

Eutrophication, sediment Phosphorus fractionation and short-term mobility study in the surface and under profile sediment of a water dam. (Okpara dam, Benin, West Africa).

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ABSTRACT. Okpara dam supplies the drinking water treatment station of Parakou town. Aquatic plants proliferation and chemical stratification of the water column in this reserve let see clear manifestation of eutrophication process. Phosphorus concentration in sediments was estimated in the range of 13.479 mg/g to 35.46 mg/g dry wet of sediment. These values are high and not common in the literature. The measured Phosphorus and a-chlorophyll values in the water column show hyper-eutrophication. From N/P ratio, Nitrogen is the limiting factor of eutrophication in Okpara dam, but this does not stop eutrophication. Phosphorus fractionation according to Rydin and Welch (1998) under oxic conditions for surface results sediment and under profile sediment was studied. It was demonstrated that: Fe-bound-P, Al-bound-P and Organic-bound-P comprise the largest phosphorus pool (30%) to 51% of Total Phosphorus). High soluble reactive phosphorus content was measured in sediment column compared to other study cases. Organic phosphorus fraction represents 90% of the Total Extracted Phosphorus content. Water and sediment column acidity could allowed iron and humic acids production from the high organic matter amount (21.42% to 28.30%) in the dam to modulate P releasing from sediment. Phosphorus short term remobilization study lets know that deeper sediment organic matters are more mineralized and released more phosphorus (95%) than surface sediment (20%). This fact is not suitable for sediment dredging to 1metter deeper because of eutrophication resumption. In oxic medium aluminum and iron orthophosphate are precipitated more in acidic solution. Phosphorus constitutes iron mobility factor in the dam. ©JASEM

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Surface water is divided into running and stored waters (stagnant). They are generally rich in dissolved gas, organic matters and suspended matters (SM) such as plankton. They are very sensitive to the mineral and organic pollution caused by nitrate and pesticide from fertilizer. The nutritive elements of origin apart from the atmospheric natural contributions after transited through the water column settle on the sediments before being given to the provision of the plants by salting out (Ba, 2006). Phosphate is the primary and the mean cause of eutrophication of numerous water bodies. Its presence in natural aquatic ecosystems is due to human activities (Correll, 1998). Okpara dam water is submitted to an eutrophication process (Zogo, 2010). Okpara dam water constitutes very significant source of drinking water to population of Parakou. Otherwise, the concentration of iron and manganese are influenced by season. Iron and in a lesser extent manganese are the most abundant metallic elements in the earth crust. But they cause esthetic and organoleptic damages. Iron and manganese were

found in surface or groundwater, (Omoregie et al., 2002). Total phosphorus content in the sediment can be a good predictor for potential eutrophication in a lake. However, characterization of sediment phosphorus, usually based on sequential chemical extractions, is also necessary. P can be exchangeable, bound to iron, aluminum and manganese hydroxides, organic matter and calcium (Rydin and Welch, 1998). The fact that iron and manganese could be bound to Phosphorus, requests the phosphorus fractionation. This fractionation allows the potential mobile P fraction under oxic and anoxic conditions to be estimated (Mama et al., 2011a; Van Hullebusch, 2000).

The main objective of this study is to establish the eutrophication state of the dam, so that to find the limiting factor of this later, to estimate the amounts and forms of potentially mobile P in surface and coring sediments by using sequential P extraction (P-fractionation) and the phosphorus impact on iron and manganese presence in the Okpara dam. A

laboratory study of short term P release (96 hours) laboratory sediment re-suspension under oxic conditions at different pH values was carried out on different sediments type.

MATERIALS AND METHODS

The present leaded Study site is the dam okpara. It situated at the commune of Tchaourou at Kika on a tributary of the Ouémé River, in the North-East of Benin at 450 km from Cotonou. The watershed of this dam is situated in the eastern part of Parakou town and extends to the districts of Tchaourou, Pèrèrè, Nikki, N'dali, then to south-east part of Bembereke district. Parakou is situated at latitude 9°21 north and longitude 2°36 east. The dam supplies the drinking water treatment station of Parakou town. Okpara dam is a reserve which fewer deep with a depth ranging between 4.5 and 9 m at N 09°17170 E 002°43366 A 1086. The aquatic plants proliferation added to the chemical water column stratification are indicative for clear eutrophication process manifestation in the tank (Zogo, 2010). Since 2000, in order to modify the algal succession and to prevent aquatic bloom, an occasional pulling up of the plants is executed. In fact, these plants push back quickly and more intensely only a few months after their pulling up by mechanical way. The water reserve is accessible to fishermen. As observation, the water is enriched in iron and manganese during low waters. December corresponds at the beginning of the dry season on the catchment area of Okpara, during which the mural valve is closed to prevent the emptying of reserve from its water. Valves are opened around July because of the arriving of the new rain water. This valve opening is accompanied by the surface sediment departure and water renewing. Hydraulic residence time was estimated to be approximately eight months. The catchment area (2070 km² with a perimeter of 217 km) is occupied

essentially by agricultural and cattle farm (80%) and weakly urbanized sector (Le Barbé, 1993).

Sampling: Water and sediments were sampling on the dam as indicated on Figure 1. Two methods were used to sample sediments: (i) a benne "Van Veen" was used to sample surface sediment (1 to 10 cm depth), this sediment corresponds to the sediment accumulated lately and to the sediment generally prone to resuspension in water dam; (ii) a polyvinyl chloride tube was used to sample the under surface profile sediment, this sediment corresponds more to the sediment accumulated over several years (Reddy et al., 1996). Sampling was carried out on nine preset areas of identical surface area each year in November (Figure 1). The collected samples were stocked in polyethylene containers previously decontaminated with HNO₃ (10%) and rinsed with ultra pure water (Milli O system) (Rubio and Ure, 1993).

Analyses: On the water samples, a-Chlorophyll was measured according to Afnor standard NFT 90 - 117. The Kjeldahl nitrogen was determined after mineralization according to the. Afnor standard NF T 90 - 110. Total phosphorus was given with the spectrophotometer after oxidation peroxodisulfate according to Afnor NF IN 1189 from French Normalization Association (AFNOR). The ratio N/P was determined to find the limiting factor of eutrophication. An N/P values lower than 16 indicated that nitrogen is the limiting eutrophication factor. The Organization for Cooperation and Economic Development (OCDE) grill was exploited to establish the eutrophication state of the dam and make some analysis and interpretation results using the tool eutrophication diagnosis of Ifremer (French Institute for research and sea exploitation).

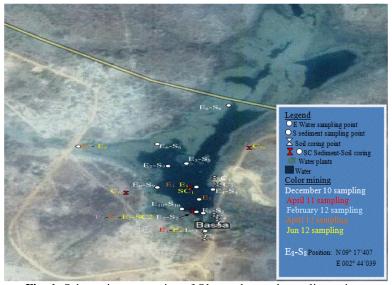


Fig: 1: Schematic presentation of Okpara dam and sampling points

*TOMÈTIN A. S. LYDE; MAMA DAOUDA; ZOGO N. DIEUDONNÉ; BOUKARI OUSMANE; BAWA L. MOCTAR In this study, after drying, the solids samples were sieved using a nylon sieve mesh (2 mm) according to the Afnor standard X31-101 (Afnor, 1994). Dry Weight (DW 40°C) and residual water were determined according to the French standard X 31-102 (Afnor, 1994). The pH was determined according to 1 / 2.5 DW sediment/water ratio described by standard NF X 31-103. Loss onignition (L.O.I.) was subsequently determined by mineralization to constant weight at 550°C for sixteen hours Norme (Afnor, 1994).

Carbonate content was determined according to the Rauret protocol (Rauret *et al.*, 1988). For total iron and phosphorus determination 0.25g of sample (DW 40°C) is placed in a furnace for organic matter calcinations at 450°C during 3h. The total digestion of sediments and soil was performed by aqua regia consisting in an addiction of 5 *ml* hydrofluoric acid (48%) and 1*ml* per hydrochloric acid (70%) on 0.25g of sediment or soil on a hotplate. The dry residue was recovered with 3.75*ml* of hydrochloric acid (38%) and 1.25*ml* nitric acid (65%) and completed in a 100 *ml* graduated flask for the total Iron (Fe-T) and TP determination according to the same method of water sample.

Iron concentration in extracted solution was determined by using orthophenanthroline method and measure at 510 nm on a JENWAY spectrophotometer model 6305 wavelength according to the standards NF T 90-017 (Afnor, 1997).

Different forms of P in sediment samples were determined by P extracting (Figure2) according to the scheme proposed by Rydin and Welch (1998). P fractions listed here were (i) Loosely bound or labile-P (including SRP) in porous water (NH₄Cl-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-P). Residual P was determined as total phosphorus (TP) minus total extracted P. Between the extraction steps, solid/liquid separation was achieved by centrifuging at 4000 rpm for 20 min, the resulting supernatant being decanted into test tube. Residues were then washed with 10 ml de-ionized water (Milli-Q), shaken for 15 min, centrifuged at 4000 rpm for 20 min, and the supernatant discarded.

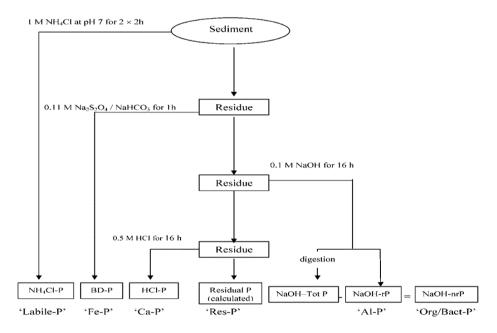


Fig: 2: Phosphorus fractionation scheme used, from Rydin and Welch (1998).

The influence of pH was studied under oxic conditions. Three pH values 3, 5 and 7 (according to the carried out pH values of the sediments) were adjusted and regulated with 0.5 M HNO₃ or 0.1 M NaOH. Two kinds of sediments were chose for the study from two sampling points (SC1 and SC2): surface sediments SS (0-5 cm and 5-10 cm) for SC1 and SC2, and those from deep sediments SP (130-

140 cm and 140-150 cm) only for SC1. These experiments were conducted in 100 ml Nalgene bottles at 25 ± 2 °C. The sediment concentration was 5 g/l in ultra pure water. After regulation of the conditions, samples were shaken on an orbital shaker for 96 hours. This equilibrium time was chosen according to Van Hullebusch work. The supernatant

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was collected as for fractionation process and the residue submitted to phosphorus fractionation

RESULTS AND DISCUSSIONS

Table 1: Total Nitrogen (TN); Total Phosphorus (TP); A-chlorophyll (A-chl); average ratio N/P; Labile Phosphorus (LP); % LP/TP value raised in each sampling point in December 2010

Sample	TN (μg/l)	PT-P (μg/l)	N/P	LP (μg/l)	% LP/TP	A-Chl	pН
E1-s	839	1053	0,8	851	80,82	10.8	
E1-p	321	37694	0,01	37439	99,32		6.50
E2-s	716	444	1,61	243	54,73	12.8	
Е2-р	648	423	1,53	223	52,72		6.43
E3-s	639	971	0,66	770	79,30	25.8	
Е3-р	739	3225	0,23	3020	93,64		6.63
E4-s	211	768	0,27	568	73,96	10.8	
E4-p	1180	18165	0,06	17939	98,76		6.75
E5-s	1757	1682	1,04	1480	87,99	28.8	
E5-p	243	464	0,52	264	56,90		6.62
E6-s	525	383	1,37	182	47,52	10.8	
Е6-р	3284	362	9,06	162	44,75		6.50
E7-s	721	281	2,57	81	28,83	14.4	
Е7-р	2809	342	8,21	142	41,52		6.89
E8-s	2503	342	7,32	142	41,52	19.8	
Е8-р	1394	13517	0,1	13297	98,37		6.80
E9-s	1885	342	5,51	142	41,52	16.2	
E9-p	3176	423	7,5	223	52,72		6.50
E10-s	2085	403	5,17	203	50,37	18	6.63
E10-p	1351	4278	2,82	4072	95,19		
Average	1351	4278	2,82	4072	66,02	*	6.63
s : surface	e p:bottom	1					

From table1 the maximum value of raised LP is 37.439 mg/l at point E1 in December 2010 at the bottom of the reserve and 1.480 mgl on the surface at the point E5. This value contributes to a hypereutrophe eutrophication state according to the grill of eutrophic state evaluation from OECD which fixes the critical level at $100 \ \mu g/l$ of LP. For all the sampled points in December 2010, the values of LP in all sampling points vary from 1.42 to 375 times the critical level of hypereutrophe state fixed according to OECD. However the bottom waters are the higher concentrated in TP and the dissolved form more important (high %LP/TP).

In December 2010 water of Okpara reserve has an average value of 2.82 N/P ratios. This value remains lower than Redfield value which is in order of 16 and seems to which found by Bloundi (2005) in Nador lagoon. These low values of N/P were noted in different lagoons ecosystems (Nixon, 1981). In August 2011, water of Okpara reserve is inpermanent flow on the level of the principal bed and its access is very risky. It is noted that ratio N/P is in order of 8.06 unit for a sample water taken on the flow bed on the level of the bridge (E3) against 63.25

unit for a sample taken on the level of a bank whatever the two samples appreciably have close orthophosphate values (0.0223 mg/l LP at the bridge and 0.0225 mg/l LP at the bank). The high presence of water plants on the banks rather than in the principal flow bed of reserve confirms this result and makes possible to put forward the limiting factor concept of nitrogen in Okpara dam. Those phosphorus values remain too strong in the water column in December and are essentially from the sediment released phosphorus. The essential of Nitrogen is under dissolved form in the water and the phosphorus combined to the particles in the water from the catchment.

The results obtained by Zogo (2010) combined with the analysis results of water sample taken in December 2010 (Table1) suggests a resumption of eutrophication intensification after a long period of water plants proliferating removal from the reserve. Indeed, the values of a-chlorophyll recorded in various points in December 2010 lie between 10.8 mg/L and 29 mg/L and indicates according to the grid of OECD eutrophic state. According to Zogo (2010), in the evolution cycle of a-chlorophyll, the

strongest chlorophyll values are observed from May to the end of the dry season. The eutrophication state in the water of reserve evolves then overall from Mesotrophe in high waters period to eutrophe state tendency (period of the dry season) and tending to Hypereutrophe on May (and of the dry season). The high values obtained by Zogo (2010) in May 2003 are already reached in December 2010.

The pH₀ of the Sediments has an acidic character with value ranged from 5.24 to 6.79 when it was measured directly on the wet sediment. After drying in oxic condition the determine pH is more acidic (weak pH) than the first determined. In front of this result we have deduced that the passage from an anoxic condition to an oxic induces the oxidation reaction in the sediment mainly the organic matter and metals. This characteristic reflects the tropical ferralitic and sandy-clay nature of the catchment area on which over studies show that the soil has an acid pH despite the basic nature of its composition (Faure, 1968; Volkoff, 1965). But the presence of organic carbon (28.41%) and humic acid toward 6.82% of soil could probably indicate the origin of the acidity. Also the iron amphoteric character combine with the basic soil nature from its composition could lead the iron to react as an acidic component. Organic matter oxidation could produce acid compound in water presence. The difference between the water-pH and KCl-pH is more than one and thus indicated a weak saturation rate in the sediment.

The carbonate content which makes possible the alkalinity expression of the sediments is very weak and consequently the percentage of so weak inorganic carbon. We have observed in the dam sediments sampled from nine sites in December 2010, an alkalinity average of 1.804% with a maximum value 2.614%. In dry season (June 2012) alkalinity recorded on the level of the dry sediments is very low and is lower than 0.230% These values remain very low in front of those found by Khribi, (2005) in Lille sediments (1.1%) and Vraimont sediment (3.5%), (which lead him to the following remark: The higher pH (7.9) of Lille sediment can be related to the more significant carbonate rate about 17.5% against 5.5% for Vraimont sediment), this parameter will influence the buffer value of the two sediments and consequently the pH of the sediments after phosphatizing. In the case of the sediments of Okpara dam which express an acid character, (the pH average 6) one can understand that the weak carbonate rate favorable to the acidity of the sediments is without influence on the sediments buffer value. According to Van Hullebusch (2000) the very low carbonate content indicates that the carbonates will thus not influence the chemistry of the sediments and not react as a pH variation factor to the action of weak acid or basic solution addition on the sediments. one can note the presence of the hydrogen carbonates in the water column (of an alkalinity of 30.5 mg/l in December 2011 with pH =

Table 2: Organic matter (OM); Total Nitrogen (TN); Total Phosphorus (TP); average ratio N/P, carbonate value raised in each sampling point in December 2010.

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	Samples	MO (%)	TN (g/kg DW)	TP (g/kg DW)	pH water	pH _{KCl}	N/P	% CO ₃ ²⁻	
_	E1	21,48	10,7	26,4712	5,75	4,5	0,4	2,61	
	E2	27,42	13,7	24,0352	5,07	3,97	0,57	0,86	
	E4	23,24	11,6	24,2788	5,25	3,97	0,48	3,32	
	E5	21,51	10,8	17,1332	5	3,8	0,63	2,23	
	E6	23,47	11,7	19,1632	4,86	3,78	0,61	1,63	
	E7	28,3	14,2	13,4792	5,25	3,89	1,05	0,78	
	E8	24,33	12,2	19,8128	5,1	3,74	0,62	1,56	
	E9	26,32	13,2	23,0608	5,81	3,74	0,57	1,54	
	E10	25,49	12,7	27,1208	5,74	4,61	0,47	1,71	
	Average %	24,62	12,31	21,62	5,31	4	0,57	4,07	

Table3: Sediments samples (E1 to E10) positioning in the Ifremer Eutrophication risk diagnostic framework grill (2000)

Variable	Very good (None eutrophication risk)		Good (low risk)		Middle (50% risk)		Bad (high risk)		Very bad (very high eutrophication risk)
MO(%)		3.5		5		7.5		10	E1-E2-E4E10
NT (g/Kg DW)		1		2		3		4	E1-E2-E4E10
PT (mg/Kg DW)		400		500		600		700	E1-E2-E4E10

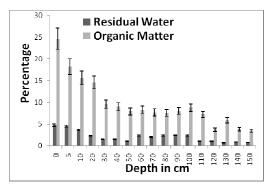


Fig: 3: Residual water and organic matter percentage in the under profile sediment sampled at the point N1 in June 2012

Organic matter: From the table 2 it could be noted that the amount of OM in the surface sediment varies from 21.42% to 28.30% (December 2010) and this are more important than those of Van Hullebusch. These high amount at the surface could be allowed to the new recently deposit sediment. For the coring sediment, OM contents (Figure 5) were similar to the results obtained by Van Hullebusch (2002) in shallow polymictic eutrophic lake (Lake Courtille). We notes according to the Figure 3 that the content of organic matter decreases regularly from top sediment (%OM = 18%) down to 80 cm of depth (% $H_2O = 7.90$ %). Thereafter this value increase light by 9% down to 100 cm of depth from where it oscillates until in fall of depth for brutally being stable around 4% to 150 cm of depth.

According to the same Figure 3 we notes that the residual water content decreases regularly from top sediment ($\%H_2O = 4.55$) down to 50 cm of depth ($\%H_2O = 1.06$). Thereafter this value increases by 2.36% where it oscillates until 2.4% to 100 cm of depth for brutally falling to 1.1% and lead to a less variation up to 0.83% to 150 cm of depth. The $\%H_2O$ content follows as the same rate/rhythm of variation as that of %MO. This traces the importance of

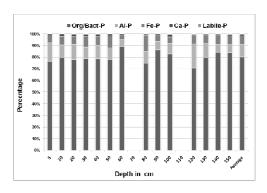


Fig: 5: Percentage of Phosphorus P-fractions (P-Lab, Fe-P, Al-P and Org/Bact-P) in the coring sediment sampled at the point N1 in June 2012

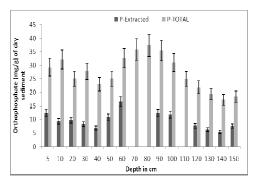


Fig: 4: Total Phosphorus and Total Extracted Phosphorus P-fractions (P-Lab, Fe-P, Al-P and Org/Bact-P) as orthophosphate in the under profile sediment sampled at the point N1 in June 2012

porous water of the sediments in the mobility of the pollutants so for the dissolved organic matter.

It is generally accepted that humic substances (HS) are formed via polycondensation reactions or oxidative derived from and hydrolytic biodegradation of plant, animal and microbial decay products, such as amino acids, phenols and sugars (humification processes). Iron in clay minerals can serve as a Lewis acid, which facilitates the polycondensation of phenolics and amino acids. It is interesting to note however that the published data pertain mainly to the so called "humic substances" (HS) and demonstrate the ability of these substances to complex metals (Mousset et al., 1997). According to Blodau (2009) it can be speculated that geogenic organic matter also supports iron and sulfate reduction in the saturated area of mine dumps and aquifers. The low efficiency of anaerobic carbon mineralization has to be considered, though, and transport of exo-enzymes with seepage water into the saturated area may be required. According to this behavior the presence of organic matter in the anoxic sediment is favorable to the iron and manganese reduction and then moving from the depth sediment to the sediment-water interface.

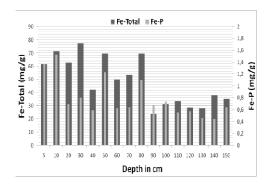


Fig: 6: Total Iron and Phosphorus bound to reducible forms of Fe and Mn (Fe-P) in the profile sediment sampled at the point N1 in June 2012

In December 2010 TP varies from 13.479 to 27.121 g/Kg of sediment value excessively high going from 19 to 39 times of the value threshold $(0,7 \ mg/g)$ making it possible to treat its sediments of bad quality according to the Ifremer (French research institute for sea exploitation) eutrophication state grill. Van Hullebusch finds TP values of about 0.94 to 1.370 mg/g on the eutrophic water level of Courtille and emits that the sediments of the lake are a potential nutriments source for the water column. Thus seen the very high value as indicates the total phosphorus content of the sediments we can deduce that the sediments of reserve constitute a source of phosphorus renewed to the water column.

For June 2012 coring sediment (Figure 4) the high total phosphorus amount (18.47 to 35.47 mg/g DW sediment) indicated that the sediment constitutes a phosphorus renewing source to the water column to a long period and justified the reason of the quickly push back and more intensely of these plants only a few months after their pulling up by mechanical removing away from the dam. Residual P determined as total phosphorus (TP) minus total extracted P is more important than the Total-Extracted (Figure 4) and indicates that Total-P consisting mainly of refractory organic P from the moment that weak values (the soil and rock of the catchment studies show that the TP fraction are lower than 0.208%.) require the use of intensive fertilizers for extensive agriculture exploitation (Faure, 1968; Volkoff, 1965). As an indication, for the cotton countryside 1998-1999, 1229 tons of nitrate fertilizers were poured in the under-basin against 745 tons over the period 2001-2002 (CeRPA Borgou-Alibori) 12145.65 tons of NPK - 5235.6 tons of urea. 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 sediment can contribute up to 99% of the total P input into some shallow lakes, even under oxic conditions at the sediment surface (Jensen and Andersen, 1992; Rydin and Brunberg, 1998). 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 lag time for ecosystem rehabilitation (Bootsma et al., 1999).

According to the high %OM, the TN and TP amount in the surface and profile sediments added to the TN and TP amount in the bottom water, the sediments are in very high eutrophication risk; then the dam could be classified as a hypereutrophe statue.

Loosely sorbed-P (labile-P) varies for each sample from 4 to 83 μ g/g DW sediment with an average of 38 μ g/g DW. The amount at the top 10 cm was 47 μ g/g DW. In the eutrophic Lake Courtille, Labile-P

fraction ranged from $6\mu g/g$ to $18 \mu g/g$ DW sediment. Our values were too high to those determined by Kaiserli et al. (2002) in shallow hypertrophic lake (1.64–1.92 $\mu g/g$ DW). Our values were low or high in comparison with the labile P determined by Rydin (2000) on the surface sediment in moderately eutrophied Lake Erken (54 $\mu g/g$ DW).

P associated to iron (Fe-P) was 1366 µg/g DW for surface (0-5 cm), more (1533 μ g/g DW) for surface (5_10 cm) and less high for the deeper sediment coring (10_150 cm) and ranged from 450 µg/g DW to 1250 μ g/g DW. Those values are very high but in similar evolution with Van hullebusch values for surface sediments in Lake Courtille were P associated to iron (Fe-P) was 230 µg/g DW for SS00 and significantly lower (160 μ g/g DW) for SS99 (old sediment). For Van Hullebusch the Fe-P initially present within new sediment sample SS00 can be partly transferred to either Al-P pool, the Fe-P pool or released into the water column, the latter way might be the major one. We make the same conclusion with Van Hullebusch that a part of total phosphorus Fe-P content in 0 to 5 cm sediment samples had been released into the water column like it's showed in Figure 6. The anoxic sediment retains more the Fe-P precipitated in the dam sediment to an acidic condition. The phosphorus constitutes a source of iron precipitation in the dam water and sediment porous water toward the sediment from which could released iron and phosphorus in the water at a redox appropriated conditions more in dry season as it was observed that phosphorus and iron have high amount in Okpara water column in the dry season (Zogo, 2010). The phosphorus thus constitutes a combine factor of the iron mobility in the dam.

The P bound to Al varies from 428 to 2302 μ g/g DW. These values are higher than those of Van hullebusch (average of 300 µg/g DW with 10 mg/g of Al content). That Al-P could be related to the Al value obtained in the soil of the catchment area by Faure (1968) and Volkoff (1965) which could reach to 55.5 mg/g of soil and 50.3 mg/g according to Pougnet (1957) and Kriatov et al. (1980). We can say that almost all of the aluminium is precipitated (estimated to 95%) under P bound to Al form more than those of Van Hullebusch (estimated to 70%) despited of the Courtille Lake treatment under alum. The P level associated with Al (Al-P), approximately 10.80% of Total-P Extracted and this value is too weak if we compared it with 30% of TP obtained by Van Hullebusch. Al-P remobilization was not able to occur in Okpara dam water according to the acidic pH (5 to 6) crossed in the sediment and the archived P remobilization study of Van Hullebusch which showed that this remobilization is impossible at pH lower than 7, weakly possible (around 6% of Al-P) from pH 8 to 10 (less 40% of Al-P). Thus alum could be used for SRP precipitation and a way for lowering

primary production and subsequent organic matter production.

Organic phosphorus is essential like the major fraction for more than 80% of total extracted phosphorus and 34.22% of TP. This result is observed in most phosphorus fractionation cases in the sediments where organic phosphorus is the major and essential part of the sediment TP and submitted to a remobilization to the water column up to 32% (Van Hullebusch et al., 2002). Also, this result follows a precedent study where suspended matters are essentially colloidal substance form in solution which allows the mobility of iron and manganese in the water dam.

The phosphorus remobilization study allowed approving sediments behavior in Okpara dam. The behavior of the surface sediments (SS) is very different from those of depth (SP) which can be appreciated as depth mineralization degree. One observes:

i) Strong Org-P release (95%) whatever is the pH and more in alkaline solution for the SP against 20% for SS but very sufficient SRP to produce an algal bloum or a strong amount of SRP in the water column. The organic matters of SS deserve for this purpose a specific study. These results also express the strong mineralization of the SP against the refractory SS. The water reserve knows a progressive reduction of its depth, the level of the sediment having increased of more than 2 meters on the level of the tower of the water point and 3 to 5 meters in North of the reserve completely invaded permanently by Echinochloa stagnina (Zogo, 2010). The state of progressive filling of the dam entrains gradual reduction in water accumulating capacity of the reserve. One thinks in these cases of the sediment dredging. Within the study framework of the reserve sediments dredging, it will be necessary to take into account a probable high resumption eutrophication owing to the fact that the mineralization and the releasing of organic phosphorus degree are very thorough in the deep sediments (SP) carrots horizons.

ii) The passage from anoxic medium to oxic of the SP supports the precipitation of Fe-P this more to pH close to that of the sediments. This phosphorus comes primarily from organic matter and the strong content of iron in the sediments. This behavior suggests that during the time when the water of reserve is richer in oxygen, for the oxic sediments, there is possibility of P accumulation in Fe-P form and when oxygen rarefies there is remobilization of iron and phosphorus Fe-P. This could explain the low P-Fe content observed towards the end of dry season on the level of the SS, the Fe-P content increase for the SP at the remobilization experimentation study in oxic condition and water

column strong iron amount in summer. Gomez et al. (1999) show that this redox potential value is variable according to the sediments pH, the presence of organic ligands and of the interstitial water salinity. Phosphorus is thus likely to be salted out in the water column with the iron when the interface water-sediment becomes anoxic (Boström et al., 1988; Gomez et al., 1999) by various mechanisms of interstitial water diffusion (Enell and Löfgren, 1988). In oxic conditions on surface sediments, there are however two possible cases: the phosphorus diffuses from sediment (anoxic) towards the interface water sediment (oxic), and where it is trapped by the iron hydroxide which is excellent phosphorus adsorbing in the presence of dissolved oxygen (Matthiesen et al., 1998). In anoxic conditions on the surface sediments, when the orthophosphates fixing to iron (III) capacity recently formed a deposit, the interface water sediment is exceeded; phosphorus is released in the water column. In anoxic sediments, other electrons acceptors are used for organic matter mineralization, like sulphates through sulfatoreduction by sulfato reducing bacteria. The sulphides produced by sulfato-reduction go then to combine with iron (II) in anoxic conditions to form FeS and FeS₂ (pyrite) and thus to immobilize iron in a layer of the sediments (Gomez et al., 1999). This phenomenon is frequently met in polluted water by sulphates resulting from the manures used in agriculture and the atmospheric deposits under sulphides form (Kleeberg, 1998; Mama et al., 2011b). The phosphates fraction related to iron is very sensitive to the sediments redox potential variations. When the redox potential is lower than 200 mV (ESH), a Fe³⁺ fraction available in the sediments is reduced to Fe²⁺. The formation of iron hydroxide will thus not have there and thus not of fixing of the phosphorus which is thus released in great quantity in the water column. These phenomenon take place in Okpara dam where organic matter mineralization in elder sediment SP procures phosphorus which is retained by iron hydroxide or diffused toward oxic sediment to be trapped in oxic condition and release in summer at anoxic condition.

- iii) Practically no variation for the SS1 which are those already emptied good part of Fe-P at the period of taking away and very weak for the SS2 which contain more Fe-P compared to SS1 and this with neutral extreme pH (high for the sediments).
- iv) Probable precipitation of Al-P for the SS and very weak (less than 10%) release of Al-P at pH 7 contrary to the SP where there is remobilization of phosphorus from Al-P (60% to 75%). We could also notice that aluminum migrated from deeper sediment to surface sediment.
- v) Released of P from Ca-P at acid pH for the SS (20% to 60%) and SP (80%).

Conclusions: The high percentage of OM, TN and TP amount in the surface and profile sediments add to the TN and TP amount in the bottom water, the sediments were in very high eutrophication risk; then Okpara dam could be classified as a hyper-eutrophic statue. Okpara dam sediment study let now that the sediment is under very bad eutrophication risk and could provide and hyper-eutrophe state to the water dam. The sediment of Okpara dam had a high P 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 sediment, and could have an impact upon the water column chemistry and the trophic state of lake following sediment resuspension and P release. The nature of sediment explains an acidic characteristic which affects the water column pH. The common characteristic (high pH) in eutrophic lakes during dry season is not observed in Okpara dam, despite intensive resuspension, and markedly internal P loading increase risk. Organic matter mineralization can also influence long term P release as illustrated by the different TP content between last and old-years sediment (profile sediment). Phosphorus release was from the organic fraction. Organic matter mineralization can also influence long term P release as demonstrated by the different behaviors between last-years sediment (SS) and the older surface sediment sample (SP); it was also demonstrated by the SRP release in Okpara water column at the end of summer. Phosphorus short term remobilization study lets know that deeper sediment organic matters are more mineralized and released more phosphorus (95%) than surface sediment (20%). This fact is not suitable for sediment dredging to 1metter deeper because of the high eutrophication resumption.

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*TOMÈTIN A. S. LYDE; MAMA DAOUDA; ZOGO N. DIEUDONNÉ; BOUKARI OUSMANE; BAWA L. MOCTAR

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