-2} \cdot \text{j}^{-1}$ ). Nürnberg and Lazerte (2004) cited by Labrecque *et al.*, (2012) stated that TL values comprised between  $2-7$   $\text{mg} \cdot \text{m}^{-2} \cdot \text{j}^{-1}$  are relevant to mesotrophic lakes. Such a rate is signaling that the lagoon Porto-Novo is in

an eutrophic state during the season considered with an internal loading estimated at  $156,03 \text{ mg}\cdot\text{m}^{-2}\cdot\text{saïson}^{-1}$ . More concretely, phosphorus weight loaded in the lagoon during the dry season and able to be released unidirectional into the water column is in the range of  $5.461.050 \text{ kg}$ , being  $5.461 \text{ tons}$ . An elevated phosphorus load is revealed in this lagoon (resulting probably from many years and seasons sedimentation process) and should be even higher omitting lagoon sand exploitation activities starting by scraping down the first centimeters of the lagoon bottom. Nonetheless, that activity may induce elsewhere phosphorus release into the water column, followed by its sedimentation with the consequence of hardening any evaluation process of phosphorus internal load.

Impact of phosphorus internal loads on the water quality depends on the availability in this mineral element. Study on phosphorus bioavailability showed certain variability of its different existing forms according to environment properties. Zhang *et al.*, (2015) studied impacts of lake water environmental conditions on bioavailable phosphorus of surface sediments. They reported that bioavailable phosphorus fraction of the lake surface sediments (0-5cm depth) under investigation and environmental indicators of the related water column in five lakes in Lixia River basin in China during three seasons, varied significantly in the different seasons. High intensity of bacterial activities combined with that of algae density as well as dissolved oxygen enhanced bioavailable phosphorus rate and contributed significantly to the eutrophication of the lake, especially in summer. In the lagoon Porto-Novo, as described above, the same phenomenon is observed during the dry season (GSS November-December) corresponding at least partly to the summer under temperate climates. Mobilizable phosphate, e.g. available for algal growth (P-labile, P-Fe, P-Ca, P-Org) represents in average about

66.39% PT. This rate is relatively lower compared to the reports of Ruban *et al.*, (1996) in the reserve of Bort-les-Orgues in France, and in the slope basin of Oum Rabiaa (Maroc) rounding 80%. Their observations may be justified by the reigning hydrodynamic conditions. However, it is sufficient to cause symptoms of eutrophication. Water swellings which mobilize sediments can move in suspension nutrients previously fixed (Oraison *et al.*, 2011). Inside stratified lakes, meteorological conditions can lead partly to the interannual variability of phosphorus dynamics in the epilimnion. The non-existence of a veritable thermal stratification within the lagoon Porto-Novo is moreover a parameter that may speed down phosphorus sedimentation in the watershed analyzed.

High phosphorus release may favorite enrichment of the water column in phosphorus, algal biomass augmentation and consequently a reduction of transparency (Labrecque *et al.*, 2012). In the watershed studied, GSS registered lower mean values in chlorophyll a and transparency, contrasting with sediment phosphorus content and its release rate in that period particularly concerning chlorophyll a, while rH is reducer. That situation should be explained by an adaptive reaction among phytoplankton and its biotope rendering the environment reducer.

Phosphorus that accumulates in sediments within the lagoon Porto-Novo arises from two main sources: slope bowl supplies and biological activity happening inside the watershed. It is more accumulated in the first stratum of sediments and under given conditions, it is moved in suspension increasing available phosphorus concentration in water. Consequently, eutrophication of the lagoon is observed. The current study showed that different fractions contribute to the phosphorus loading in this lagoon, and mobilizable phosphorus rate reaches 66.39%

of total phosphorus measured. Among those fractions, P-Org is more abundant, consequence of organic matter accumulation sourcing from the slope bowl through anthropoid activities and moreover from plant and animal organic matters present on the watershed. Phosphorus release rate estimated in dry season is indicating that the lagoon Porto-Novo remains in more or less degraded state needing from local and national stakeholders and other authorities urgent actions insight a reduction of phosphorus, notably that arising from the slope basin.

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