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Extracellular enzyme activities of estuarine mudflats in French Guiana in relation with environmental factors across spatial and seasonal scales

Mathieu Luglia^{a,*}, Stéven Criquet^a, Max Sarrazin^b, Daniel Guiral^a

ABSTRACT

The main aim of this study was to investigate the dynamic of extracellular enzyme activities within estuarine intertidal mudflats and to explore their potential environmental driving factors. Estuarine sliques of the main rivers of French Guiana were sampled during two annual contrasted hydro-climatic seasons (wet and dry) over a two-year period ($n = 38$). The spatio-temporal variability of four enzyme activities (alkaline phosphomonoesterase, arylsulfatase, β -glucosidase, urease) was assessed and physico-chemical analyses (dry bulk density, salinity, pH, carbon, nitrogen and sulfur content) of sediments were carried out. Results showed that the hydro-sedimentary specificities of each estuary, combined with the alternation of hydro-climatic seasons, had a strong influence on sediment physico-chemical characteristics. They revealed a gradient of mudflats under mainly continental versus marine influence. Mudflats under mainly continental influence were characterized by oligohaline pore-waters, more acidic pH and relatively high organic matter content, and conversely for sliques under mainly marine influence. Crossing of physico-chemical and functional data showed that the main factor associated with enzyme activities was the total nitrogen content. To a lesser extent, pH and organic carbon content were also related to enzyme activities, but these relationships could not be generalized to all enzymes. Moreover, relationships between enzyme activities and physico-chemical variables were not dependent on the mudflat types, except for the β -glucosidase which showed higher activity under mainly marine influence. Finally, relationships between enzyme activities and physico-chemical variables were not dependent on the seasons, except for alkaline phosphomonoesterase and urease activity, which showed opposite patterns according to seasons.

1. Introduction

Along the whole of the 1600 km of coastline extending from the Guiana Shield to the Orinoco Delta, the coastal oceanic currents are responsible for vast inputs of sediments ($1.5 \cdot 10^8 \text{ t y}^{-1}$; Eisma et al., 1991), carried down by the Amazon River, then discharged into the Atlantic Ocean where they form mobile mud banks (Froidefond et al., 1988; Allison et al., 2000). In the upper part of the intertidal zone of French Guiana, the deposition and maturation of these sediments lead to the formation of consolidated mud banks (Froidefond et al., 1988; Allison and Lee, 2004; Lefebvre et al., 2004; Anthony et al., 2010). In this general context of southeasterly-northwesterly sedimentary transport, the swells and tidal cycles towards the coast are the cause of intensive re-mobilization of these mud deposits, generating high hydro-sedimentary instability at regional-scale (Aller, 1998; Lefebvre et al., 2004). The alternation of hydro-climatic seasons and the

geomorphological characteristics of the various estuaries of French Guiana are additional sources of temporal and spatial variability of this hydro-sedimentary dynamic at estuary-scale. The physico-chemical characteristics of sediments and the biogeochemical processes within estuarine mudflats can therefore show strong spatio-temporal variations that derive from 1) alternations of bank exposure and immersion phases related to semidiurnal (low/high water), diurnal, and synodic (low/high astronomical tide) tidal cycles, 2) the intertidal mudflat dynamic impacted by seasonal cycles which determine rainfall regimes (Allison and Lee, 2001), and thus river and estuarine hydrology, and modulate the angle of incidence and intensity of swell to the coast (Guiral and Le Guen, 2012), and 3) the import/export balance of mineral, organic, dissolved and particulate materials from sedimentary deposits, modulated by the hydrological cycles of the rivers and tides (Aller et al., 2004; Allison and Lee, 2004; Lam-Hoai et al., 2006; Anthony et al., 2013).

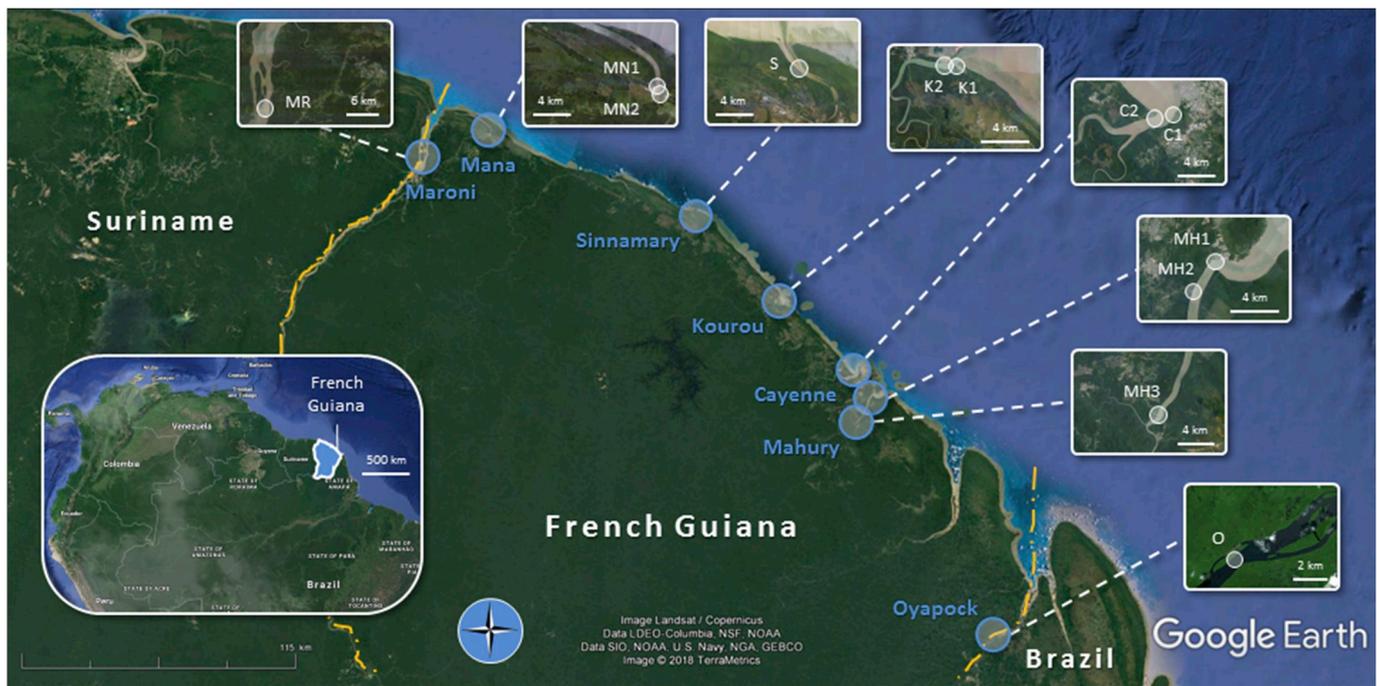


Fig. 1. Location of the study area, the 7 estuaries referred to as Maroni, Mana, Sinnamary, Kourou, Cayenne, Mahury, and Oyapock, and the 12 stations investigated in French Guiana (see also [Online Resource 1](#)). Sources: www.geoportail.gouv.fr; www.google.fr; Google Earth Pro.

The heterotrophic microbial communities and their extracellular enzymes are central actors in biogeochemical processes (Alongi, 1996; Dinesh et al., 1998; Holguin et al., 2001; Sjöling et al., 2005; Liu et al., 2008). The enzymes support essential functions of the transformation and recycling of organic matter (OM) in ecosystems. In particular, they play a major role in their functioning by ensuring the regulation of the bioavailability of many nutrients. Initially, the organic polymers are broken down into oligo- and monomers by the extracellular enzymes produced by the living cells, or released during cell death and lysis. These steps, requiring numerous hydrolytic enzymes, depend on the capabilities of heterotrophic microbial communities, and are considered as the most limiting in the bioelement cycles within marine sediments (Meyer-Reil, 1987). These enzyme activities provide microbial cells with the opportunity to acquire the necessary energy and mineral elements, in an assimilable form, for energy supply and biomass production (Rejmankova and Sirova, 2007). Thus, the multiple enzymatic systems are collectively involved in syntrophic interactions linking energy resource quality to microbial community metabolisms. In addition, these enzymes are involved at all trophic levels of ecosystems by allowing the organisms to ensure the essential functions of fixation, transformation and mineralization of the various bioelements constituting the living matter. The proliferation of saprotrophic microorganisms from particulate or dissolved OM determines the establishment of a food chain based on microbes (picoplankton) (Hoppe et al., 2002). This chain has a greater number of trophic levels and its involvement in food webs is particularly important in nutrient-poor environments such as oceans, marine sediments, freshwater lakes and streams. Therefore, the extracellular enzymes constitute a key component for the understanding of ecological functions and ecosystem services provided by estuarine environments. Therein, the study of enzyme activities involved in the biogeochemical cycles of carbon, nitrogen, phosphorus and sulfur offers the means to provide information on the dynamics of OM breakdown processes, nutrient recycling and energy flows in estuarine systems. Furthermore, while studies have been devoted to the microbial functional ecology of intertidal sediments, rarer are those focused on mangrove-fringed mudflats (Liu et al., 2008; Luglia et al., 2014).

The expression and conservation of enzyme activities in soils and sediments vary in space and time (Burns, 1978). Numerous environmental factors, such as water content, OM, substrate type and availability, texture, adsorption surfaces, temperature, pH, nature of primary producers or seasonality, are known to significantly influence enzyme expression in terrestrial and freshwater ecosystems (Cébron et al., 2011; Arnosti et al., 2014). However, significant associations of these factors with enzyme activities in marine ecosystems have still not been evidenced (Arnosti et al., 2014). Thus, the driving forces behind the observed variability in enzyme activity of microbial communities in marine ecosystems remain to be established (Arnosti et al., 2014). Furthermore, while such approaches are conventionally deployed for the assessment of soil fertility and health (Dick, 1997; Masto et al., 2008), they are seldom used for the study of estuarine sliks (Duarte et al., 2012), especially in the intertropical context.

This study fits into this conceptual framework, the aim being to investigate and understand the variability of microbial extracellular enzyme activities involved in the main biogeochemical cycles of estuarine systems of French Guiana. In a major effort to take into account spatial and seasonal variabilities, a wide range of estuaries were sampled during two annual contrasted hydro-climatic seasons (*i.e.* wet and dry) over a two-year period. This extended sampling campaign provided the opportunity to measure changes in microbial activity in the estuaries in relation with environmental factors across large spatial and seasonal scales. In particular, we sought to explore to what extent changing environmental factors may affect OM and nutrient cycling assessed through the activity of extracellular enzymes.

2. Materials and methods

2.1. Study sites

The study sites were established in 7 of the 9 estuaries of the major rivers of French Guiana. They extend from the Suriname border to that of Brazil (*ca.* 350 km), thus covering the entire coastal zone affected by the dispersal of freshwater and sediment inputs from the Amazon River, the estuary of which is situated about 400 km from the eastern border.

From west to east, these estuaries are: Maroni (MR), Mana (MN), Sinnamary (S), Kourou (K), Cayenne (C), Mahury (MH), and Oyapock (O) (Fig. 1). In the near-coastal zone, 12 stations were chosen among these 7 estuaries to include the various land-use effects of rivers (agricultural, urbanization and industrial impact), as well as the gradient from a freshwater to a marine ecosystem. They correspond to fringing intertidal mudflats (slikkes) of mangrove stands at various stages of development. From west to east and by estuary, these stations are: MR; MN1 and MN2; S; K1 and K2; C1 and C2; MH1, MH2 and MH3; O (Fig. 1).

2.2. Sediment sampling

The sampling campaign took place over a two-year period (2009–2010) during two annual contrasted hydro-climatic seasons characterizing the wet equatorial climate: a wet season (W, May to July) and a dry season (D, September to November). Locations and sampling dates of stations are given in [Online Resource 1](#). Each sediment sample ($n = 38$) was constituted of 5 sub-samples randomly collected from a 100 m² plot and pooled to form a composite sample. Each sub-sample corresponded to 1 m² from 0 to 0.5 cm sediment depth (surface sediment). Following sampling and homogenization, all composite samples were stored at 25 °C in darkness, except those for enzyme activity (4 °C), ammonium content (4 °C), and acid-volatile sulfide content (–20 °C) measurements.

2.3. Physico-chemical analyses of sediments

2.3.1. Dry bulk density and *in situ* water content

The sediment dry bulk density (ρ) and *in situ* water content were determined after drying 100 mL of sediment at 50 °C in a ventilated oven to a steady dry mass (DM). Then, the dry sediments were ground to 200 μ m and stored at 25 °C before use. The ρ is expressed in grams DM per milliliter of sediment.

2.3.2. pH, conductivity, and salinity

pH and conductivity were measured (inoLab[®] pH and Cond Level 2, WTW) in supernatant of a 1/2.5 (v/v) sediment/distilled water suspension. The salinity was measured using the Practical Salinity Scale. The salinity of *in situ* sediment pore-water was extrapolated from the slope of the linear regression between chloride concentration (automated colorimetric dosage with a continuous flow autoanalyzer Technicon II, mercuric thiocyanate reagent) and conductivity, and then adjusted to the initial sediment water content.

2.3.3. C, N, and S elemental analyses

20–50 mg DM of sediment (<200 μ m) was used for the determination of total C, N (TN) and S (TS) content carried out on a CHNS elemental analyzer (AS2100, ThermoQuest). Due to the almost total lack of carbonates in coastal sediments of French Guiana, total C can be attributed to the total organic C (TOC) ([Marchand et al., 2004](#); [Walcker et al., 2018](#)). The results are expressed in grams per kilogram DM of sediment (TOC, TN, and TS). The C:N molar ratio was computed from these contents.

2.3.4. Ammonium and acid-volatile sulfide content

The ammonium (NH₄⁺) content was measured according to the method of [Koroleff \(1969\)](#) as modified by [Grasshoff and Johannsen \(1972\)](#). 2 mL of sediment sample were suspended in 10 mL of 1 M acidified KCl solution, then agitated for 30 min at 3.8 Hz to extract NH₄⁺ ions, and finally centrifuged for 20 min at 2000 g. The dosage of NH₄⁺ was done on 2.5 mL of supernatant with 1 mL of phenol-prussiate reagent and 1 mL of alkaline dichloroisocyanurate reagent. At 6 h later in darkness, the absorbance was measured at 660 nm (spectrophotometer Specord 205, Analytik Jena).

The acid-volatile sulfide (AVS) content was measured according to

the methods of [Chaudhry and Cornfield \(1966\)](#), and [Rodier et al. \(1978\)](#). 20 mL of frozen sediment and 100 mL of degassed distilled water were placed in a glass flask under helium stream and heated at 60 °C during 1.5 h. After 5 min, 2 mL of a 4 M HCl solution were added. The AVS, displaced in the form of H₂S by the helium stream, was trapped in a 2 M zinc and sodium acetate solution and assayed by iodometry (potentiograph E 536, dosimat 665, Metrohm).

The results are expressed in milligrams per kilogram DM of sediment (NH₄⁺ and AVS).

2.4. Activities of extracellular enzymes

The enzyme activities assayed were alkaline phosphomonoesterases (AIP, EC 3.1.3.1, phosphate monoester mineralization, P cycle), arylsulfatases (ArylS, EC 3.1.6.1, sulfate ester mineralization, S cycle), β -glucosidases (β -glu, EC 3.2.1.21, cellobiose degradation, C cycle), and ureases (Ure, EC 3.5.1.5, urea mineralization, N cycle). The enzyme assays were performed in 3 replicates and one control (substrate added after incubation) for each sample. A unit (U) of enzyme activity was defined as micromoles of hydrolyzed substrate per minute. Results were obtained from calibration curves performed under the same experimental conditions as for incubations, and are expressed in mU (nmol.min⁻¹) per gram DM of sediment.

The AIP activity was assessed by measuring the *p*-nitrophenyl phosphate hydrolysis to *p*-nitrophenol (*p*-NP) according to the method of [Tabatabai and Bremner \(1969\)](#), using a modified universal buffer (MUB) pH 11 ([Tabatabai, 1994](#)). The ArylS activity was assessed by measuring the *p*-nitrophenyl sulfate hydrolysis to *p*-NP according to the method of [Tabatabai and Bremner \(1970\)](#). The β -glu activity was assessed by measuring the *p*-nitrophenyl β -D-glucopyranoside hydrolysis to *p*-NP according to the method of [Eivazi and Tabatabai \(1988\)](#). The Ure activity was assessed by measuring the urea hydrolysis to NH₄⁺ according to the method of [Kandeler and Gerber \(1988\)](#). Full details are given in [Luglia et al. \(2014\)](#).

2.5. Statistical analyses

A principal component analysis (PCA) was carried out to explore relationships among physico-chemical variables, and to display the distribution of observations ($n = 38$) along these variables. For the similarity matrix calculation, the Pearson correlation coefficient was used. From PCA, a mudflat typology was defined using TN, TOC, pH and salinity data. The clustering of stations (mudflat type) was done by the *pam* function of the cluster package version 2.0.6 ([Maechler et al., 2017](#)), using the square root of a Manhattan distance matrix after data standardization performed by the *daisy* function of the cluster package. The number of clusters was previously determined using the *clvalid* function of the *clvalid* package version 0.6–6 ([Brock et al., 2008](#)). Thereafter, a permutational multivariate analysis of variance (permanova), using the *adonis2* function of the vegan package version 2.5–2 ([Oksanen et al., 2018](#)), was performed on this matrix to test the effect of mudflat type factor on physico-chemical characteristics, with a permutation test ($n = 9999$) at a significance level of $p < .05$. Then, another permanova was performed to test the effect of season factor on physico-chemical characteristics, using mudflat types as strata within which permutations were constrained, with a permutation test ($n = 9999$) at a significance level of $p < .05$. Tests for homogeneity of multivariate dispersions were first done at a significance level of $p < .05$, using the *betadisper* function of the vegan package, which compare within-group spread among groups using average distances between individual observations and their own group centroid.

The Pearson correlation coefficients were used to assess the degree of linear relationship among physico-chemical variables and extracellular enzyme activities of mudflats ($n = 38$), at a significance level of $p < .05$.

In order to explore and to rank the environmental factors having

potential influences on extracellular enzyme activities of mudflats, linear models for each enzyme activity were built and estimated from quantitative (*i.e.* physico-chemical; ρ , pH, salinity, TOC, TN, NH_4^+ , TS, AVS) and qualitative (*i.e.* mudflat type and season factors; two levels each: CI and MI mudflats, and W and D seasons, respectively) variables. Beforehand, assumptions of linear models and collinearity among variables were checked. To select the 'best' subsets of explanatory variables and to obtain parsimonious and explanatory models, heuristic methods were used. To this end, stepwise selection procedures of variables were applied by minimization of a penalized criterion using the Akaike (AIC) or Bayesian (BIC) Information Criterion. The range of models examined in the stepwise search was from null model to full model without interaction.

All of these analyses were conducted using XLSTAT software version 2018.6 (Addinsoft), RStudio software version 1.1.453, and R software version 3.5.0 (R Core Team, 2018).

3. Results

3.1. Characteristics of estuarine systems

Hydrological (Table 1) and physico-chemical (Online Resource 2) data were used to determine the spatial and seasonal patterns of environmental characteristics of the seven estuaries, and to investigate the relationships between extracellular enzyme activities and estuary characteristics over time.

Hydrological characteristics indicate two distinct groups of rivers. Related to significant catchment area and length of rivers, the average discharges of the Maroni, Mana, Sinnamary and Oyapock rivers are far higher than those of the Kourou, Cayenne and Mahury rivers (Table 1). The alternation of wet and dry seasons, corresponding to flood and low water periods, results in major changes in the hydrological regime of rivers. In particular, the Kourou, Cayenne and Mahury rivers show extremely low discharges during the dry season and low water (Table 1).

Physico-chemical characteristics of intertidal mudflats showed broad patterns across spatial and seasonal scales (Figs. 2 and 3). The PCA highlighted a physico-chemical gradient depicted on PC1, accounting for 36.8% of total variance (Fig. 2a). It contrasted the sediment OM, represented by its TOC and TN content, with the pH and pore-water salinity. The TOC corresponded to the most contributive variable to this axis (27.9%) and was negatively correlated with the pH

($r = -0.66$, $p < .001$) and salinity ($r = -0.51$, $p < .01$) (Fig. 4). Strong positive correlations were observed between TN and TOC ($r = .85$, $p < .001$), and between salinity and pH ($r = .73$, $p < .001$) (Fig. 4). The station of Maroni, and to a lesser extent those of Mana, Sinnamary and Oyapock generally exhibited higher TOC and TN content, as well as higher C:N ratios than the stations of Kourou, Cayenne and Mahury (Figs. 2b and 3, Online Resource 2). Conversely, this distinction also occurred concerning pH and was far more marked for pore-water salinity (Figs. 2b and 3, Online Resource 2). The stations of Maroni, Mana, Sinnamary and Oyapock generally showed acid pH or close to neutrality and salinities from strictly continental to oligohaline waters (Fig. 3, Online Resource 2). In contrast, the stations of Kourou, Cayenne and Mahury generally presented alkaline pH or close to neutrality and salinities from meso- to ultrahaline waters. In addition, for the stations of Mana, Kourou, Cayenne and Mahury, an upstream-downstream gradient was observed. The upstream stations generally exhibited higher TOC and TN content, as well as higher C:N ratios, and lower pH and salinities than downstream stations (Fig. 3, Online Resource 2). Therein, physico-chemical characteristics of the station farthest upriver in the Mahury River (MH3) were quite similar to those of stations of Mana, Sinnamary and Oyapock. The clustering performed on physico-chemical characteristics evidenced two distinct groups of estuarine mudflats, depending on major continental versus marine influence (permanova, pseudo- $F_{1,36} = 13.3$, $p < .001$). A first group under mainly continental influence (CI mudflats, $n = 16$) was composed by MR, MN1, MN2, S, MH3, and O stations, and a second one under mainly marine influence (MI mudflats, $n = 22$) was composed by K1, K2, C1, C2, MH1, and MH2 stations (Fig. 2b).

Within this CI-MI mudflat distinction, a secondary differentiation occurred along this physico-chemical gradient depending on seasons (permanova, pseudo- $F_{1,36} = 2.3$, $p < .001$) (Fig. 2b). The TOC and TN content, as well as C:N ratios, generally decreased during the dry season, while the pH and salinities increased during this period (Fig. 3, Online Resource 2). For salinity, TOC and TN, this seasonal trend was differentiated between and within some estuaries. While a lack of variation (Maroni and Oyapock stations) or slight increases (Mana and Sinnamary stations) of salinity were observed between wet and dry seasons, huge seasonal salinity variations were recorded in the stations of Kourou, Cayenne and Mahury (Fig. 3, Online Resource 2). Concerning the TOC and TN content of Kourou, Cayenne and Mahury stations, this seasonal trend was not always evident due to generally low variations (Fig. 3, Online Resource 2). With higher TOC and TN content

Table 1

Hydrological characteristics of the seven rivers of French Guiana investigated and the Amazon River, the estuary of which is situated about 400 km from the eastern border of French Guiana.

River watershed	Monitoring station	Period	Discharge					Catchment area ¹	Length ¹	
			Average		Decennial					
			Inter-annual	Monthly		Specific	Flood	Low water	km ²	km
				May–June (W)	Oct–Nov (D)					
			m ³ .s ⁻¹			L.s ⁻¹ .km ⁻²	m ³ .s ⁻¹			
Maroni	Langa Tabiki	1950–2003	1672	3296–3280	477–376	27.4	6226	76	60,930	612
Mana	Saut Sabbat	1953-62/1967–77/ 1985-2003	315	565–568	113–122	30.7	1268	27.1	10,225	462
Sinnamary	Petit-Saut ²	1982–93	237	439–378	103–117	40.3	1095	40	5880	290
Kourou	Upstream ^{3,4}	2005	85	1687–1488	48.2–49.6	42.5	10	10	2000	144
Cayenne	Tonnégrande - ONF	1992–2003	7.2	17.0–14.5	1.6–3.1	55.8	67	0.47	129	44
Mahury	Comté - Saut Bief	1969–2003	101	199–164	32–38	57.4	502	8.7	1760	169
Oyapock	Saut Maripa	1953–2003	832	1687–1488	241–199	33.1	3514	78	25,120	403
Amazon	Óbidos	1902–99	163,000	213,500–224,000	109,400–104,200	34.7	260,000	78,000	4,676,000	6500

After Callède et al. (2002), Monfort and Ruf (2005); ¹, in French Guiana; ², station flooded during the impoundment of the dam; ³, Adèle et al. (2006); ⁴, Radoux and Parizot (2012); W, D, wet and dry seasons, respectively; *italic values*, min or max monthly average discharge over an annual hydrological cycle.

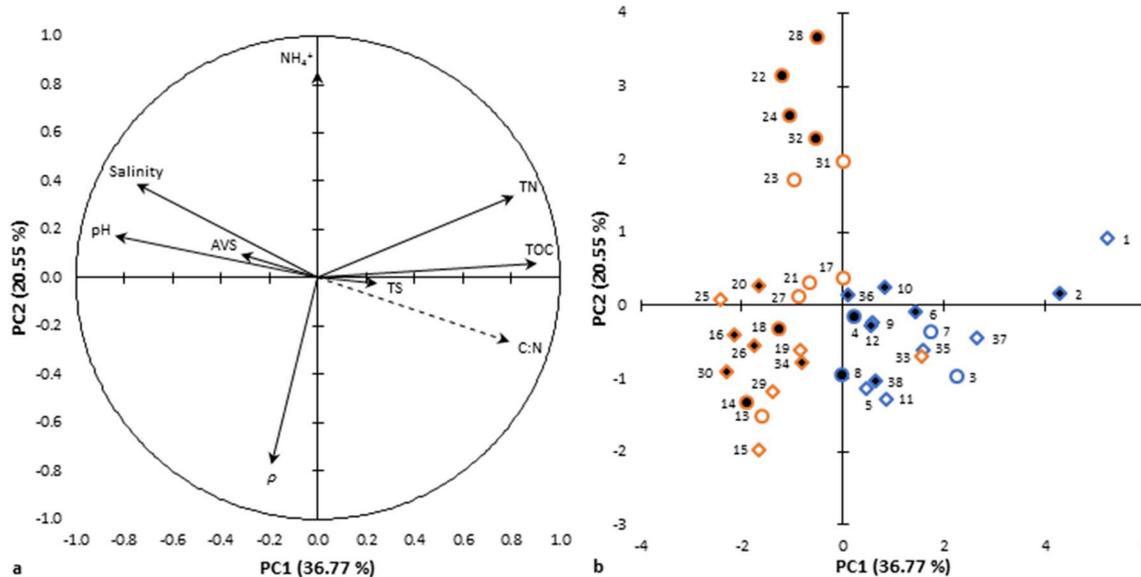


Fig. 2. Principal component analysis (Pearson) on physico-chemical characteristics of mudflats accounting for 57.3% of total variance. **(a)** Factorial map of variables with correlation circle; hatched arrow, illustrative variable (C:N); ρ , dry bulk density; TOC, total organic carbon; TN, total nitrogen; TS, total sulfur; AVS, acid-volatile sulfide. **(b)** Factorial map of observations ($n = 38$); circle, 2009; diamond, 2010; white font, wet season; black font, dry season; blue outline, mudflats under mainly continental influence (CI, $n = 16$), orange outline, mudflats under mainly marine influence (MI, $n = 22$); numbering corresponds to observations; 1–2, MR station; 3–6, MN1 station; 7–10, MN2 station; 11–12, S station; 13–16, K1 station; 17–20, K2 station; 21–22, C1 station; 23–26, C2 station; 27–30, MH1 station; 31–34, MH2 station; 35–36, MH3 station; 37–38, O station (see also [Online Resource 2](#)). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

in dry than in wet seasons, the seasonal pattern even seemed to be reversed in downstream stations of Kourou (K1) and Mahury (MH1) and in both stations of Cayenne (C1, C2).

The PCA also contrasted the NH₄⁺ content with the dry bulk density (ρ) on PC2, accounting for 20.6% of total variance (Fig. 2a). The NH₄⁺ corresponded to the variable most strongly contributive to this axis (44.3%) and was weakly and negatively correlated with the ρ ($r = -0.45$, $p < .01$) (Fig. 4). This axis, disconnected from spatial and seasonal patterns depicted on PC1, mainly highlighted relatively very high NH₄⁺ content, ranging from 163 to 305 mg kg⁻¹ DM, in stations C1, C2, MH1 and MH2 of Cayenne and Mahury estuaries during the year 2009 (Fig. 2b, [Online Resource 2](#)).

3.2. Extracellular enzyme activities

Significant positive correlations were observed among enzyme activities, the ArylS and β -glu showing the highest correlation ($r = .64$, $p < .001$) (Fig. 4). However, the Ure was not significantly correlated with the ArylS and AIP. Results showed that the average activity levels varied among enzymes in the order Ure » AIP » ArylS \approx β -glu (Fig. 5). Ure and AIP activities also exhibited higher variations than the other two (Fig. 5). Extracellular enzyme activities of intertidal mudflats showed broad patterns across spatial and seasonal scales (Fig. 5). Overall, the average activity levels were similar between CI and MI mudflats (Fig. 5). The Maroni station stood out from the others with the highest average ArylS and β -glu activity levels (Fig. 5, [Online Resource 3](#)). For Mana, Kourou, Cayenne and Mahury stations, an upstream-downstream gradient was observed for all enzyme activities. The upstream stations generally exhibited higher enzyme activities than downstream stations (Fig. 5, [Online Resource 3](#)). Overall, seasonal trends were also evidenced. The ArylS, β -glu and Ure activities were generally higher in dry than in wet seasons, this trend being far more marked for Ure (Fig. 5, [Online Resource 3](#)). In contrast, the AIP activity was frequently lower in dry than in wet seasons, especially varying widely for the stations MR and MN2 of Maroni and Mana estuaries. If these seasonal trends were evident for the Mana, Sinnamary and Mahury estuaries, they were far less so for the other estuaries,

especially the Maroni which showed consistently lower activities in dry than in wet season (Fig. 5, [Online Resource 3](#)).

3.3. Extracellular enzyme activities versus environmental factors

Firstly, simple linear correlations between enzyme activities and physico-chemical variables were performed (Fig. 4). The AIP was significantly and positively related with the TN ($r = .55$, $p < .001$) and NH₄⁺ ($r = .40$, $p < .05$) content. The ArylS showed significant positive correlations with the TOC ($r = .82$) and TN ($r = .87$) content (both $p < .001$) and the C:N ratio ($r = .43$, $p < .01$), as well as a significant negative correlation with the pH ($r = -0.34$, $p < .05$). Significant and positive relationships were observed between the β -glu and TOC ($r = .53$) and TN ($r = .65$) content (both $p < .001$). Finally, no significant association between the Ure and physico-chemical variables was observed.

Secondly, results obtained from multivariate linear models showed that the TN content was significantly and positively related with all enzyme activities (Table 2). It was also the factor most strongly contributive to the variance explained by the models of AIP, ArylS and β -glu. The TOC was also significantly and positively related with the ArylS, as well as the pH with the AIP and ArylS. Spatially, results showed that the relationships between AIP, ArylS, and Ure and physico-chemical variables were not dependent on the mudflat type under mainly continental (CI) versus marine influence (MI). In contrast, results indicated that after controlling for the effect of the TN, there was a significant difference between CI and MI mudflats with respect to the activity level of β -glu ($F_{1,35} = 4.2$, $p < .05$); the MI mudflats showing a higher β -glu activity level than the CI mudflats (Table 2). Seasonally, results showed that the relationships between ArylS and β -glu and physico-chemical variables were not dependent on the season. In contrast, results indicated that after controlling for the effects of the physico-chemical variables, there was a significant difference between dry and wet seasons with respect to the activity levels of AIP ($F_{1,34} = 5.2$, $p < .05$) and Ure ($F_{1,35} = 13.0$, $p < .001$) (Table 2). However, this seasonal effect resulted in opposite patterns of enzyme activities, the dry season showing a lower AIP and a higher Ure activity level than the wet season.

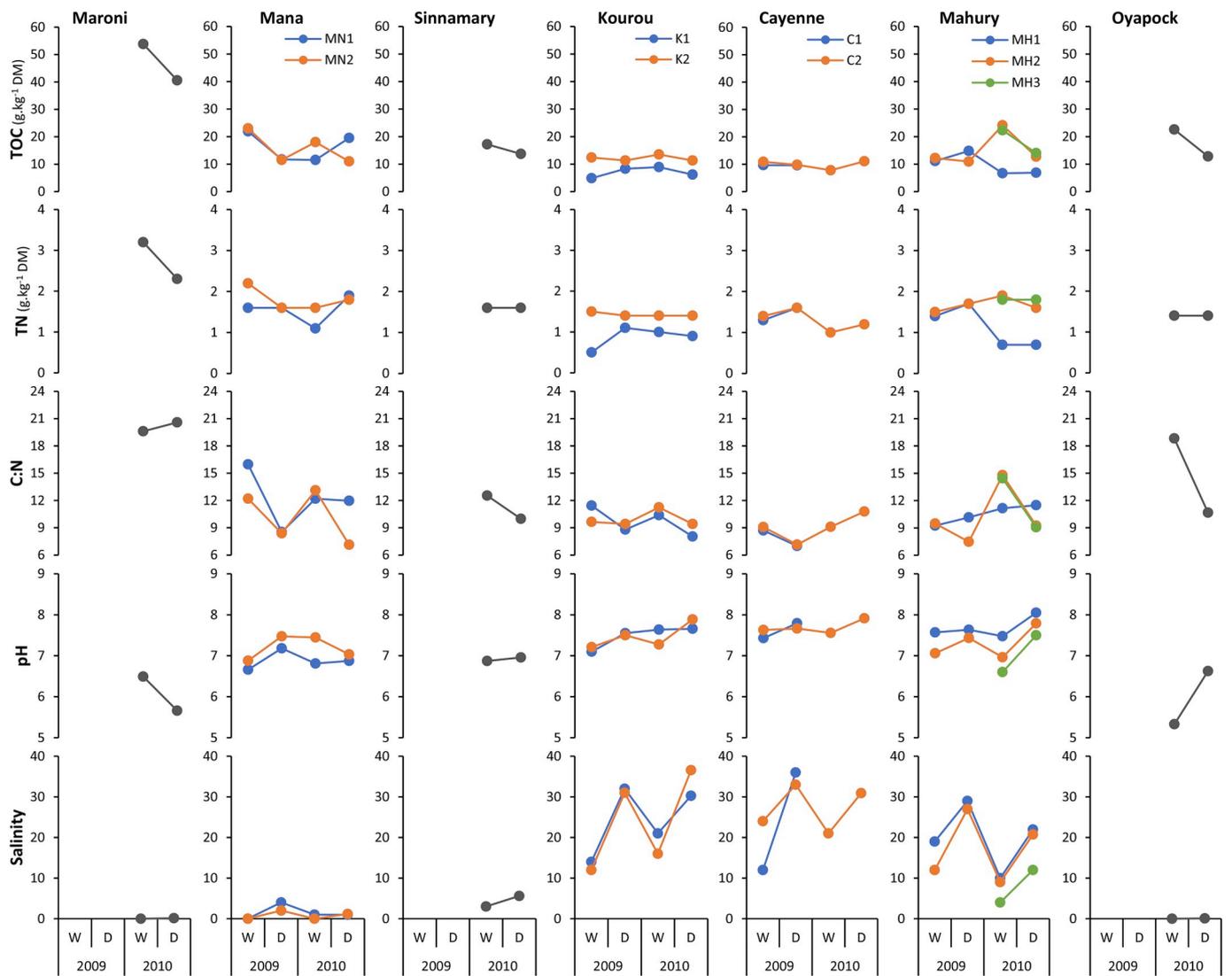


Fig. 3. Total organic carbon (TOC) and nitrogen (TN) concentrations, C:N ratio, pH and pore-water salinity of mudflats over time. Lines connect consecutive sampling periods (seasons); DM, dry mass; W, D, wet and dry seasons, respectively.

4. Discussion

4.1. Typology and dynamic of estuarine intertidal mudflats

The study of physico-chemical characteristics of mudflat surface slurries made it possible to identify two types of estuarine intertidal mudflats in French Guiana. The first type of mudflats showed oligohaline pore-waters (median of 1) and sediments close to neutrality (6.9) with relatively high OM content (17.6 and $1.6 \text{ g kg}^{-1} \text{ DM}$ for TOC and TN). In contrast, the second type of mudflats exhibited meso- to ultrahaline pore-waters (22) and alkaline sediments (7.6) with relatively low OM content (10.9 and $1.4 \text{ g kg}^{-1} \text{ DM}$ for TOC and TN). This broad spatial distinction reflected different degrees of influence of marine and continental inputs to estuarine systems. At estuary scale, this was naturally modulated according to the location of mudflats along the upstream-downstream gradient. These degrees of influence mainly depended on river hydrology and estuary geomorphology. The mudflats identified as being mainly under continental influence (CI mudflats) actually belonged to the Maroni, Mana, Sinnamary and Oyapock rivers, which exhibited significant catchment areas and lengths and therefore high average discharges. Conversely, the mudflats located in estuaries of the Kourou, Cayenne and Mahury rivers, of relatively short length, draining smaller areas and therefore of very low discharges, were

mainly under marine influence (MI mudflats).

The alternation of wet and dry seasons, corresponding to flood and low water periods, resulted in profound changes in the hydrological regime of rivers, and consequently seasonal shifts in the physico-chemical characteristics of mudflats. The impact of these hydro-climatic seasons on the physico-chemistry of CI and MI mudflats was similar. In contrast, the amplitude of the induced variations was different according to the type of mudflats and was primarily determined by the level of river discharge; the Kourou, Cayenne and Mahury rivers of the MI mudflats exhibited extremely low discharges during the dry season and low water.

The higher pH and pore-water salinities observed during the dry season reflected lower freshwater contributions to estuaries by (i) the rivers while in low water period, and by (ii) the reduced rainfall at that time of the year, which also contributed to higher evaporation during the intertidal mudflat exposure phase at low tide. The TOC content, of which the range was very wide, was on average higher than that observed for Amazonian muds transiting along the coastline of French Guiana (Aller and Blair, 2006). The C:N ratios of CI mudflats (median of 12.2) denoted detrital OM of mixed origin, with both marine and continental inputs by tides and rivers. However, the low C:N ratios of MI mudflats (9.4) characterized detrital OM predominantly of marine origin and enriched with proteinaceous material (Meyer-Reil, 1987).

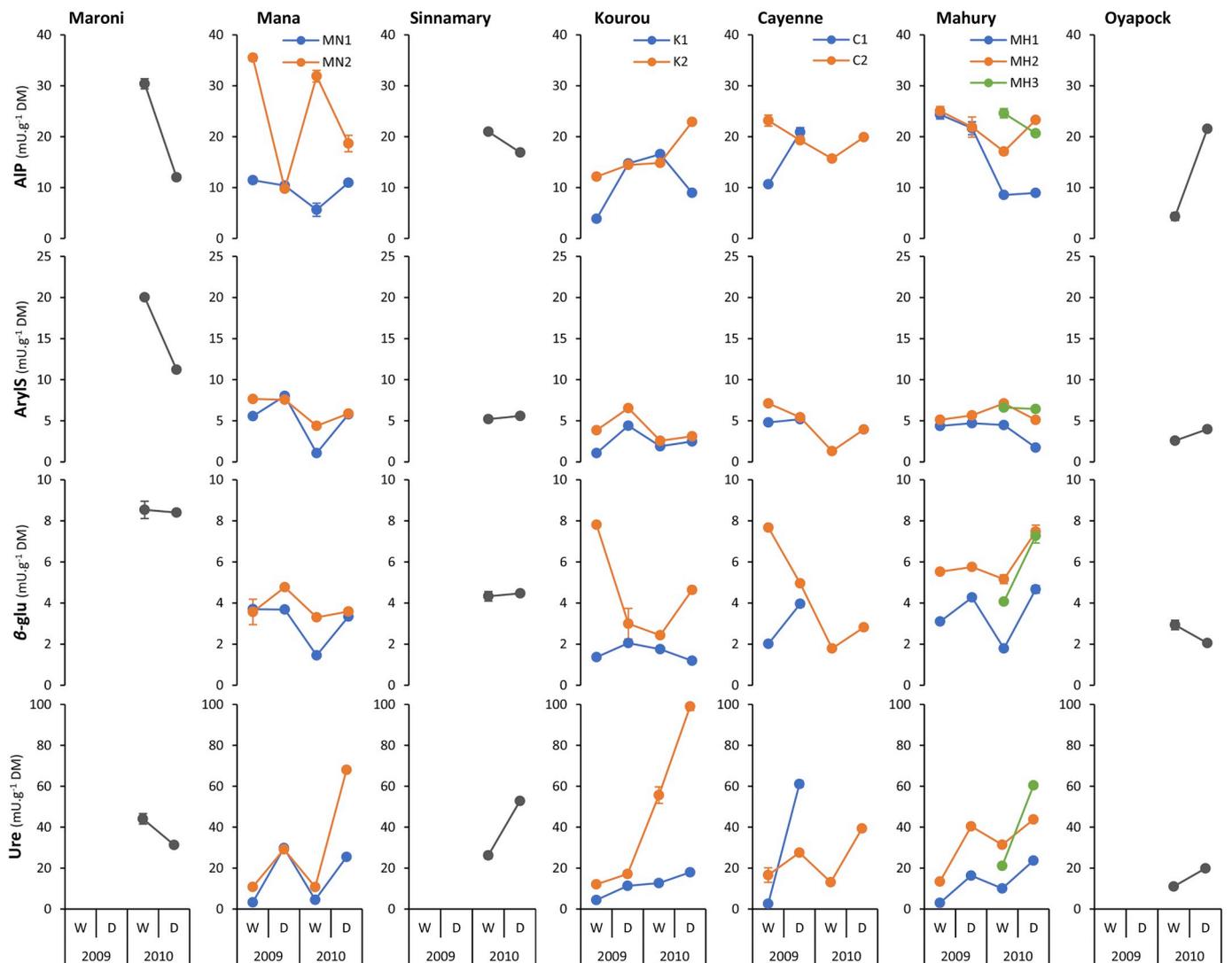


Fig. 5. Extracellular enzyme activities of mudflats over time. Symbols depict means ($n = 3$) with standard deviations (in brackets); lines connect consecutive sampling periods (seasons); AIP, alkaline phosphomonoesterase; ArylS, arylsulfatase; β -glu, β -glucosidase; Ure, urease; mU, nanomoles of hydrolyzed substrate per minute; DM, dry mass; W, D, wet and dry seasons, respectively.

organic matter, reflecting internal production of N-rich organic matter, while total organic carbon would include both labile and refractory organic compounds of various origins in estuarine systems. Moreover, the OM of mudflats under mainly marine influence was found to be predominantly of marine origin and enriched with proteinaceous material, while an OM of mixed origin with both marine and continental inputs from tides and rivers was observed for mudflats under mainly continental influence.

As a corollary, another interesting result was that the functional relationship between β -glucosidase activity and total nitrogen content was dependent on the mudflat types; the mudflats under mainly marine influence showing higher activity levels than those under mainly continental influence. This finding may suggest a control of β -glucosidase activity by the sediment OM quality, as observed in the supratidal part of mudflats (Luglia et al., 2014). In such marine environments, the OM quality shows a wide diversity of initial carbon structures (Wakeham et al., 1997) along with a significant imprint of primary producers (Luglia et al., 2014). In French Guiana, the intertidal mudflat surfaces are colonized at low tide mainly by microphytobenthic diatoms (Sylvestre et al., 2004; Debenay et al., 2007). These communities are known to produce large amounts of extracellular polymeric substances (EPS), consisting of polysaccharides and glycoproteins (Smith and

Underwood, 1998; Underwood and Smith, 1998; Taylor et al., 1999; Haynes et al., 2007), resulting in the formation of biofilms at the water/air-sediment interface. Because of life traits of these microalgae, this OM is found exclusively concentrated within the surface sediments of intertidal mudflats (Decho, 1990, 2000; Underwood et al., 1995; Goto et al., 2001; Debenay et al., 2007). Thus, the β -glucosidase substrates may originate in part from EPS produced by mobile phytobenthic diatoms during the daytime bank exposure phases. Moreover, it has been shown that the EPS produced by the diatom biofilms could induce similar effects to rhizodeposits, leading to an increase of β -glucosidase activity in the sediments (Hiroki et al., 2007). These labile compounds, readily biodegradable, did indeed constitute preferred energy and carbon sources for the microbial communities (Sala et al., 2005, 2008; Oliveira et al., 2010). Conversely, the mudflats more subjected to continental inputs from fringing mangroves and, further upstream, from forest stands drained by the rivers, generally exhibit an OM of lower quality and more recalcitrant to microbial degradation (i.e. low nitrogen content, high tannin amount), and therefore the expression of mineralizing functions can be considerably slowed down in such environments. Thereby, the qualitative variations of energy and carbon sources observed would explain this distinction of β -glucosidase activity levels depending on the mudflat type.

Table 2
Results of linear models on extracellular enzyme activities of mudflats.

<i>AIP</i>	<i>Source</i>	<i>df</i>	<i>SS^{III}</i>	<i>MS</i>	<i>F</i>	<i>p</i>	ω^2/ω_p^2
R² .566	Model	3	20.9	7.0	14.8	< .0001	.521
	pH	1	9.3	9.3	19.6	< .0001	.329
	TN	1	19.6	19.6	41.4	< .0001	.515
	Season	1	2.4	2.4	5.2	.030	.099
	Error	34	16.1	.5			
	Corrected total	37	37.0				
	<i>Parameter</i>	<i>Estimate [95% Conf Int]</i>			<i>SE</i>	<i>t</i>	<i>p</i>
	Intercept	-.269	[-.600; .061]		.163	-1.7	.107
	pH	1.028	[.556; 1.499]		.232	4.4	< .0001
	TN	1.727	[1.181; 2.272]		.268	6.4	< .0001
	Season-D	0 ^c					
	Season-W	.539	[.057; 1.021]		.237	2.3	.030
	<i>Season</i>	<i>Mean [95% Conf Int]</i>			<i>SE</i>		
	D ^a	-.269	[-.600; .061]		.163		
	W ^b	.269	[-.061; .807]		.163		
<i>ArylS</i>	<i>Source</i>	<i>df</i>	<i>SS^{III}</i>	<i>MS</i>	<i>F</i>	<i>p</i>	ω^2/ω_p^2
R² .808	Model	3	29.9	10.0	47.6	< .0001	.786
	pH	1	1.2	1.2	5.8	.021	.113
	TOC	1	2.1	2.1	9.8	.004	.189
	TN	1	2.4	2.4	11.6	.002	.219
	Error	34	7.1	.2			
	Corrected total	37	37.0				
	<i>Parameter</i>	<i>Estimate [95% Conf Int]</i>			<i>SE</i>	<i>t</i>	<i>p</i>
	Intercept	.000	[-.151; .151]		.074	.0	1.000
	pH	.442	[.070; .815]		.183	2.4	.021
	TOC	.060	[.021; .099]		.019	3.1	.004
	TN	1.058	[.428; 1.688]		.310	3.4	.002
<i>β-glu</i>	<i>Source</i>	<i>df</i>	<i>SS^{III}</i>	<i>MS</i>	<i>F</i>	<i>p</i>	ω^2/ω_p^2
R² .479	Model	2	17.7	8.9	16.1	< .0001	.442
	TN	1	17.2	17.2	31.3	< .0001	.443
	Type	1	2.3	2.3	4.2	.049	.077
	Error	35	19.3	.6			
	Corrected total	37	37.0				
		<i>Parameter</i>	<i>Estimate [95% Conf Int]</i>			<i>SE</i>	<i>t</i>
	Intercept	-.334	[-.747; .079]		.203	-1.6	.109
	TN	1.660	[1.057; 2.262]		.297	5.6	< .0001
	Type-CI	0 ^c					
	Type-MI	.578	[.002; 1.153]		.283	2.0	.049
	<i>Type</i>	<i>Mean [95% Conf Int]</i>			<i>SE</i>		
	CI ^a	-.334	[-.747; .079]		.203		
	MI ^b	.243	[-.101; .587]		.170		
<i>Ure</i>	<i>Source</i>	<i>df</i>	<i>SS^{III}</i>	<i>MS</i>	<i>F</i>	<i>p</i>	ω^2/ω_p^2
R² .343	Model	2	12.7	6.4	9.2	.001	.300
	TN	1	3.2	3.2	4.6	.040	.086
	Season	1	9.0	9.0	13.0	.001	.240
	Error	35	24.3	.7			
	Corrected total	37	37.0				
		<i>Parameter</i>	<i>Estimate [95% Conf Int]</i>			<i>SE</i>	<i>t</i>
	Intercept	.488	[.100; 1.195]		.876]	.191	2.6
	TN	.613	[.030; 1.195]		.287	2.1	.040
	Season-D	0 ^c					
	Season-W	-.976	[-1.526; -.427]		.271	-3.6	.001
	<i>Season</i>	<i>Mean [95% Conf Int]</i>			<i>SE</i>		
	W ^a	-.488	[-.876; -.100]		.191		
	D ^b	.488	[.100; .876]		.191		

Enzyme activities (dependent variables) were normalized ($n-1$) and physico-chemical data (independent variables) were centered; R^2 , R-squared; df , degrees of freedom; SS^{III} , type III sum of squares; MS , mean square; F , F-ratio; p , p-value; ω^2/ω_p^2 , omega-squared and partial omega-squared (size effect); *Conf Int*, confidence interval; *SE*, standard error; t , t-ratio; *TN*, total nitrogen; *TOC*, total organic carbon; *W*, *D*, wet and dry seasons, respectively; *CI*, *MI*, types of mudflats under mainly continental or marine influences, respectively; *bold values*, significant at $p < .05$; ^a, ^b, significant difference in mean enzyme activity between seasons or mudflat types at $p < .05$; ^c, this parameter is set to zero because it is redundant.

Urease and alkaline phosphomonoesterase activities were also found to be related to seasonality but interestingly this resulted in opposite patterns in enzyme activities. The dry season, featuring reduced rainfall and minimum river discharge, is conducive to marine ingress and therefore to inputs by sedimentation of OM essentially of marine origin, mainly proteinaceous (Mayer, 1989; Wakeham et al., 1997), and of relatively high nitrogen content. In this context, a stimulation of urease activity was observed; urea being one of the intermediates of amino-acid degradation (urea cycle), including the amino-acids of proteins and nitrogenous bases of nucleic acids, as energy and nitrogen sources for the microorganisms. The same seasonal pattern was also reported from another estuarine system where, moreover, the urease activity exhibited a negative correlation with the C:N ratio, and was found to relate closely with the gross nitrogen mineralization rate (Li et al., 2015; Lin et al., 2016). Thus, it appears that the variability in urease activity observed may relate to changes in nutrient availability and OM characteristics (as discussed above), which are mediated by the alternation of seasons through its impact on estuarine hydrology. On the other hand, in response to changes in hydro-climatic conditions (e.g. longer bank exposure phase) and OM characteristics during the dry season, the structure and composition of benthic communities (e.g. microbial, algal) may fluctuate and potentially affect the activity of urease (as discussed above) and other enzymes (Costa et al., 2007). During the wet season, high rainfall and river discharge occur, leading to significant inputs of organic, inorganic, dissolved and particulate materials to estuaries by river runoff and flood, which also cause intensive re-mobilization of mud deposits. In this context, higher alkaline phosphomonoesterase activities were observed; the organic phosphorus compounds serving as energy and phosphate sources for the microorganisms through enzyme hydrolysis of phosphate monoesters into orthophosphate and OM. This suggests an important seasonal contribution to phosphate estuarine production and enrichment of coastal waters by alkaline phosphomonoesterase activities. This is an interesting result, given that production of phosphate by microbial mineralization of organic phosphorus compounds is rarely considered as a potential source of phosphate in estuaries, studies rather focusing on physico-chemical processes especially concerning the mineral particulate phases of phosphate (Labry et al., 2016). Without data on the phosphate concentrations in estuaries, alkaline phosphatases being a mainly inducible enzyme for which the induction or repression mechanisms of their synthesis are regulated by substrates or end-product availability or depletion (Chróst, 1990), the factors underlying these variations remain uncertain. However, one can hypothesize that higher alkaline phosphomonoesterase activities could be related to high amounts of suspended material during the wet season, with particle-attached bacteria. The importance of particle-attached bacteria in the occurrence of high alkaline phosphomonoesterase activities has been reported from other marine environments (Smith et al., 1992; Zoppini et al., 2005; Labry et al., 2016). Moreover, the attachment of bacteria to particulate OM is thought to be an important factor in the induction of alkaline phosphatase synthesis, and more broadly the starting point for synthesis of enzyme pools to decompose OM, leading to an enrichment of the surrounding waters in hydrolysates supporting the productivity of estuarine systems (Smith et al., 1992; Labry et al., 2016). Similarly, the adsorption of phosphatases onto mineral surfaces, especially clays, may also have contributed to high alkaline phosphomonoesterase activities in estuaries during the wet season.

Finally, alkaline phosphomonoesterase and arylsulfatase activities were also related with the pH. Concerning the alkaline phosphomonoesterase activity, a positive correlation was observed, as reported in other studies (Turner and Haygarth, 2005; Wang et al., 2014). pH can act as a control factor of microbial activity and enzyme synthesis (Frankenberger and Johanson, 1982) along with microbial diversity (Bååth and Anderson, 2003; Fierer and Jackson, 2006). The effect of pH on the activity kinetics of phosphomonoesterases in alkaline soils has been demonstrated by Eivazi and Tabatabai (1977); the pH effect of the

soil-buffer mixture ranging from 4 to 12, leading to an increase in activity until reaching an optimum for a pH close to 10. For arylsulfatase activity, the relationship with the pH, a proxy of marine influence closely associated with salinity, was unclear since both positive and negative correlations were observed. This enzyme catalyzes the hydrolysis of phenolic sulfate esters; substrates widespread within sediments and which may represent up to 30% of total sulfur content (King and Klug, 1980). A negative relationship with the pH was expected as it is well known that with regard to the sediment pore-water quality, in particular, the increase of pH and salinity may exert a negative feedback both on the enzyme and its synthesis by microorganisms (Fitzgerald and Cline, 1977; King and Klug, 1980; Ash and Fitzgerald, 1982; Roy and Williams, 1989; Ganeshamurthy and Nielsen, 1990).

5. Conclusions

This study addresses a conceptually important topic as understanding the dynamic of extracellular enzyme activities involved in the main biogeochemical cycles and their relationships with environmental factors is a crucial factor in organic matter and nutrient cycling, food webs and productivity of coastal regions. In this framework, our aim was to investigate and understand some of the complexities of these interactions in highly dynamic estuarine systems specific to French Guiana across wide spatial and seasonal scales.

For the whole set of descriptive variables studied, wide spatio-temporal variations in the physico-chemical characteristics of estuarine mudflats have been recorded. Results showed that the hydro-sedimentary specificities of each estuary, combined with the alternation of hydro-climatic seasons, were environmental factors having strong influences on physico-chemical characteristics of mudflats and are the basis for their distinction in two types according to a continental versus marine influence gradient. Mudflats under mainly continental influence were characterized by oligohaline pore-waters, more acidic pH and relatively high organic matter content, and conversely for slikkes under mainly marine influence.

The total nitrogen content, relating to relatively more labile OM, appeared as the main environmental factor related to all enzyme activities involved in the sediment OM mineralization, and thus, more broadly, in the CNPS biogeochemical cycles. The organic carbon content and pH have been also identified as factors potentially involved in the regulation of these enzyme functions, but they could not be generalized to all enzymes studied. Moreover, it has been shown that the relationship between β -glucosidase activity and total nitrogen content was dependent on the mudflat type, the mudflats under mainly marine influence showing higher activity levels than those under mainly continental influence. This finding may suggest the control of β -glucosidase activity levels by the sediment OM quality. In particular, the phyto-benthic communities, via their EPS production, and more broadly the benthos (phytobenthos, meio- and macrofauna), via their biomass and bioturbation activity, would be expected to be directly involved in these dynamics and qualitative variations of sediment OM. Finally, it has been shown that the relationships between alkaline phosphomonoesterase and urease activities and physico-chemical variables were dependent on the seasons; alkaline phosphomonoesterase activity being lower during the dry season, and conversely for the urease activity.

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