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SEASONAL DYNAMICS OF PHOSPHORUS FRACTIONS IN ARTIFICIAL MARINE ESTUARY: VRIDI CHANNEL (CÔTE D'IVOIRE)

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ABSTRACT
Seasonal dynamics of some phosphorus fractions in Vridi channel have been the focus of this study. In its implementation, the monthly sediment samples were taken over one year in this artificial estuary (from April 2014 to March 2015). Olsen modified method and Van Eck modified method were used for the assessment of phosphorus fractions. The results showed that seasonal and annual fractions of particulate bioavailable phosphorus and authigenic apatite phosphorus are the most important, while those of detrital apatite phosphorus and dissolved bioavailable phosphorus are the weakest. Seasonal dynamics of phosphorus fractions are particularly importance in the last two seasons with the advent of Comoé River in this channel. The use of component analysis principal shows that pH, conductivity and redox potential of these sediments would be directly involved in the biogeochemistry of almost all phosphorus fractions evaluated, except for exchangeable phosphorus and phosphorus detritic apatite. For these two phosphorus fractions, moisture and salinity directly influence their biogeochimism over the study period.

KEYWORDS: Atlantic Ocean, Ébrié system, Eutrophication, Olsen modified method, Van Eck modified method.

INTRODUCTION
Phosphorus (P) is known for its fundamental rule in the physiology of living organisms (Wang *et al*., 2018; Zhang *et al*., 2018). However, it is also one of main factors of surface waters eutrophication (Lemley and Adams, 2018; Stutter *et al*., 2018). Eutrophication causes the destruction of aquatic ecosystems. So, it impacts all entire ecosystem (Ménesguen and Lacroix, 2018; Lemley and Adams, 2018; Stutter *et al*., 2018). This phenomenon knows a real expansion in the world, particularly in developing world where releases of any kinds were discharged back into surface waters without preliminary treatments (Yao *et al*., 2010; Yao *et al*., 2016). Therefore, P studies in aquatic ecosystems are global major concern, in particular that concerning its distribution and mobility in sediments (Abboud *et al*., 2018; Cao *et al*., 2016; Defforey and Paytan, 2018; Huang *et al*., 2015).
This nutrient is present in several forms in aquatic ecosystems, the best-known of which are: Authigenic Apatite Phosphorus (AAP); Detrital Apatite Phosphorus (DAP); Dissolved Bioavailable Phosphorus (DBP); Particulate Bioavailable Phosphorus (PBP); Exchangeable Phosphorus (EP); Phosphorus bound to Oxyhydroxides of Fe, Mn and Al (PO); Reducible Phosphorus (phosphorus bond to Fe) (RP); Labile Phosphorus (LP) and Organic Residual Phosphorus (ORP) (Cao *et al*., 2016; Huang *et al*., 2015; Kwak *et al*., 2018). The presence and stability of these different P forms is bond to several complex processes. These processes depend on the hydroclimate and hydrosystem (topology, geology, currents, tides *etc*.) of aquatic entities (Kwak *et al*., 2018; Mendes *et al*.,

2018), but also on intense biogeochemical activities which take place in them (Wang *et al*., 2018a; Zhu *et al*., 2017; Zhu *et al*., 2018). pH, redox potential (U), conductivity, salinity, moisture and organic matter are among physical and chemical factors that influence P mobility and distribution in sediments (Bai *et al*., 2017; Defforey and Paytan, 2018; Missong *et al*., 2018; Ngatia *et al*., 2017; Zhu *et al*., 2018).The formation of AAP and DAP is favored in basic environment at high temperatures, particularly in silty sediments, rich in nitrogen and organic carbon (Heindel *et al*., 2018), where this process is recurring. On the other hand, a drop in pH under 5 (caulibaly, 2014) favors these P forms remobilization (Gaoa, 2012). This is achieved following the reduction of negative surfaces of sediments, accentuated by a competition of major cations (K^+, Na^+ et Mg^{2+}) with Ca^{2+} on different sites (Li and al., 2017), but also by a high presence of sulfur in sediments (März and al., 2018). These P forms remobilized can be bioavailable through biogeochemical and physical processes. It is the same for DAP, which by mineralization becomes potentially bioavailable with the increase of the temperature (Bai *et al*., 2017; Zhu *et al*., 2017). With regard to PO, their stability depend both on the combined action of pH and U, but also on the nature and composition of sediments (Bai *et al.,* 2017; Mengxin *et al*., 2018). For illustration, during the degradation of organic matter in anoxic and sulphate-rich sediments, the transformation of Fe (hydr)oxides into iron sulphide or siderite ($FeCO_3$) causes a decrease in P adsorption capacity on iron (oxy)hydroxides (Missong *et al*., 2018). In general, sediments of sandy nature and rich

in quartz grains have a low P sorption with these (oxy) hydroxides, while those from clays are more (Abboud *et al*., 2018; Fonseca *et al*., 2011). In most cases, the content of RP is correlated with that of iron in sediments (Fonseca *et al*., 2011). Its adsorption on sediments is considerably favored by Na^+, Mg^{2+} and Ca^{2+} (Li *et al*., 2017). However, a drop of U, most often due to the degradation of organic matter under anaerobic conditions with an increase of temperature, leads to its reduction and the P and Fe release in sediments (Mengxin *et al*., 2018). This is especially true in sulphide-rich sediments, where iron is released under iron sulphide (FeS) (März *et al*., 2018). As concerned to LP, it is very sensitive to dilution effects from tributary freshwater inflow and extended evapotranspiration (Mendes *et al*., 2018; Xu *et al*., 2018). Under anaerobic conditions, increased pH promotes LP remobilization from sediments from sediments to water overlying (Gaoa, 2012), as well as the formation of iron phosphate (II) (März *et al*., 2018). This P loss in the sediment solution is compensated by EP, which constitutes a reserve for LP (Xu *et al*., 2018). This is generally observed for pH values close to neutral at low temperatures (Gaoa, 2012).

With a population of nearly 5,000,000, Abidjan district is the most populous city in French-speaking West Africa. This district knows a real extension following a strong industrialization and a galloping urbanization. This established fact is source of numerous ecological conflicts. Indeed, all anthropogenic discharges from this district are directly rejected in Ébrié system and/or in Atlantic Ocean without prior treatment (Gnagne *et al*., 2015). Thus, these two ecosystems present a darkening ecological future as a result of anthropogenic pressures they are undergoing, particularly for Ebrié system where this situation is mentioned by several recent studies (Coulibaly *et al*., 2018; Diarra and Kablan, 2014; Kouamé *et al*., 2016; Tia, 2017). This is also the case of Vridi channel, which represents the only pass between these two aquatic ecosystems. For illustration, works of Yao *et al.* (2017) and Yao and Trokourey (2018a and b) have shown that this channel is subject to relatively important metallic pollution, with considerable ecological risks. So, it is important to seriously assess the level of pollution of this estuary, especially that it shelters an impressive and unique biotope. And this, in anticipation of possible decision-making and implementation of techniques that aims it's short and/or long term protection for its sustainable development. It is in this context, this study was carried out. Its main objective is the seasonal monitoring of P distribution and mobility in Vridi channel, with the subsequent objective of studying the influence of some physical and chemical parameters of these sediments (pH, conductivity, salinity, redox potential (U), organic matter and moisture) on this phenomenon.

MATERIALS & METHODS
Study area
As mentioned by Yao *et al*. (2017) and Yao & Trokourey (2018a and b), Vridi channel is located in Southern of Côte d'Ivoire, at precisely 4°0'50 " West longitude at 5°15 '23" North latitude. This channel is 2.7 km long and 370 m wide. Its depths are ranging from 12 to 15 m with pits of 10 to 25 m (Affian, 2003). Because of its position, this channel possesses an impressive hydrological network, composed of Ébrié system and Atlantic Ocean on the one hand, and contributions in fluvial waters, the most important of which are Mé River and Comoé River in South-East, and Agneby River, to West on the other. Its water seasons are characterized by five seasons: a hot season from February to April; a rainy season from May to July; a great cold season from August to September; a flood season from October to November and a short cold season from November to December (Yao and Trokourey, 2018b).

The entire area from Ébrié system to Atlantic Ocean has its remarkable biodiversity threatened by trace metals pollution caused by strong anthropogenic pressures, like Vridi channel. Indeed, there is autonomous harbour of Abidjan near this channel, which shelters the biggest industrial area of Côte d'Ivoire (2/3), with the only oil industrial zone of this country installed on banks of this estuary. The second industrial zone close to this estuary belongs to Yopougon (Fig. 1) (Yao *et al*., 2017). This marine estuary is currently the only pass of all types of pollutants from Abidjan district to Atlantic Ocean, but also those drained by fluvial contributions (Gnagne *et al*., 2015).
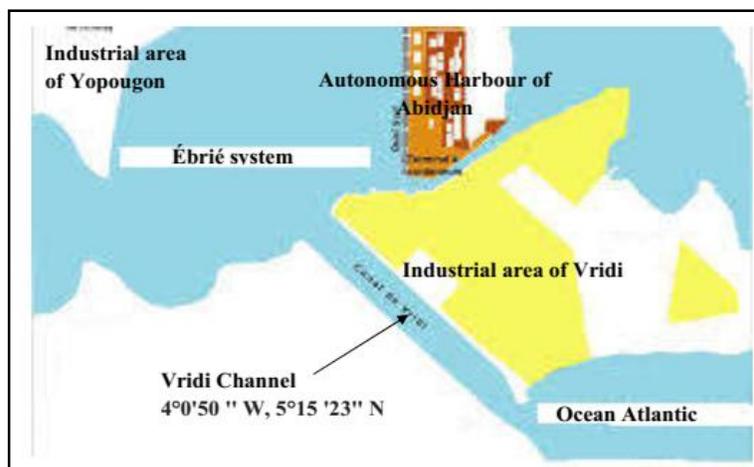
FIGURE 1: Vridi channel and its environments.

Collection and analytical pre-treatments of samples
This study was conducted jointly with those of Yao *et al.* (2017) and Yao and Trokourey (2018 a and b), that is over a year (from April 2014 to March 2015).The collection of samples was performed on the same sites as theirs shown in fig. 2, as well as their pre-treatment. Thus, sediment samples were taken monthly at 5 cm below superficial sediments using a Van-Veen type grab according to

AFNOR X 31-100 standard (1992), and immediately stored in polyethylene bottles. In lab, they are first cleared of coarse elements, followed by their freeze-drying to a constant weight (NF EN ISO 16720 (2007)). They are subsequently reduced to diameters of less than 2 mm by grinding (NF X 31-107 (2003)) and stored in polyethylene bottles.These flasks are stored in the dark at approximately 20°C for future analyzes.

FIGURE 2: Sampling sites

Determination of the content of total P (TP) and those of its forms studies in samples
Determination of the content of TP
The determination of the total phosphorus (TP) in different samples of dry sediments was doing by acid mineralization according to NF X31-147 standard (1996). 0.2 mg of dry sample in 25 ml of concentrated sulfuric acid is heated at 400°C for about 30 minutes in a mineraliser. After cooling, the mineralized material is treated with 150 ml of distilled water. 10 ml of the solution obtained is measured by automatic colorimetry according to the Murphey and Riley method (AFNOR T90-023 (1982)). The content of TP (mg/g) in sediment samples is obtained according to the formula (1):

$$C = \frac{A \times V \times f}{m} \qquad (1)$$

where:
- A : concentration in mg.l^{-1}, after carrying the absorbance in the calibration
curve;
- V : volume of extractant used in ml;
- f : dilution factor;
- m : mass of dry sediment (g) (corrected for moisture content at (105 ± 5)°C).
P speciation
The P speciation in samples collected was doing in two phases. The first phase concerned the determination of LP, EP, RP, PO, AAP, DAP and ORP; and the second was for the determination of PBP and DBP. The implementation of the first phase was done in accordance with Van Eck method (1982) modified by Moore and Reddy (1994) (Van Eck modified method). The second phase was doing according to Olsen method (Olsen et al., 1954) modified by Colwell (1963) (Olsen modified method).
For the first phase, it was determined first LP by treating 0.5 g of dry sediment with 25 ml of deionized water by vertical agitation during 2 hours. The content of this P

form was obtained by measurement of liquid phase, got back after centrifugation of the mixture at 1500 tr/mn, by automatic colorimetry of according to Murphey and Riley method (AFNOR T90-023 (1982)). The sediment residue was got back and treated with 25 ml of 1M NH$_4$Cl solution by vertical agitation during 2 hours. The mixture was centrifuged as previously and the liquid phase collected was measured as previously to obtain the content of EP. The sediment residue from this second step is taken up again with 25 ml of a combined solution of 0.11M Na$_2$S$_2$O$_4$ and 1M NaHCO$_3$. The mixture obtained was again treated as previously to have the content of RP. Again, the sediment residue from this sequence was treated with 25 ml of a 1M NaOH solution by vertical agitation during 16 hours, and treated as previously for obtaining of the content of PO. The sediment residue resulting from this step was subsequently treated with 25 ml of acetic buffer solution (0.1M CH$_3$COOH/ CH$_3$COONa at pH = 4) by vertical agitation during 6 hours, and treated as previously for obtaining of the content of AAP. The sediment residue was subsequently treated with 25 ml of 1M HCl by vertical agitation during 16 hours, and treated as previously for obtaining of the content of DAP. Finally, the sediment residue from all these steps was calcined at 550 ° C for 3 hours, cooled to room temperature, followed by treatment with 25 ml of 1M HCl by vertical agitation during 16 hours, and treated as previously for obtaining of the content of ORP.
For the second phase, 2 g of dry sediment is treated with 25 ml of 0.56 M NaHCO$_3$ solution at pH = 8.5, by vertical agitation during 2 hours. The mixture was centrifuged and the liquid extract was collected and treated for the obtaining of the content of DBP as in the first phase. The sediment residue is taken up in 25 ml of 0.11M NaOH solution and shake vertically also for 2 hours and centrifuged and treated as before for the obtaining of the content of PBP. These analyzes were performed in triplicate.

Recovery rate

In order to verify whether there was any interference during the implementation of different processes, which could lead to significant differences between TP and the sum of different P fractions evaluated, the recovery rate of these methods was calculated. This rate (R) is obtained as follows:

$$R\ (\%) = \frac{\sum_i^n P_i}{TP} \qquad (2)$$

with Pi, P fraction i

Source of data and statistical treatment of results

The data of pH, U, conductivity, salinity, organic matter and moisture of sediments over the period from April 2014 to March 2015 were provided by Yao and Trokourey (2018b) (Table 1). In addition to the standard statistical techniques concerning mean (m), Variation Coefficient (VC), standard deviation (s), minimum-maximum values (Min-Max), Component Analysis Principal (CAP) and Spearman's nonparametric correlation coefficient (r') has been used. The purpose of using CAP was to evaluate seasonal correlations between different parameters studied. This analysis was done for significant correlations at $p < 0.5$. Performed within a 5% confidence interval according to the student test, r' allowed to the evaluation of correlations between these parameters over the entire study period. All these statistical calculations were doing from the software Statistica version 10.0.

TABLE 1: Some physical and chemical characteristics of sediments of Vridi Channel (Yao and Trokourey, 2018b)

		HS	RS	GCS	FS	SCS	Annual
pH	m	7.64	7.79	8.07	7.51	7.80	7.76
	s	±0.18	±0.31	±0.61	±0.09	±0.21	±0.20
	VC (%)	2.40	3.97	7.60	1.20	2.71	2.60
	Min	7.49	7.61	7.61	7.41	7.59	7.48
	Max	7.85	8.15	8.78	7.57	8.02	8.77
Conductivity (mS/cm)	m	5.02	1.59	2.55	5.23	5.72	4.02
	s	±1.70	±0.28	±2.14	±2.06	±3.69	±1.22
	VC (%)	33.84	17.42	83.64	39.30	64.56	30.29
	Min	3.64	1.27	0.93	3.72	2.45	0.93
	Max	6.92	1.75	4.97	7.58	9.72	9.72
U (mV)	m	-29.72	-31.82	-32.43	-25.70	-29.76	-29.88
	s	±3.51	±1.38	±0.55	±4.64	±2.53	±1.73
	VC (%)	11.82	4.35	1.71	18.05	8.52	5.80
	Min	-32.44	-33.10	-32.95	-30.53	-31.88	-33.10
	Max	-25.75	-30.35	-31.85	-21.28	-26.95	-21.27
Salinity (‰)	m	1.69	0.74	1.25	0.90	0.62	1.04
	s	±0.78	±0.50	±0.13	±0.19	±0.24	±0.27
	VC (%)	45.95	67.82	10.48	21.29	38.02	25.88
	Min	1.08	0.21	1.14	0.68	0.35	0.21
	Max	2.57	1.21	1.40	1.03	0.79	2.56
Organic matter (%)	m	14.09	11.28	18.74	15.18	15.18	15.38
	s	±12.44	±11.73	±21.74	±21.74	±9.82	±5.32
	VC (%)	88.30	103.95	115.99	115.99	64.71	34.61
	Min	5.81	1.84	3.43	3.43	5.87	1.84
	Max	28.39	24.40	43.63	43.63	25.45	43.63
Moisture (%)	m	1.16	0,63	0.73	0.61	0.70	0.77
	s	±0.83	±0,55	±0.54	±0.35	±2.27	±0.78
	VC (%)	71.60	87,46	73.55	56.95	322.59	102.0
	Min	0.34	0,26	0.33	0.36	1.06	0.26
	Max	1.99	1,26	1.34	0.85	2.77	2.77

HS: Hot Season; RS: Rainy Season; GCS: Great Cold Season; FS: Flood Season; SCS: Short Cold Season.

RESULTS

Seasonal dynamics of P forms studied

The results obtained are shown in Table 2. Over the study period, PBP has the most important seasonal and annual proportions, followed by those of AAP. These two P fractions both represent about 40% of the P fractions considered in this study. The lowest seasonal and annual proportions are noted for DAP and DBP, all of which are less than 11% (Fig. 3).

TABLE 2: Seasonal and annual mean (mg/Kg), standard deviation (s), variation coefficient (VC in %), minimum-maximum (Min-Max) of P forms studied and TP

		HS	RS	GCS	FS	SCS	Annual
LP	m	7.84	6.14	9.24	15.72	14.37	10.66
	s	±9.26	±2.76	±7.63	±12.52	±16.44	±5.15
	VC (%)	118.19	45.01	82.63	79.67	114.39	48.29
	Min	2.09	2.95	3.80	4.81	2.46	2.09
	Max	18.54	7.74	17.95	26.43	33.11	33.11
EP	m	13.19	22.80	18.09	24.20	20.48	19.75
	s	±16.04	±31.36	±23.35	±18.84	±19.77	±5.91
	VC (%)	121.60	137.61	129.13	77.86	96.58	29.93
	Min	1.14	4.26	1.18	10.67	4.28	1.14
	Max	33.68	59.01	44.73	45.72	42.51	59.01
RP	m	10.06	9.99	5.91	11.18	12.55	9.94
	s	±7.06	±8.98	±3.71	±4.86	±12.83	±3.61
	VC (%)	70.20	89.91	62.86	43.49	102.23	36.32
	Min	2.52	1.52	1.74	6.21	0.63	0.63
	Max	16.51	19.40	8.84	15.92	26.12	26.12
PO	m	8.35	3.58	4.18	12.44	7.44	7.20
	s	±6.50	±3.69	±4.16	±14.61	±6.10	±4.42
	VC (%)	77.90	103.04	99.56	117.46	81.96	61.35
	Min	3.15	-	-	0.05	0.52	0.05
	Max	15.63	7.12	7.31	28.55	12.01	28.55
AAP	m	14.64	19.15	27.24	40.44	33.01	26.90
	s	±17.30	±18.14	±27.26	±38.33	±33.46	±9.26
	VC (%)	118.21	94.73	100.10	94.82	100.38	34.41
	Min	4.46	-	-	0.11	0.16	0.11
	Max	34.62	35.56	53.30	76.40	67.05	76.4
DAP	m	5.38	3.66	5.74	12.11	10.44	7.47
	s	±6.50	±3.70	±4.59	±7.34	±6.16	±1.48
	VC (%)	120.78	100.92	80.20	60.66	59.05	19.83
	Min	0.63	0.54	1.38	4.07	3.33	0.54
	Max	12.78	7.74	10.51	18.45	14.23	18.45
ORP	m	8.39	31.87	11.59	10,97	10.62	14.69
	s	±4.90	±39.87	±4.63	±4,94	±7.99	±15.38
	VC (%)	58.35	125.11	39.98	45,00	75.20	104.72
	Min	4.69	7.98	6.34	6,84	5.10	4.69
	Max	13.94	77.90	15.11	16,44	19.76	77.9
DBP	m	5.61	4.25	5.10	13.26	7.50	7.14
	s	±2.72	±2.36	±3.23	±16.23	±4.35	±5.89
	VC (%)	48.67	55.65	63.41	122.45	58.09	82.46
	Min	2.67	1.94	3.03	3.58	4.33	1.94
	Max	8.05	6.67	8.82	32.01	12.46	32.01
PBP	m	34.91	42.14	31.12	62.48	56.53	45.44
	s	±10.73	±23.25	±16.11	±27.55	±34.95	±9.49
	VC (%)	30.76	55.19	51.81	44.00	61.84	20.89
	Min	26.89	20.42	19.01	31.09	31.74	19.01
	Max	47.11	66.67	49.47	82.70	96.51	96.51
TP	m	34.33	34.83	42.53	56.48	68.22	47.28
	s	±17.61	±22.66	±17.54	±9.97	±12.45	±4.95
	VC (%)	51.32	65.06	41.23	17.66	18.26	10.48
	Min	22.20	13.90	27.40	23.75	50.20	13.90
	Max	59.00	37.85	61.75	85.35	101.15	101.15

HS: Hot Season; RS: Rainy Season; GCS: Great Cold Season; FS: Flood Season; SCS: Short Cold Season.

A) Hot season

B) Rainy season

C) Great cold season

D) Flood season

E) Small cold season
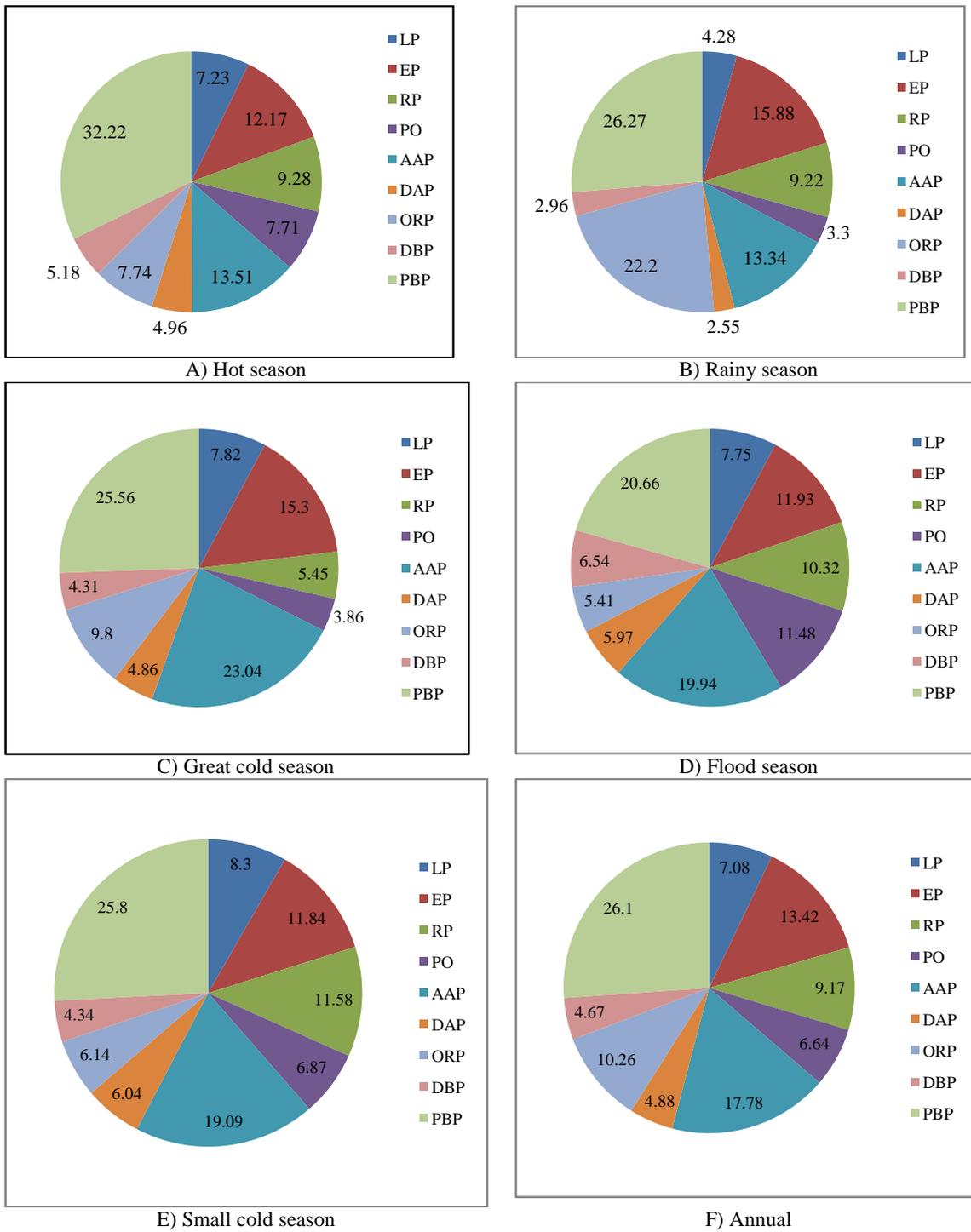
F) Annual

FIGURE 3: Seasonal and annual proportion of P fractions studied

The increasing order of seasonal and annual contents of different P fractions studied in sediments of Vridi Channel is as follows:

- Hot season: DAP < DPB < LP < PO < ORP < RP < EP < AAP <PBP;
- Rainy season: DAP < PO < DPB < LP < RP < AAP < EP < ORP < PBP;
- Great cold season: PO < DBP < DAP < RP < LP < ORP < EP < AAP < PBP;
- Flood season: ORP < RP < DAP < PO < DPB < LP < EP < AAP < PBP;
- Small cold season: PO < DBP < DAP < ORP < RP < LP < EP < AAP < PBP;
- Annual: DBP < PO < DAP < RP < LP < ORP < EP < AAP < PBP.

In seasons with high oceanic influences, seasonal contents of LP, DAP and PBP are relatively low in these sediments, particularly in rainy season for LP and DAP, and in great cold season for PBP. However, in seasons of high

influence of Comoé River on Vridi channel, their contents are relatively considerable, in particular in flood season, where they all present their maximum seasonal content. Their seasonal variations are relatively low over the study period. The importance of PO, ORP and DBP in these entities is observed in only one season, namely in rainy season for ORP and in flood season for DBP and PO. Their contents are relatively low in other seasons, with seasonal minima observed in hot season for ORP and in rainy season for DBP and PO. Their seasonal variations are all important over the study period. In contrast to PO, ORP, DBP, RP and AAP are relatively important in all seasons, except for great cold season for RP and in hot

season for AAP, with low seasonal variations over the study period. EP shows it's most important contents in these sediments in seasons when inland water contributions are significant in this estuary (rainy season, flood season, small cold season). This is especially true in flood season with the presence of Comoé River in this aquatic ecosystem. Its lower contents in these sediments are observed in great cold season, and especially in hot season. Its seasonal variations are also very low. TP gradually increases from hot season to small cold season with low seasonal variations. The seasonal recovery rate remains high over the entire study period (Table 3).

TABLE 3: Seasonal and annual recovery rate of P

Seasons	HS	RS	GCS	FS	SCS	Annual
R (%)	315.67	412.23	277.94	359.07	253.50	315.52

HS: Hot Season; RS: Rainy Season; GCS: Great Cold Season; FS: Flood Season; SCS: Short Cold Season

Assessment of the influence of some physical and chemical parameters on seasonal dynamics of P fractions studied

The first two factors of CAP express at 78.46% the information relating to seasonal variations of P fractions and physical and chemical parameters considered in this study (53.93% for F1 and 24.53% for F2) (Fig. 4). This result reflects the relevance of these physical and chemical parameters to the dynamics of these P forms. The highest eigenvalue of 8.90 is associated with F1, and the second eigenvalue of 3.68 is at F2. F1 highlights the opposition two seasonal groups, the one formed by rainy season and great cold season to the other formed by hot season and

small cold season. pH ($r = 0.66$), conductivity ($r = -0.74$), U ($r = -0.91$), LP ($r = -0.94$), PO ($r = -0.87$) , AAP ($r = -0.85$), PAD ($r = -0.97$), DBP ($r = -0.95$), PBP ($r = -0.94$) and RP ($r = -0.67$) are strongly correlated with F1. Thus, F1 would highlight the influence of pH, conductivity and U in the biogeochemistry of LP, PO, AAP, DAP, DBP, PBP and RP in these seasons. As concerning F2, it allows to distinguish clearly hot season to rainy season (Fig. 4B). Salinity ($r = -0.84$), moisture ($r = -0.86$), EP ($r = 0.82$) and RAP ($r = 0.82$) show a strong correlation with F2. This fact would show the impact of moisture and salinity on the biogeochemistry of EP and ORP in these two seasons (Fig. 4A).

A

B
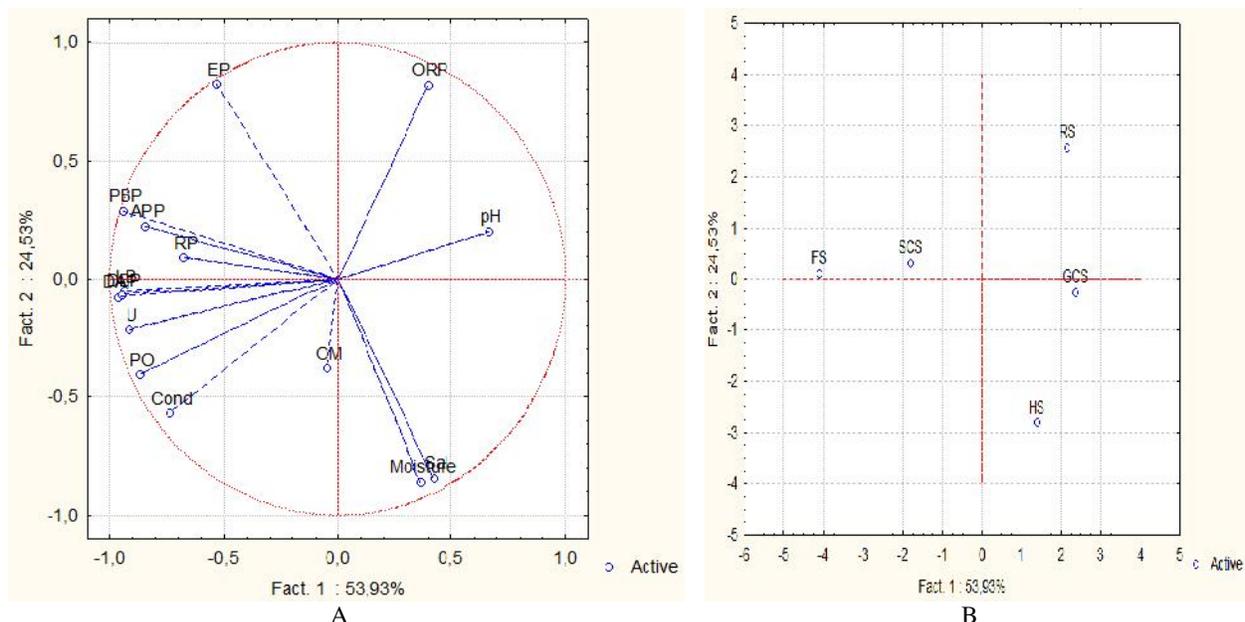
FIGURE 4: 2D projections of variables (A) and individuals (B).
Cond: Conductivity; OM: Organic Matter, Sal: Salinity.

The different Spearman coefficients show the existence of very strong correlations between LP and DBP ($r ' = 0.66$), LP and AAP ($r' = 0.65$), LP and PBP ($r '= 0.65$), U and EP ($r ' = 0.60$), DBP and PO ($r '= 0.71$), PBP and AAP ($r ' = 0.77$), DAP and PBP ($r '= 0.61$), DBP and PBP ($r'= 0.76$),

RP and PO ($r '= 0.58$), AAP and DBP ($r = 0.66$), AAP and PBP ($r = 0.77$), AAP and DAP ($r '= 0.75$).

DISCUSSION
In its design, Vridi channel should answer two major concerns: the realization of autonomous harbour of

Abidjan and the evacuation of solid wastes from various industries near this harbour to Atlantic Ocean. To prevent the rise of solid wastes in Ébrié system and avoid its rapid siltation, this estuary was oriented to South-East (in the direction of the canyon) at North-West, accentuated by the construction of discarded and wing walls, but also by a carpet fascinage weighted riprap (Monde *et al*., 2011; Wango *et al.,* 2015). This situation has evolved considerably with the population growth and the unprecedented development of human activities which has seen the village of Abidjan become the city of Abidjan then Abidjan district today. The discharges resulting from different anthropogenic activities are sources of many ecological problems, particularly the pollution of Ébrié system and Atlantic Ocean being among their main receptacles (Gnagne *et al*., 2015, Wognin *et al*., 2017). The majority of these discharges transit through Vridi channel which is the only pass between these two ecosystems. This fact is amplified by fluviatile contributions of Mé River, Agnéby River and especially Comoé River during their different flood seasons (Yao *et al*., 2017; Yao et Trokourey 2018a, 2018b). Most of sedimentary inputs in this channel are mainly of terrigenous origin because the presence of the canyon in front of this channel at the level of Atlantic Ocean prevents massive migration of marine sediments (Yao *et al*., 2018; N'Douffou *et al*., 2015). Thus, most of it comes from detrital organic matter from highly evolved terrigenous particles and/or plant debris from Ébrié system (Irié *et al*., 2018); to which would be added those resulting from the good mineralization of organic matter in this estuary, favored by physical and chemical conditions and the hydrosystem of this entitie (Yao and Trokourey, 2018b). They are dominated by silts, clays and coarse average sands (N'Douffou *et al*., 2015, Yao *et al*., 2017). This established fact would justify the relatively high abundance of PBP, but also the very low relative proportion of ORP in these sediments over the study period. The environmental conditions would also favor partial P remobilization from PBP. This would contribute to the formation of LP, DAP, DBP and especially AAP; if it is referred to strong correlations of these fractions with PBP on the one hand, and that between DAP and AAP on the other. The relatively high presence of AAP in its sediments, due to the marine character of this estuary (Yao *et al*., 2017), is thought to be more attributed to a precipitation of hydroxyapatite (Heindel *et al*., 2018). This reaction would be done in this case by the P absorption released from PBP, LP and DBP by $CaCO_3$, given strong correlations observed AAP with these P fractions. Relative low contents of DBP in these sediments observed during the entire study period can be explained by this reaction and by the partial conversion of this P form to PO and LP, again by the P remobilization in DBP. The strong correlations between PO and DBP, LP and DBP would illustrate this process. Due to the high presence of iron relative to manganese (Yao and Trokourey, 2018b), the majority of PO would consist of RP, as illustrated by the strong correlation between PO and RP. EP would come almost entirely from the degradation of organic matter, partly favored by the reducing nature of these sediments, as shown by the strong correlation between EP and U.

In seasons of high oceanic influences, contributions of meteorite runoff waters and those of Mé and Agnéby Rivers would enrich sediments of this channel in P. This nutrient input into these entities would increase with inflow of marine waters inflows from the great marine upwelling. This would justify the gradual increase of TP from hot season to great cold season. In hot season, most of P in this estuary comes from more or less evolved organic detritus of Ébrié system. This contribution would result in the observation of the lowest seasonal content of ORP in these sediments over the study period, as illustrated by CAP. This relatively low input would be affected by high biogeochemical reactions favored by the temperature and strong hydrodynamism of this estuary. These reactions lead to partial P remobilization and solubilization (Labry *et al*., 2013), but also to its sedimentation (Glaucia *et al*., 2015). Also, their very slightly basic character in this season would contribute to P remobilization in these P fractions, and cause its solubilization (Gaoa, 2012). This process would be achieved by reducing negative surfaces induced by their pH (Li *et al*., 2017; Noronha-D'Mello and Nayak, 2016, Wang *et al*., 2017). These reduced surfaces would be subject to high competition between major ions, due to their high presence (showed by the high conductivity of these sediments) induced by the high presence of marine waters in this estuary (Abdu and Mohammed, 2016, Zhao *et al*., 2013). This type of process would affect more PO, RP; and particularly AAP, which has its lowest seasonal content in these sediments over the study period in this season. For RP, the high presence of sulphide in this marine estuary (Yao and Trokourey, 2018b) would also help reduce its presence (Missong *et al*., 2018). Despite the relatively high reductive character of these sediments in this season, the high presence of chloride ions (Cl^-) would cause the P remobilization from EP (Nasrin *et al*., 2016), followed by its solubilization favored by a relative high moisture of these sediments in this period (Chagas *et al*., 2015, Abbasi *et al*., 2015). These processes would be shown by results obtained by CAP. In rainy season, meteorite runoff waters, Mé and Agnéby Rivers would take P mainly in particulate form, coming from both highly evolved organic detritus and soil erosion (geological origin). These contributions would explain the highest seasonal content of ORP in these sediments recorded this season. The organic detritus intake very highly evolved by these waters is confirmed by the growth of PBP, but also by the very low presence of DAP (its lowest annual seasonal content) in these sediments. As in rainy season, this estuary is also the site of high biogeochemical reactions. Correlatively, these contributions lead to a slight increase in the basic character of these sediments (Yao and Trokourey, 2018b). This increase should significantly increase the number of negative surfaces. In spite of this fact, pH would produce more of same effects as rainy season on all P fractions studied except DAP and EP, as shown by CAP. This pH effect would cause declines in RP, particularly LP, PO and DBP, which have their lowest annual seasonal content in this period. For AAP, the decrease in conductivity and salinity, due to these inputs, would partially inhibit the effect of pH and lead to an observed increase of its content in these sediments from hot season to rainy season. Also, these contributions in continental waters would cause there a modification of waters circulation in this estuary. This established fact would lead to a decrease in moisture and

salinity of these sediments in this season. The decrease of these two physical and chemical parameters would favor the high presence of DAP in this season, but also the relative growth of EP from hot season to rainy season, as illustrated by CAPN. Also, this phenomenon could explain the relative decline of LP in this season. In great cold season, waters of the great marine upwelling are cold, rich in carbonates and sulphides (Eric *et al*., 2018, Wang *et al*., 2018b). By water-sediment exchange favored by the strong hydrodynamism of this estuary, these waters would enrich these sediments by adding P that they would mainly transport in dissolved form. This would result in lower contents of PBP and ORP in these sediments of hot season to great cold season. The same effects observed in hot season would occur there but with relatively reduced amplitude. This would be due to the increase of reductive and basic characters, but also to decreases in salinity, conductivity and moisture of these sediments compared to hot season. This would justify an increase in the content of PBP, LP, PO, DAP and the high presence of AAP, which has its highest seasonal content in this season. Also, it would be explained the sharp decline of PBP, ORP, EP and especially of RP who presents its lower seasonal content in this season.

In flood season, due to its impressive watershed (Kouakou *et al.,* 2016, Ouattara *et al*., 2016), Comoé River would drain a high P influx, almost essentially in particulate matter from highly evolved organic detritus (Ouattara *et al.*, 2016). This situation would be demonstrated by the highest seasonal content of DBP and DAP in these sediments observed this season, but also by the quasi non variation of ORP from great cold season to flood season. This input would have a larger soluble fraction than would be provided by meteorite runoff waters, Mé and Agnéby Rivers in rainy season, which have a very small watershed with respect to Comoé River (Kouadio *et al*., 2010). This fact would contribute to the relatively important presence of DBP, AAP, and especially LP and EP who also present their maximal seasonal content in these sediments in this period. The character of the largest provider of trace metals in Ébrié system (Pottier *et al*., 2008) and Vridi channel (Yao *et al.,* 2017) of Comoé River is illustrated by the high presence of RP and especially PO, which also has its seasonal maximum content in this season; and those in spite of the high conductivity of these sediments induced by a high contribution of major ions by this river (Ouattara *et al*., 2016). In the presence of this river, it is observed the rise of cold marine waters during the small season of the marine upwelling in small cold season. These marine waters would bring P essentially in dissolved form as in great cold season. However, this contribution, less important than that of these waters in great cold season, would have same effects as that carried out in this season but with relatively low amplitudes and some nuances. This would be reflected by a relatively large decline in the seasonal content of PBP, AAP, PO, DAP, EP and DBP, the near-no variation of ORP and LP; and the relatively high increase of RP, having its maximum seasonal value in this season. The dynamics of these P forms are directly influenced by physical and chemical conditions of these sediments, affected by the advent of this river in these last two seasons. Indeed, because of its characteristics (slightly acidic, oxidizing, desalted, charged with major ions (Yao *et al*., 2017)), the presence of Comoé River leads to the

decrease of basic and reducing characteristics of these sediments, as well as their salinity and moisture, but increases their conductivity and the presence of organic matter. During these seasons, the very slightly basic character of these sediments would be unfavorable for all these P fractions with the exception of ORP and EP. As for the reduction of their reducing character simultaneously with the increase of their conductivity, they would increase the formation and/or the presence of DAP, LP, DBP and PO, but would inhibit those of PBP and AAP, as illustrated by CAP.

The high seasonal recovery rates obtained over the entire study period are explained by the underestimation of TP due to the acid digestion process (H_2SO_4) used in this study. Indeed, as in the case of assessment of trace metals in sediments (Durand et al., 2016, Xie et al., 2018, Wali *et al*., 2014), the high calcium content in these sediments (Yao and Trokourey, 2018a) would form precipitates, interfering with the implementation of process. In addition, whether TP and/or all of P fractions evaluated, their seasonal and annual levels are much lower than those obtained by Wedepohl (1995) in the continental upper continental crust (from 665 mg.kg^{-1} dry sediment). This would confirm the role of cleaning pollutants of continental origin to Atlantic Ocean assigned to this channel in its realization. As a result, most of P drained in this estuary would be in transit to the ocean, where it sediments (Liu and Chen, 2014, Ruttenberg, 2014). Nevertheless, the contents of these fractions, particularly those of DBP, would testify to eutrophication of this estuary, therefore of Atlantic Ocean coasts in front of Abidjan district.

CONCLUSION
This study has revealed that P essential present in this estuary is of anthropic origin. It comes almost entirely from highly evolved terrigenous particles and/or plant debris. This fact is shown by proportions of PBP that are the most important in these sediments over the entire study period. Whatever the season, P fractions and their distribution are important. These processes are due to high biogeochemical reactions that take place there, favored by physical and chemical conditions and the strong hydrodynamism of this estuary. This phenomenon knows a particular importance in the last seasons with the advent of Comoé River in this site. The conditions of this aquatic ecosystem favor P remobilization from these different fractions, followed by its solubilization and/or sedimentation. This channel is suspected to be hypereutrophic, given the relatively high content of PBD in these sediments. This could probably be the case of Atlantic Ocean coasts in front of Abidjan district. Therefore, this study could extend to the study of eutrophication of this ocean coasts. Also, distribution and fractionation of P could be considered in sediments of Atlantic Ocean coasts. It would be possible the study of phosphorus sorption on these sediments under particular conditions.

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