Linking sediment biodegradability with its origin in shallow coastal environments

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Abstract

In coastal areas and estuaries, such as those encountered in the western part of France (Brittany region), the recycling of carbon and nutrients from sediments can participate in the development of micro and macro-algal

15   blooms with harmful consequences for these ecosystems. One of the main processes controlling this recycling is the microbial mineralization of sedimentary organic matter (SOM). Mineralization is controlled by the origin, quantity and accessibility of the SOM, three factors whose relative importance remain, however, poorly quantified, mainly due to the great diversity of OM sources in coastal areas. The first objective of the present work was to assess the variability of the SOM origin at the regional scale representative of the complexity of the sources likely

20   to be involved. The second objective was to determine the link between the SOM origin and its biodegradability, and how the OM sources can drive nutrient dynamics at the sediment-water interface. To this end, a broad sediment sampling campaign was carried out on Brittany mudflats, particularly affected by the eutrophication, during the spring period. A total of 200 samples were collected at 45 sites. They were characterized by their porosity and grain-size, as well as their chemical composition through elemental, isotopic and molecular biomarker analysis. A

25   wide range of OM sources were identified in the sediments, including both natural (bacteria, algae, macrophytes, terrestrial plants), and anthropogenic (combustion products, crude oil, petroleum products - e.g. from the processing of crude oil at refineries- and fecal matter) sources. Sediment slurry incubations were carried out to determine the spatial variability of potential mineralization rates under oxic conditions. In addition, the measurements of NH_4^+ and PO_4 fluxes at the sediment-water interface were made from sediment core incubations

30   under realistic redox conditions of sediment. The physical and chemical sedimentary characteristics explained 58 % of the variability of mineralization rates under oxic conditions, with a negligible independent effect of the SOM origin (3 %). Conversely, under *insitu* redox conditions, the prevalent role of SOM origin over quantity/accessibility on the sediment biodegradability was highlighted with a significant effect 5 and 1.5 fold higher on the PO_4 and NH_4^+ fluxes respectively. The anthropogenic inputs from the watershed to the coastal

35   sediment, through agricultural runoff and/or sewages discharge, seem to significantly drive the nutrient dynamics at the sediment-water interface. Higher values of NH_4^+ and PO_4 fluxes were measured for the sediment with a chemical composition impacted by human activities.

1. Introduction

40   Nutrient cycling in coastal ecosystems, especially in shallow environments, are impacted by both biotic and abiotic processes (e.g. Boynton et al., 2018; Santshi et al., 1990; Stahlberg et al., 2006). One of the major processes occurring at the sediment-water interface is the microbial degradation of sedimentary organic matter (SOM). This process is largely involved in the effluxes of inorganic carbon (CO_2), ammonium (NH_4^+) and phosphate (PO_4) from the sediment. The SOM biodegradability depends, among other factors, on the SOM sources and

45   composition, the mineral protection, the temperature, the terminal electron acceptor (TEA) availability (O_2, NO_2^- or NO_3^-, Mn(IV), Fe(III), SO_4^{2-}), and the microbial and macrobenthic activities (Arndt et al., 2013; Freitas et al., 2020; LaRowe et al. 2020 and references therein). As Freitas et al. (2020) highlighted, "the relative significance of each of these factors remains poorly quantified", compromising the ability to predict the effect of climate and environmental changes on carbon and nutrient budgets in eutrophicated coastal systems. The diversity of OM

50   sources as well as the interactions with environmental parameters (e.g. oxic conditions) complicate the chemical structure and the understanding of SOM biodegradability (e.g. Bianchi and Bauer, 2011; LaRowe et al. 2020). Efforts are thus required to better characterize the SOM composition and to quantify the relative significance of OM sources on the sediment biodegradability.

The composition of SOM is the resultant of a large diversity of allochthonous and autochthonous primary

55   producers such as phytoplankton, benthic macroalgae, microphytobenthos, seagrasses, woody plants as well as human activities in coastal areas (Bianchi and Bauer, 2011 and references therein). Differences in isotopic and elemental signatures, and specific chemical biomarkers are used to discriminate OM sources. The C:N ratio allows to distinguish terrestrial higher plants (C:N > 20) from macrophytes (C:N ≈ 10-20) and microalgae (C:N ≈ 6-10). In addition, the C:N ratio can be combined with the stable isotopes of carbon and nitrogen (e.g. Dubois et al., 2012;

60   Liénart et al., 2017; Meyers, 1994) to distinguish the SOM origin. A depletion in carbon isotopic ratio ($\delta^{13}C$ varying from -28 to -26 ‰) of OM is typical for the riverine end members, whereas the marine end member is more enriched, with a $\delta^{13}C$ varying from -22 to -20 ‰ (e.g. Cook et al., 2004; Li et al., 2016; Ogrinc et al., 2005). Furthermore, the variability of the nitrogen isotopic ratio ($\delta^{15}N$) has been shown to discriminate contrasting anthropogenic loading. High $\delta^{15}N$ in sediment (> 8 ‰) can result from treated sewage (e.g. Savage, 2005),

65   pollution from petroleum products (e.g. Rumolo et al., 2011), agricultural runoff (e.g. Finlay and Kendall, 2007) and/or effluents of aquaculture ponds (e.g. Yokoyama et al., 2006). Unlike the bulk elemental and isotopic signatures of end members which can be partially reset by decay processes (Bianchi and Bauer, 2012), chemical biomarkers usually survive explaining why their use has become popular in characterizing OM sources (Derrien et al., 2017; Meyers, 2003). Lipids have successfully been used as sensitive biomarkers of OM in coastal systems,

70   due to a chemical stability and a diversity in the compound classes. Distribution or ratios of *n*-alkanes, *n*-alcohols, fatty acids and steroids are useful in determining the contribution of microalgae, aquatic macrophytes, terrestrial plants and bacteria in the SOM composition (e.g. Cook et al., 2004; Derrien et al., 2017; Ficken et al., 2000; Jaffé et al., 2001; Pisani et al., 2013). In addition, input of sewage discharges or agricultural runoff may be revealed by the presence of specific 5β-stanols (Derien et al., 2012; Leeming et al., 1996; Harrault et al., 2019). Anthropogenic

75   activities in coastal and catchment areas are also indicated by the presence of polycyclic aromatic hydrocarbons (PAH) in sediment. The accumulation of PAH in sediment generally can results from the incomplete combustion

of fossil fuels, burning of biomass or oil spill (e.g. Benlahcen et al., 1997; Sporstol et al., 1983, Yunker et al., 2002).

Most investigations on the spatial variation of the origin and composition of the SOM have been carried out so far
at local scale, within a bay (e.g. Dubois et al., 2012; Gu et al., 2017), in lakes (e.g. Dunn et al., 2008; Fang et al., 2014) or along an estuary (e.g. Kumar et al., 2020; Meziane et al., 2006). There are only few studies on the regional scale e.g. Lee et al., 2019). Here we are interested in this scale through the case of Brittany, a region in the west of France particularly affected by coastal eutrophication phenomena (e.g. Perrot et al., 2014; Schreyer et al., 2019). In this region, marine intertidal mudflats are influenced by river discharges and large tidal fluctuations. The agricultural intensification and the urbanization of watersheds have led to the coastal eutrophication, where macroalgal "green tides" are regularly occurred in spring (Ménesguen et al., 2019; Perrot et al., 2014; Schreyer et al., 2019). We therefore expect that the isotopic and lipid markers tools used in the SOM characterization allow to describe the variability of OM sources - natural or anthropogenic - which affect the coastal and estuarine systems in Brittany.

The range of possible sources and hence the great potential diversity of the chemical structure of SOM makes it difficult to relate the biodegradability to SOM composition and ultimately, the biodegradability to the source of SOM. Biopolymers such as proteins have been shown to be more biodegradable than refractory biopolymers specific to vascular plants (e.g. cutan) (Tegelaar et al., 1989). It is thus widely assumed that the terrestrial OM is more refractory than the marine algal OM due to its chemical composition both dominated by higher resistant compounds, and impacted by the aging during the transport (Arndt et al., 2013). The SOM mineralization is thus controlled, in part, by its origin but also by the deposition rate of OM in the sediment (Khalil et al., 2018). To our knowledge, no investigation has dissociated and quantified the respective effects of OM quantity and source on the sediment biodegradability. Recently, Albert et al., 2021 have attempted to highlight the prevalent role of the OM quality on the benthic processes in coastal sediments, but in a context dominated rather uniform OM source materials (spring and summer plankton).

The aim of this work was i) to assess the variability of OM composition within coastal sediments of Brittany, at the scale of the entire region, ii) to use this variability to go back to the variability of OM sources, and finally iii) to determine how changes in OM source affect its biodegradability . To this end, 200 sediments were sampled at 45 sites in macrotidal mudflats on the Brittany coast. The SOM characterization was carried out by combining bulk elemental, isotopic and chemical biomarkers analysis. To determine the link between the origin and degradability of SOM, mineralization rates from sediment slurry incubations under oxic conditions and benthic nutrient fluxes (NH_4^+ and PO_4) from core incubations were carried out for all the sediments. In addition, the sediments were characterized by their physical properties (grain size distribution and porosity), which impact the accessibility of SOM for the microorganisms, as well as their element contents (C, N, P). Canonical redundancy analysis (RDA) and variance partitioning were used to explain the spatial variability of the NH_4^+ and PO_4 fluxes and the mineralization rates into independent parameters related to 1) the variation of SOM composition and origin and 2) the variation of the chemical composition and physical properties of sediment.

2. Materials and Methods

2.1. Study sites and sampling

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115   All study sites were macrotidal mudflats, located in Brittany, north-western France, and have been already fully described in a companion paper (Louis et al., 2021). Overall, 200 sediment samples were collected on 45 sites and classified into 12 mudflats (Fig. 1) during the spring period (year 2019). Sediment cores were sampled with one PVC core (diameter = 6 cm, h = 20 cm) in the upper 10 cm sediment layer for the measurements of nutrient benthic flux, and another one core (diameter = 9 cm, h = 5 cm) was sampled for carrying out sediment slurry incubations

120   as well as for characterization of the surface sediment (elemental, isotopic and lipidic composition; grain-size distribution and porosity).
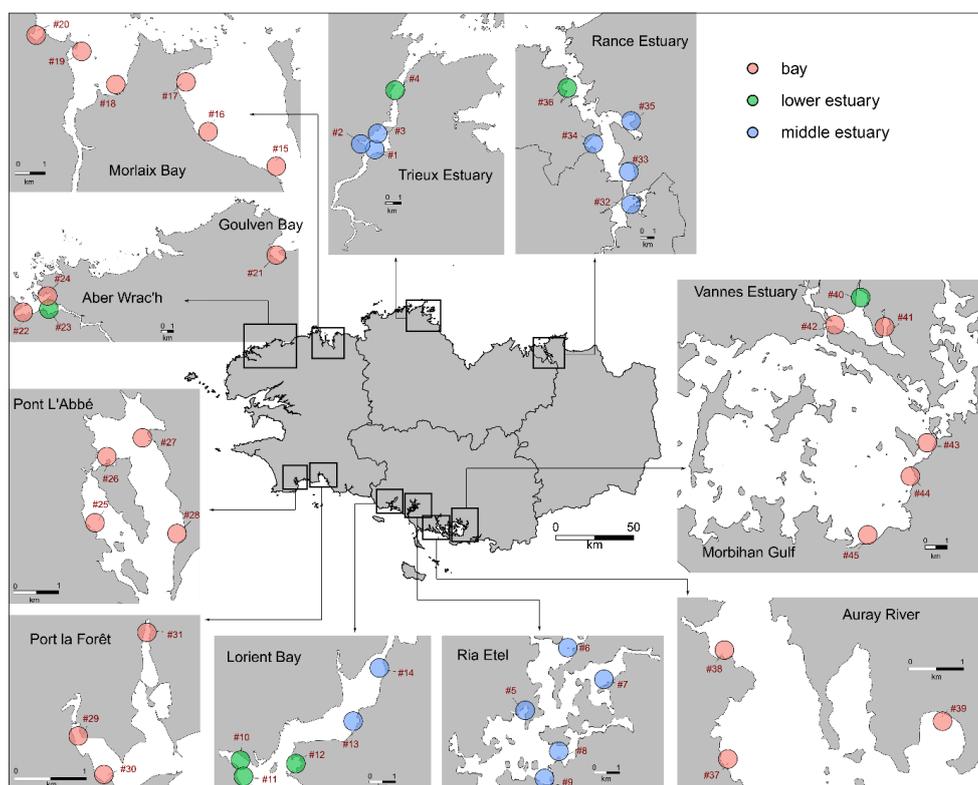
Figure 1. Location of mudflats (n=12) and sites of sampling (n=45) on the Brittany coast. The sampling sites were divided into 3 groups according their geographic locations: "bay", "lower estuary" and "middle estuary".

125   **2.2.   Grain-size and porosity measurements**

A sample of known volume and weight taken in the upper 5 cm layer of the core sediment was maintained at 4°C and used for porosity measurement. The porosity was calculated by using the amount water determined after drying the sample at 60°C, with the sediment density set at 2.55 (Berner, 1980). The particle size distribution (< 2 mm) was measured using a laser diffraction instrument (Malvern Mastersizer). "Mud" is defined as the sum of the clay and silt particles, with a diameter of less than 63 µm (e.g. Keil and Hedges, 1993; Pye and Blott, 2004)

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2.3.   Bulk elemental and isotopic analysis

The total organic carbon and nitrogen (TOC and TN) contents and the carbon and nitrogen isotopic ratios (δ^{13}C and δ^{15}N) were determined using an element analyzer (FLASH™ EA 2000 IRMS) coupled with an isotopic ratio mass spectrometer (DELTA V™ plus).

135 An aliquot of freeze-dried and crushed sediment was acid-treated with 2N HCl to remove the carbonate and was subsequently rinsed with deionized water. After centrifugation, the carbonate-free sample was dried at 60°C, and ground before being placed into a tin capsule for the TOC and δ^{13}C analysis. A second aliquot without an acidification treatment was used for the TN and δ^{15}N analysis. All isotopic data were expressed in the conventional delta notation:

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$$\delta^{13}\text{C}_{\text{sample}} \text{ or } \delta^{15}\text{N}_{\text{sample}} (‰) = \frac{R_{\text{sample}}}{R_{\text{reference}} - 1} \times 1000$$

with :

$$R = \frac{^{13}\text{C}}{^{12}\text{C}} \text{ or } \frac{^{15}\text{N}}{^{14}\text{N}}$$

The reference is (Pee Dee Belemnite) PDB for δ^{13}C and atmospheric N_2 for δ^{15}N. Analysis uncertainty was less than 0.2‰.

145 The phosphorus (P) speciation in the surface sediment was made from determining the iron oxide-bound P (Fe-P) and organic P (Org-P) contents, which represented the pool of potentially bioavailable P. The analytical method was totally described in the companion paper Louis et al. (2021). Briefly, the Fe-P content was determined using a Dithionite-Bicarbonate solution (Ruttenberg et al., 1992), and the Org-P content was quantified by calculating the difference between the total P and inorganic P (sums of Fe-bound P, Ca-bound P and detrital P) contents as 150 described in Andrieux-Loyer et al. (2008).

The TOC, TN, Org-P and Fe-P contents were expressed as the mass of the carbon, nitrogen and phosphorus in the total dry mass of the sediment.

The C:N and TN:Org-P ratios (mol:mol) were calculated from the TOC, TN and Org-P contents.

2.4. Lipid analysis

155 Approximately 30g of freeze-dried and crushed sediment was extracted with dichloromethane using an accelerated solvent extractor (Dionex™ASE™ 200) according to the following conditions: 33 mL cells, 5 min heating at 100°C and 60 bars, 10 min static phase, completed with 80% flush and 20-s purge with nitrogen. Elemental sulfur was removed from the total lipid fraction by reduction on metallic copper. The total lipid extract was then weighed and fractionated into aliphatic hydrocarbons, aromatic hydrocarbons and polar compounds on a silica column by 160 successive elution with cyclohexane, cyclohexane/dichloromethane (2/1, v/v) and methanol/dichloromethane (1/1, v/v). After this fractionation step, the mass of each fraction was weighed.

Polar fractions were analyzed by capillary gas chromatograph-mass spectrometer (QP2010SE GC-MS, Shimadzu) after derivatization using a mixture of N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMSC) (99/1, v/v), while aliphatic and aromatic fractions were analyzed without further 165 treatment. The injector used was in splitless mode and maintained at a temperature of 310°C. The chromatographic separation was performed on a SLB-5MS capillary column (length= 60m, diameter=0.25mm, film thickness=0.25µm) under the following temperature conditions: 70°C (held for 1 min) to 130°C at 15°C/min, the 130°C to 300°C (held for 15 min) at 3°C/min. The helium flow was maintained at 1 ml/min. The chromatograph was coupled to the mass spectrometer by a transfer line heated at 280°C. The analyses were performed in fullscan

mode. Quantification of the organic compounds was performed by adding internal standard in the solutions containing the aliphatic hydrocarbons, the aromatic hydrocarbons and the polar compounds according to Jeanneau et al. (2008).

These analyses provided the total concentration of lipid compounds in the dry mass sediment, as well as the concentration of each lipid marker. The results were also expressed as the proportion of each lipid marker against the sum of all lipid compounds quantified in the sediment.

2.5. Nutrient benthic fluxes from sediment core incubations

The measurement method of NH_4^+ and PO_4 fluxes was totally described in the companion paper Louis et al. (2021). Briefly, the sediment cores were incubated in the dark during 4 hours directly on site in a mobile laboratory under controlled temperature ($19 \pm 2°C$) within one hour upon sampling. The overlying water was replaced by 150 mL of nutrient-free artificial seawater ([NaCl] = 33 g.L^{-1}, [NaHCO$_3$] = 0.2 g.L^{-1}, pH ≈ 8) and gently aerated and stirred by bubbling in order to preserve the oxic conditions in the overlying water and to prevent the build-up of concentration gradients at the sediment-water column interface. The NH_4^+ and PO_4 fluxes ($\mu mol.m^{-2}.h^{-1}$) across the sediment-water interface were estimated by using the change in the molar concentration of the solute in the known volume of overlying water as a function of incubation time and the surface area of the sediment core.

2.6. Mineralization rate from sediment slurry incubations

The assessment of the biodegradability of the SOM was carried out by sediment slurry incubations in hermetically closed glass flasks, placed in the dark during 4 hours directly on site in a mobile laboratory under controlled temperature ($19 \pm 2°C$), agitation (150 rpm.min^{-1}) and oxic conditions. A wet aliquot sediment (m=5g) was used and mixed with a known volume of artificial seawater (V=20mL). The mineralization rate of SOM by microbial degradation, was determined by the measurements of the CO_2 concentrations in the headspace of flasks before and after incubation by micro gas chromatography (Agilent ™ 3000A micro GC). The mineralization rate (μmol $CO_2.g^{-1}.h^{-1}$) was calculated as follows:

$$\text{Mineralization rate} = \frac{[CO_2]_{T4} - [CO_2]_{T0}}{V_m} \times \frac{V_{air} + V_{liq} \times \text{bunsen coef}}{t \times m}$$

with:

[CO_2] the concentration of CO_2 measured in the headspace before and after incubation ($\mu mol.mol^{-1}$); Vm the molar volume (24.055 L.mol^{-1}); V_{air} the air volume in the headspace of flask (L); V_{liq} the sum of the volume of artificial seawater added and the volume of sediment porewater (L); t the incubation time (hour); m the dry sediment mass (g); Bunsen coefficient set at 1.49.

The sediment reactivity can be expressed as the first-order rate constant (e.g. Berner, 1980), calculated as follows:

$$k \ (yr^{-1}) = \frac{R \times Mc}{C_{TOC}}$$

with:

R the mineralization rate ($\mu mol \ CO_2.g^{-1}.yr^{-1}$); C_{TOC} the content of organic carbon in the dry mass of sediment ($\mu g.g^{-1}$); and M_c is the molar mass of carbon ($M_c = 12$).

2.7. Data analysis

2.7.1. Selection of lipid markers of OM sources in sediment

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A total of 109 lipid markers were selected as tracers of OM sources from the scientific literature (Table S1). For each source of OM identified, the lipid markers were classified according to their functional groups as well as the correlations among them established by a Principal Component Analysis (PCA). In all, the lipid markers were divided into 16 groups (Table 1).

210   PCA analysis were performed using the R-studio software with the package "FactoMineR". The proportions of lipid makers were previously standardized.

source	group	lipid markers *	Ref
Fecal matter	Fecal	Coprostanol Epicoprostanol	[1]
Combustion products	Combustion 1	Phenanthrene Anthracene Pyrene	
	Combustion 2	Benzo(a)anthracene Chrysene Benzo(a)pyrene	
Oil and by-products	Petroleum product	nC11-nC14 bicyclohexane	[2]; [3]
	Crude oil	Phytane Hopane Pristane	[3]
Bacterial matter	Bacteria 1	Iso 17:0 Anteiso 17:0	[4]; [5]
	Bacteria 2	Iso 15:0 Anteiso 15:0	[4]; [5]; [14]
Terrestrial plants	Plants 1	n-alkanes C24-nC35	[6]; [7]; [8]
	Plants 2	Campesterol Stigmasterol	[8]
	Plants 3	Alcohol C20-C30	[9]
	Plants 4	Fatty acids 22:0 to 30:0	[4]; [5]
Phytoplankton	Phytoplankton	Cholesta-5,22(E)-dien-3b-ol Brassicasterol	[14]; [15]
Pelagic and benthic microalgae	Microalgae	n-alkanes C15-nC16	[8]; [12]
Algal matter (micro and macro)	Algae	neophytadiene	[10]; [11]
Macrophytes	Macrophytes	n-alkanes C20-nC26	[6]; [12]; [13]
Green macroalgae	Green macroalgae	Fucosterol Isofucosterol	[16]

Table 1. Identification of lipid markers analyzed in the sediment samples according the scientific literature, and divided into 16 groups. *complete data in supplementary information (Table S1). [1] Leeming et al., 1996; [2] Emsbo-Mattingly

215 **et al (2018); [3] Peters and Moldowan, 1993; [4] Derrien et al (2017); [5} Meziane and Tsuchiya 2000; [6] Chevalier et al (2015); [7] Fang et al (2014); [8] Pisani et al (2013); [9] Eglinton et Hamilton (1967); [10] Lopez-Rosales et al, 2019; [11] Santos et al, 2015; [12] Jaffé et al (2001); [13] Ficken et al (2000); [14] Cook et al. (2004); [15] Volkman (1986); [16] Iatrides et al (1983).**

2.7.2. Co-inertia analysis between the data discriminating OM sources

A co-inertia analysis was carried out to assess how the proportion of lipid markers in SOM varies with the isotopic
220 and elemental signature of sediment (Dray et al. 2003). Unlike constrained analyzes, co-inertia has no causal link (no multiple regression) and just represents the two descriptor datasets in the common space of samples after two simple ordinations. It allows to determine how it varies together by superimposing the two points clouds of stations. The link between the two tables is thus performed a posteriori, by maximizing the square of covariance between initial projections of samples in the separate ordinations. Being unconstrained geometric data analysis, there is no
225 limitation in the variables from each table. A representation of the isotopic and elemental ratios was thus made in the common space with the lipid group proportions. The co-inertia was performed using the package ADE4 on two PCA ordinations, one on centered-reduced lipid composition and one on centered-reduced isotopic and elemental signature of sediment (Dray et al. 2007). The significance of the correlation between the two tables has been checked through a Monte-Carlo permutation test, by aleatory permuting rows and columns of one table and
230 calculating a reference distribution of the correlation coefficient (RV).

2.7.3. Canonical Redundancy Analysis (RDA) and variance partitioning

In order to explain spatial variability in NH_4^+ and PO_4 fluxes and mineralization rates (response variables), two constrained analyses were carried out in parallel. For the first analysis, explanatory variables were SOM sources (elemental and isotopic ratios and the proportions of lipid markers groups), hereafter called "SOM origin".
235 Explanatory variables for the second analysis were sediment composition (the contents of TN, TOC, Fe-P, Org-P, and total lipids) and the accessibility of SOM for the microorganisms (percentage of mud and porosity), hereafter called "physico-chemical composition". Canonical Redundancy Analysis (RDA) was chosen in both cases, assuming a linear relationships between responses and explanatory variables. This dissymmetrical analysis combines the concepts of ordination and regression, with explanatory variables used to recalculate the response
240 variables. The new canonical axes are thus a linear combination of the initial explanatory variables. The best explanatory variables in each matrix were selected by the "ordistep" function of the "vegan" package (R software ; Borcard et al. 2018; Oksanen et al., 2013) based on Akaike Information Criterion (AIC) through an automatic permutation tests of the ordination model and forward model selection. The non-collinearity between selected variables was then checked with the Variance Inflation Factor (VIF) (a threshold value was set at 10).

245 In order to determine the linear relationships between all previously selected variables and the potential biodegradability of sediment (mineralization rates and nutrient fluxes), a RDA was performed and tested by the permutation test. A hierarchical cluster analysis was then run from the projection of all sediment samples on this canonical ordination by the Ward2 Algorithm (Murtagh and Legendre, 2014).

With the selected explanatory variables, the variance partitioning was then used to quantify the variance proportion
250 of NH_4^+ and PO_4 fluxes and mineralization rates independently explained by both the variables "SOM origin" and the "physic-chemical composition" (Borcard et al. 1992). Therefore, a comparison between the effects of the SOM

origin on the sediment biodegradability with those of other known sedimentary characteristics was established. The significance of each fraction of interest was tested by the permutation test.

The "rda", "vif.cca", "anoca.cca" and "varpart" functions of the "vegan" package (R software) were used to perform the RDA, the VIF calculation, the permutation test and the variance partitioning respectively. The "dist.dudi" function of the "ade4" package and the "hclust" function (R software) were used to perform the hierarchical cluster analysis. Each data was previously standardized with the "scale" function before multivariate analysis.

3. Results

3.1. Elemental composition and physical characteristics of surface sediment

Over all sediment samples, the percentage of mud averaged 68 ± 17 % with the clay and silt particles representing respectively 5 ± 2 and 64 ± 15 % of the particle size distribution (Table 2). A large proportion of the surface sediment collected was classified as sandy mud (38 %) and slightly sandy mud (49 %) (Flemming, 2000). The average porosity was 70 ± 10 %. The TOC and TN contents averaged 2.2 ± 1.2 % and 0.24 ± 0.12 % of dry mass, respectively. The pool of bioavailable P (sum of Fe-P and Org-P contents) represented, on average, 0.033 ± 0.018 % of sediment, with the fraction of Fe-P (mean = 0.007 ± 0.005 %) lower than that for Org-P (mean = 0.026 ± 0.014 %) (Table 2).

	Mean (± sd)	median	Min-Max	Q1-Q3
Mud [clay + silt] (%)	68 ± 17	73	15 - 93	56 – 82
Porosity (%)	70 ± 10	70	46 - 87	63 – 79
TOC %	2.2 ± 1.2	2.1	0.2 – 7.7	1.1- 3.0
TN %	0.24 ± 0.12	0.22	0.06 – 0.64	0.15 – 0.32
Fe-P %	0.007 ± 0.005	0.006	0.001 – 0.033	0.004 – 0.009
Org-P %	0.026 ± 0.014	0.023	0.004 – 0.065	0.013 – 0.034
Total lipids (µg.g^{-1})	16.8 ± 11.5	13.8	0.7 – 76.0	8.7 – 20.7

Table 2. Composition and physical characteristics in the top 5cm of sediment. Q1 and Q3 represent the 25th and 75th percentile respectively.

3.2. SOM characterization by elemental, isotopic and lipid analysis

3.2.1. Elemental ratio

The C:N and TN:Org-P ratios (mol:mol) averaged 10.0 ± 2.1 and 23.1 ± 6.9 respectively over all sediment samples. The highest C:N ratios were measured in the sediments collected in the Goulven Bay (site #21, mean = 17.8 ± 3.9). The Lorient Bay presented also relatively high values of C:N ratio over all sampling sites (mean = 11.94 ± 1.32). Lowest C:N ratios were measured in the Ria Etel, particularly at the site #6 (mean = 4.8 ± 0.7). At the regional scale, no difference in C:N ratio was evidence between the samples collected in bays, in lower estuaries and or middle estuaries (Fig. 2a). At the local scale (scale of a given mudflat), rather systematic variations of the C:N ratio are observed depending on the location of the sampling station. In the Trieux Estuary, for example, samples taken further upstream of the estuary yielded systematically the highest C:N ratios (site #2, mean = 11.8 ± 0.4; site #4, mean = 7.4 ± 1.1). This is also true for the Aber Wrac'h were sediments collected in the lower estuary (site #23) gave higher C:N ratios (mean = 11.5 ± 1.3) than those collected directly in the bay (Figure 2A). With

regard to the TN:Org-P ratios, the sediments sampled in the Rance Estuary presented lowest values over all sampling sites (mean = 16.0 ± 7.6). In the Lorient Bay, the sites located further downstream of the estuary presented sediments with higher TN:Org-P ratios (Fig. 2b), particularly for sites #10 (mean = 36.3 ± 19.8) and #11 (mean = 36.7 ± 4.8). Elevated values of TN:Org-P ratio (up to 25) were also measured in sediments collected in the bay of Aber Wrac'h (sites # 22 and 24), in the Goulven Bay, and in the Gulf of Morbihan (Fig. 2b).

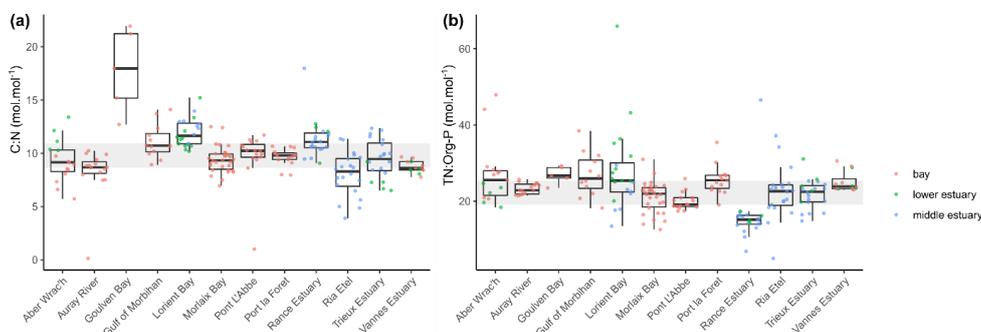



Figure 2. Boxplot of the C:N (A) and TN:Org-P (B) molar ratios for the 12 studied mudflats. Within the boxes, medians are the black lines. First and third quartiles are hinges. The grey area represents the values between the first and third quartiles calculated overall data.

3.2.2. Isotopic ratio

The $\delta^{13}C$ values varied from -24.3 to -16.2 ‰, with the highest values measured in the Gulf of Morbihan (mean = -17.0 ± 0.6 ‰). Lower values of $\delta^{13}C$ (< -22 ‰) corresponded to sediments collected in the upstream sites of the Lorient Bay (sites #13 and #14), the Trieux Estuary (sites #1 and #2), and Port la Forêt (site #31) (Fig. 3). The $\delta^{15}N$ values varied from 5.8 to 10.5 ‰. Higher values of $\delta^{15}N$ were measured in the Vannes Estuary (site #41, mean = 9.5 ± 0.7 ‰), as well as in the Rance Estuary (mean = 8.4 ± 0.4 ‰). In general, sediments collected in the mid estuary tended to have higher values of $\delta^{15}N$ and lower values of $\delta^{13}C$; the opposite was generally observed for the sampling sites located in the bay (Fig. 3).

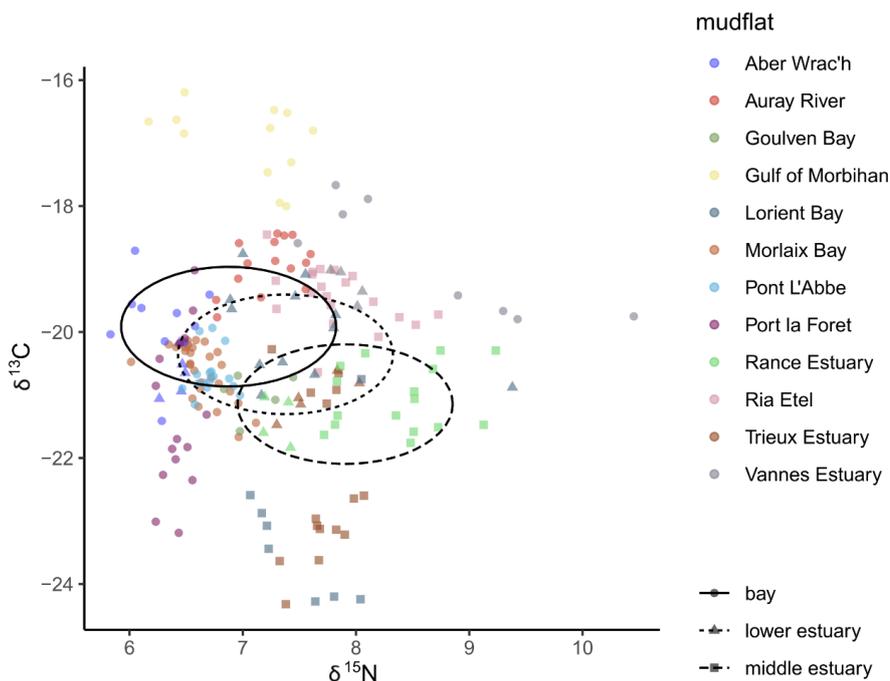
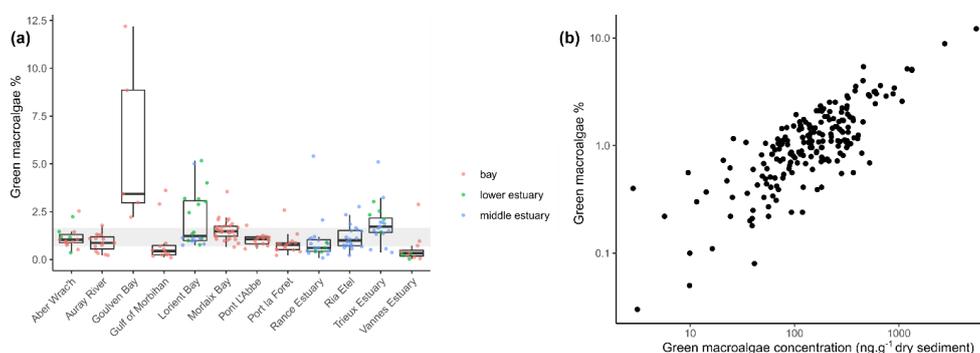



Figure 3. Biplots of the nitrogen (δ^{15}N) and carbon (δ^{13}C) isotopic ratios over all sediment samples (n=200). The three ellipses representing the sediments collected in a bay, in a lower and middle estuary, were drawn by computing the Euclidean distance of each sample from the center.

3.2.3. OM sources from lipid markers

A wide range of OM sources were identified in the sediments, including both natural (bacteria, algae, macrophytes, terrestrial plants), and anthropogenic (combustion products, crude oil, petroleum products - e.g. from the processing of crude oil at refineries- and fecal matter) sources. Overall, lipid markers originating from terrestrial plants were the most important quantified markers, representing, on average, 31.3 ± 9.9 % of the lipid pool (Fig. S1a). In contrast, the bacterial OM markers represented only a small proportion of the lipid pool for all sediments, with an average of 1.3 ± 0.9 % (Fig. S1b). The sites in the upstream section of the Lorient Bay were distinguishable from all other sites at the Brittany scale by the highest proportions of terrestrial plants markers (site #13, mean = 47.1 ± 5.6 %; site #14, mean = 45.9 ± 2.8 %), coupled to the highest concentrations of these compounds in the sediment (Fig. S1c).

Lipid markers specific to algae and macrophytes represented on average 8.5 ± 3.3 % of the total lipid pool. Higher proportions of microalgae (pelagic and benthic) markers were measured in the sediments collected in the Gulf of Morbihan (mean = 5.7 ± 2.3 %), the Morlaix Bay (mean = 5.2 ± 1.5 %) and the Rance Estuary (mean = 5.7 ± 2.3 %) (Fig. S2a). For the Morlaix Bay, this was mainly due to a higher proportion of phytoplankton biomarkers (mean = 4.2 ± 1.5 % against 2.5 ± 1.5 % for overall sediments). In the sediments of the Morbihan Gulf, the high proportions of microalgae markers were clearly associated to larger concentrations of these compounds in the sediments (mean = 1,952 ng.g^{-1} against 741 ± 777 ng.g^{-1}) (Fig. S2b). Largest proportions of green macroalgae

320   markers were observed in the Goulven Bay, the Trieux Estuary and in the downstream sites of the Lorient Bay
(Fig. 4a). In these areas, the sediment composition was directly related to the highest amounts of green macroalgae,
given the positive relationship between the proportions and concentrations of these biomarkers over all sediment
samples (Fig. 4b).

325   **Figure 4. Boxplot of the biomarkers proportion (%) specific to green macroalgae in the lipid pool of sediment samples
collected on the 12 studied mudflats. The grey area represents the values between the first and third quartiles calculated
overall data (A). Biomarkers proportion (%) of green macroalgae in the lipid pool of sediment in function of its
concentration (ng.g⁻¹ of dry sediment) overall samples (n=200) (B).**

In addition to the natural OM sources, anthropogenic OM markers were present in the sediments, with an average
330   proportion in the lipid pool of 19.2 ± 15.5 %. The high spatial variability of anthropogenic markers was mainly
due to a high variation of marker proportions of petroleum products (e.g. creosote) (mean = 12.3 ± 15.4 %). A
second group of oil and by-products markers was specific to crude oil (Table 1). This proportion over all samples
averaged 3.0 ± 3.5 %. No correlation was observed between the marker proportion of petroleum products and
crude oil (Fig. 5a), and the samples could be divided into two classes according their location: north and south
335   coast (Fig. 5b). The sediments collected on the southern Brittany coast were characterized by highest proportions
of petroleum products markers, while those collected in the northern Brittany coast had lower proportions. For the
crude oil markers, the opposite was observed: the sampling sites located at the north Brittany coast presented
higher proportions than those located at the south (Fig. 5b). In general, an increase in proportion of petroleum
product markers resulted from an increase in these compounds in the sediment (Fig. 5c), as well as for the crude
340   oil markers (Fig. 5d). In the present study, 4 stanols specific to human and animal waste were identified and
quantified in the SOM: coprostanol, epicoprostanol, 24-ethylcoprostanol and 24-ethylepicoprostanol, with relative
abundances of 28 ± 9 %, 8 ± 5 %, 44 ± 8 % and 21 ± 6 % respectively. The proportion of these fecal markers in
the lipid pool of the sediment samples was on average 1.7 ± 0.9 %. Relative higher values were measured in the
Goulven Bay (mean = 4.3 ± 1.1%), the Lorient Bay (mean = 2.4 ± 1.2%) and the Rance Estuary (mean = 2.1 ± 0.7
345   %) (Fig. 6). Except for the Rance estuary, this was mainly due to an enrichment of fecal matter in the sediment
(Fig S3). Markers of combustion products were also detectable, with an average proportion of 2.3 ± 4.2 %. In the
sediments collected in the Auray River, the Lorient Bay and Ria Etel, both largest proportions and concentrations
of these combustion markers were measured (Fig. S4).

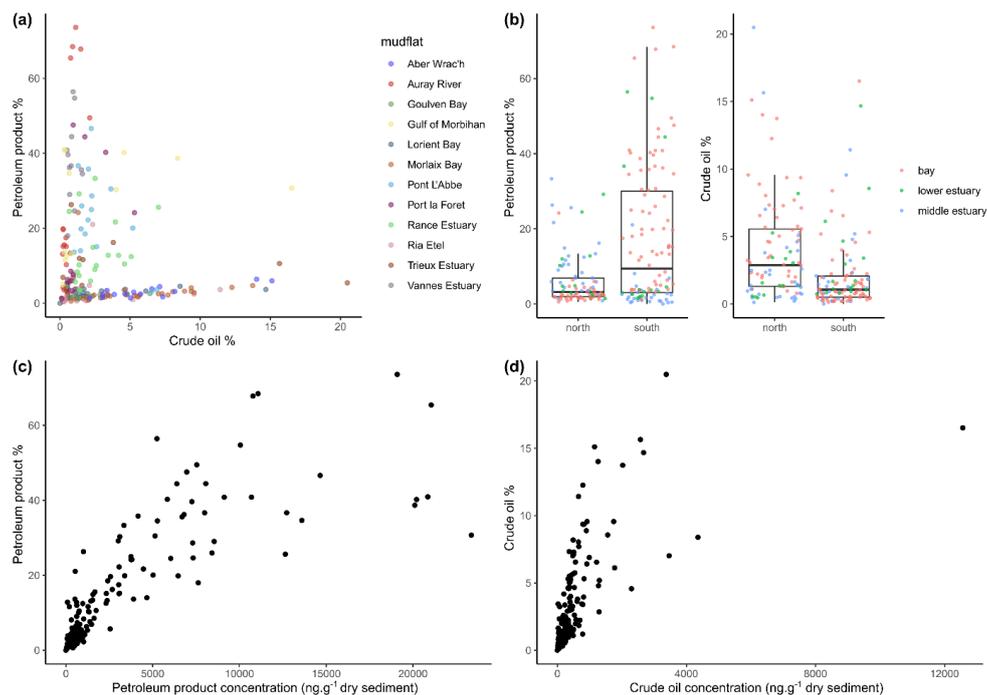



Figure 5. Markers proportion (%) of petroleum products *versus* crude oil, measured in the lipid pool of each sediment samples (n=200) (A). Distribution of markers proportion (%) of petroleum products and crude oil between the sites located at the south and the north of the Brittany coast. The grey area represents the values between the first and third quartiles calculated overall data (B). Markers proportions (%) in function of their concentrations in the lipid pool of sediment (ng.g^{-1} of dry sediment) for petroleum products (C) and crude oil (D).

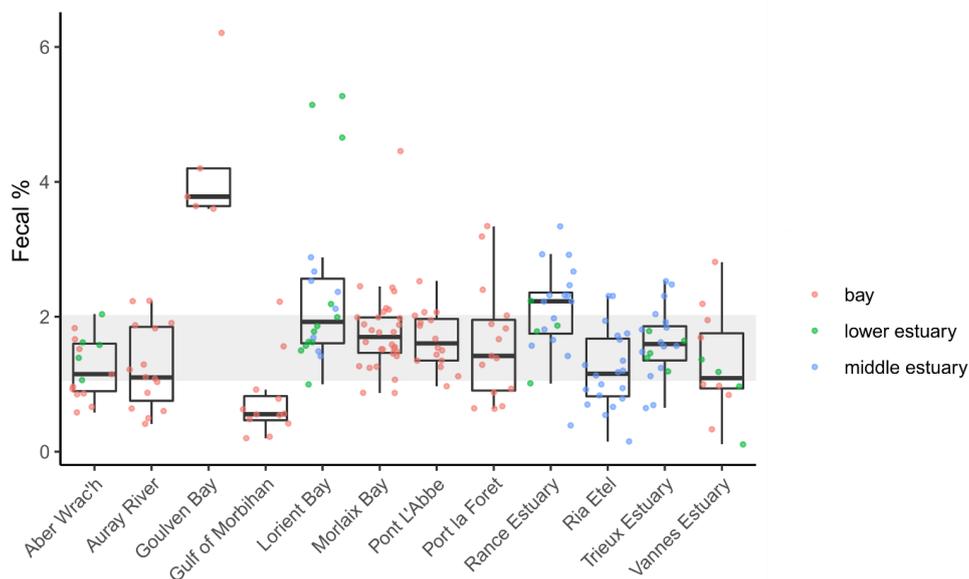



Figure 6. Boxplot of the biomarkers proportion (%) specific to fecal matter in the lipid pool of sediment samples collected on the 12 studied mudflats. The grey area represents the values between the first and third quartiles calculated overall data.

3.3. Potential SOM biodegradability

360   The slurry sediment incubations allowed assessing the SOM biodegradability under oxic conditions. The mineralization rate was determined from the CO_2 production measured during the incubation from the microbial respiration of SOM. The average CO_2 production over the 200 sampling points was 0.40 ± 0.58 µmol C.g^{-1}.h^{-1}. The sampling sites located in the Goulven Bay, Pont L'Abbé, Port la Forêt (site #31), and in the upstream section of the Trieux Estuary (sites #1 and #2) were characterized by relative high sediment mineralization rates (Fig.

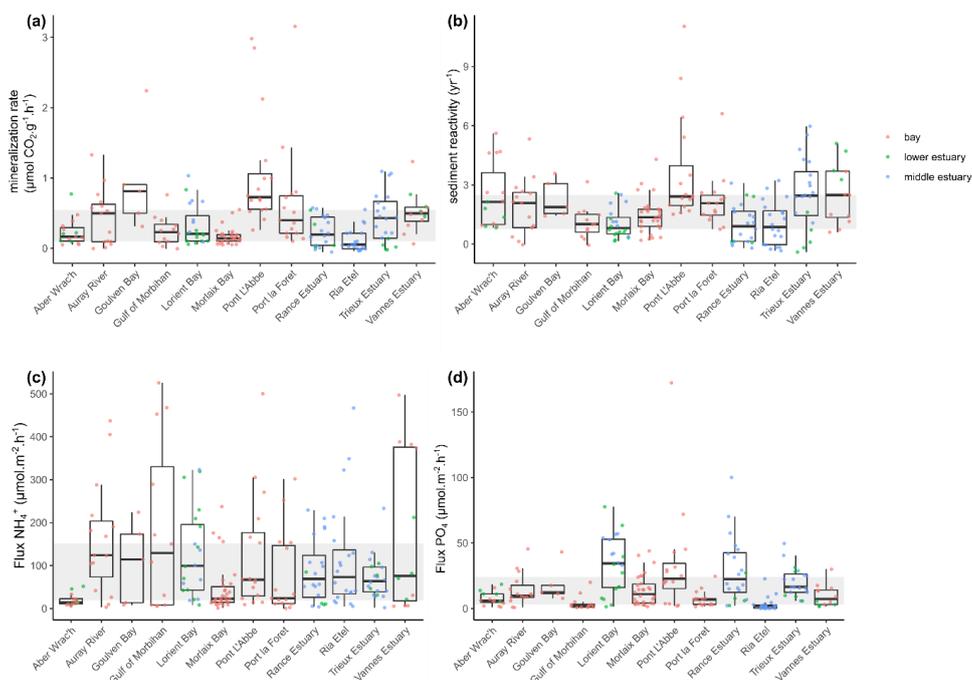
365   7a).The sediment reactivity (k), deduced from the CO_2 production and the sediment organic carbon content, averaged 1.9 ± 1.6 yr^{-1}, with a maximal value of 11.0 yr^{-1}. Highest sediment reactivity was determined in Pont L'Abbé and the upstream Trieux Estuary, similar to the mineralization rates. In addition, another sampling site located in the lower estuary of Vannes (site #40), was characterized by high sediment reactivity (mean = 4.2 ± 0.8 yr^{-1}) (Fig. 7b).

370

Figure 7. Boxplot of the mineralization rate (µmol C.g^{-1}.h^{-1} of dry sediment) (A) and sediment reactivity "k" (yr^{-1}) (B) determined from sediment slurry incubations for the 12 studied mudflats. Boxplot of the benthic NH$_4^+$ flux (A) and PO$_4$ flux (B) (µmol.m^{-2}.h^{-1}) at the sediment-water interface determined from core incubations for the 12 studied mudflats. The grey area represents the values between the first and third quartiles calculated overall data.

375   ### 3.4. Potential benthic nutrient fluxes

Potential benthic NH_4^+ and PO_4 fluxes were determined via sediment core incubations (see more details in Louis et al., 2021). The NH_4^+ fluxes averaged 101 ± 117 µmol.m^{-2}.h^{-1}. A large spatial variability of NH_4^+ fluxes was observed at both the regional and local (mudflat) scale (Fig. 7c). Large differences were for example observed within the Vannes Estuary with, on average, 410 ± 58 µmol.m^{-2}.h^{-1} for the sampling site #41, while it was only 12 ± 12 µmol.m^{-2}.h^{-1} for the site #42. The PO_4 fluxes were generally 20-fold lower than the NH_4^+ fluxes, with an average flux of 17 ± 20 µmol.m^{-2}.h^{-1} (Fig. 7d). High PO_4 fluxes were observed for the sites located in the Lorient Bay (e.g. site #13, mean = 51 ± 7 µmol.m^{-2}.h^{-1}), Pont L'Abbé (e.g. site #28, mean = $66 +71$ µmol.m^{-2}.h^{-1}) and along the Rance Estuary (e.g. site #33, mean = 54 ± 42 µmol.m^{-2}.h^{-1}).

3.5. Statistical processing of data

3.5.1. Co-inertia analysis

To assess how the proportion of lipid markers in SOM varies with the isotopic and elemental signature of sediment, a co-inertia analysis (see Materials and Methods 2.7.2) was done by comparing the two descriptors' datasets represented in the common space of sampling sites (Fig. S5).

The co-inertia analysis between the isotopic and elemental ratios and the lipid marker proportions, indicated a correlation coefficient (RV) of 0.13. The first and second axis represented 60.1 and 18.8 % respectively of the co-inertia. The groups of lipid markers which contributed 79 % of the first axis were "Fecal" (29.3%), "Petroleum products" (15.3%), "Green macroalgae" (15.8%) and "Plants 3" (18.3%). Regarding the second axis, the groups "Macrophytes" (23.7%), "Green macroalgae" (24.5%), "Phytoplankton" (9.6%), "Microalgae" (11.6%) and "Plants 2" (10.4%) contributed 80 %. $\delta^{13}C$, C:N and TN:Org-P ratios contributed to the two first axis, contrary to $\delta^{15}N$ with a minor contribution. $\delta^{13}C$ and C:N ratio had a contribution of 43 and 57 % on the first axis respectively. TN:Org-P contributed 52 % of the second axis. The correlations between the lipid groups mentioned above, and the elemental and isotopic ratios, are presented in the Table 3. The groups "Fecal" and "Plants 3" were positively correlated with the C:N ratio (pearson coef = 0.39 and 0.29, p<0.001), while they were negatively correlated with $\delta^{13}C$ (pearson coef = -0.32 and -0.29, p<0.0001). For the markers of petroleum products, the opposite was observed. The markers of green macroalgae were positively correlated with the C:N (pearson coef = 0.40, p<0.001) and TN:Org-P ratios (pearson coef = 0.20, p<0.01). For the markers of microalgae, they were positively correlated with $\delta^{13}C$ (pearson coef = 0.23, p<0.001) and $\delta^{15}N$ (pearson coef = 0.21, p<0.001).

	C :N	TN :Org-P	$\delta^{13}C$	$\delta^{15}N$
Fecal	0.39 ***	0.07	-0.32 ***	0.10
Petroleum products	-0.24 ***	0.02	0.28 ***	0.11
Green macroalgae	0.40 ***	0.20 **	-0.11	0.004
Plants 3	0.28 ***	0.02	-0.29 ***	-0.11
Macrophytes	0.05	0.18 *	0.13	0.16 *
Phytoplankton	-0.15 *	-0.09	-0.05	-0.05
Microalgae	0.05	-0.02	0.23 ***	0.21 **
Plants 2	0.07	0.21 **	-0.11	0.03

Table 3. Pearson's coefficient between the isotopic and elemental ratios (C:N, TN-Org-P, $\delta^{13}C$ $\delta^{15}N$), and the proportions of biomarker groups "Fecal", "Petroleum products", "Green macroalgae", "Plants 3", "Macrophytes", "Phytoplankton", "Microalgae" and "Plants 2". *** p <0.001; ** p <0.01; * p <0.05

3.5.2. Variance partitioning and canonical redundancy analysis (RDA)

To relate biodegradability to OM sources considering sediment properties, the significant variables from the different datasets were selected (see Materials and Methods 2.7.3). In the data matrix "SOM origin", the selected variables were $\delta^{13}C$, $\delta^{15}N$, and the lipid markers groups "Fecal", "Petroleum products", "Microalgae", "Plants 3" and "Plants 4". Regarding the data matrix "physico-chemical composition", the selected variables were the TN, Fe-P, Org-P and total lipids contents, the percentage of mud and the porosity. With these selected variables in both data matrices, the variance partitioning of mineralization rate, NH_4^+ and PO_4 fluxes was carried out and the results are presented in Fig. 8. The selected parameters from "SOM origin" and "physico-chemical composition" explained 58 % of the variance of the sediment mineralization rates. A large part was the result of the significant and independent effect of the "physico-chemical composition" variables (F=28.2, p=0.001) (Fig. 8). On the contrary, the variations of NH_4^+ and PO_4 fluxes were more correlated with the "SOM origin" than with the "physico-chemical composition" variables (Fig. 8). The variables "SOM origin" significantly explained 15 and 14 % of variance of NH_4^+ fluxes (F=4.8, p=0.003) and PO_4 fluxes (F=5.2, p=0.001) respectively, compared to 9 and 3 % with the "physico-chemical composition". The variables "SOM origin" and "physico-chemical composition" shared between 10 and 16 % of the variance partitioning of NH_4^+ and PO_4 fluxes respectively.

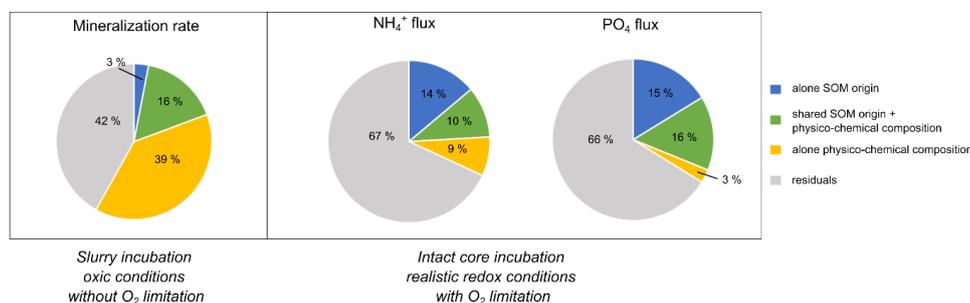
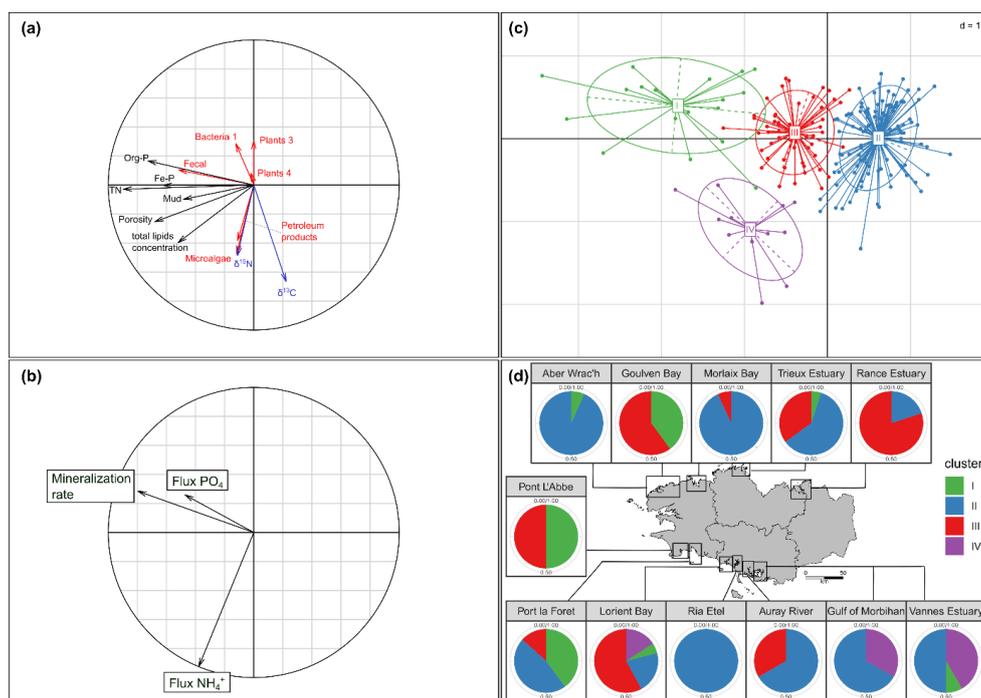



Figure 8. Variation partitioning of the mineralization rate, NH_4^+ and PO_4 fluxes. "SOM origin" corresponds to $\delta^{13}C$, $\delta^{15}N$ and the proportions of lipid markers groups previously selected (see Materials and Methods in section 2.7.3). "physico-chemical composition" corresponds to the selected parameters related to the composition (TN, Fe-P, Org-P and total lipids contents) and physical properties (percentage of mud and porosity) of sediment.

In order to explain the sediment mineralization rates and nutrient fluxes in relation to the selected variables, a canonical redundancy analysis (RDA) was performed. The canonical ordination constrained by both selected variables "SOM origin" and "physico-chemical composition" significantly explained 42 % of the responses of sediment (F = 9.3, p = 0.001), of which 84 % was carried out by the first two axis. The NH_4^+ flux was mainly correlated with the second axis (correlation coef = -0.92). This second axis was associated to the isotopic ratios $\delta^{13}C$ and $\delta^{15}N$, the proportion of microalgae biomarkers and, to a lesser extent, the proportion of petroleum products markers (Fig. 9a, b). The mineralization rates were mainly correlated with the first axis (correlation coef = -0.80), and with the third axis (correlation coef = 0.53). The opposite was observed for the PO_4 flux, which was mainly correlated with the third axis (correlation coef = -0.84) and with the first axis (correlation coef = -0.47). On the first axis, the mineralization rate and the PO_4 flux were associated to the variables related to the sediment composition (TN, Org-P, Fe-P and total lipids contents) and physical properties (percentage of mud and porosity) (Fig. 9a, b). On the axis 1 and 3, they were associated to the proportion of fecal biomarkers.

The RDA discriminated four groups of sediments from the hierarchical cluster analysis (see Materials and Method 2.7.3) (Fig. 9c). A first cluster was related to the highest mineralization rates, Org-P and TN contents, and porosity

440 (cluster "I"). Another cluster represented the lowest mineralization rates, nutrient fluxes, porosity and percentage of mud, and the sediments with the lowest contents in TN, Org-P, Fe-P and total lipids (cluster "II"). The cluster "III" was intermediate between the clusters "I" and "II". The last cluster represented the highest NH_4^+ fluxes, microalgae markers proportions and isotopic ratios (cluster "IV"). The spatial distribution of these groups is presented in Fig. 9d. The sediment collected in the Goulven Bay and Pont L'Abbé would represent those for which

445 the selected variables "SOM origin" and "physico-chemical composition" would explain both higher mineralization rates and PO_4 fluxes (clusters "I" and "II"). Some of sediments collected in the Lorient Bay (site #10), the Gulf of Morbihan and the Vannes Estuary (site #41), would represent those of which the selected variables would explain the highest NH_4^+ fluxes (cluster "IV").

450 **Figure 9. Correlation circles of the Canonical Redundancy Analysis (RDA) showing the correlations between the explanatory variables, related to the SOM origin, composition and physical properties of sediment, (A) and the response variables (mineralization rate, NH_4^+ and PO_4 fluxes) (B). The first and second axis represent respectively 63.5 and 20.1 % of data. Representation of the hierarchical cluster analysis on the canonical ordination (C) with which all sediment samples were divided into 4 clusters. Spatial repartition of these 4 clusters for the 12 studied mudflats (D). Each**

455 **sediment sample is listed according to the 4 clusters in the supplementary information (Table S2).**

4. Discussion

4.1. Spatial variability of OM sources in Brittany intertidal mudflats

4.1.1. Marine *versus* continental natural sources

In the investigated river-dominated studied mudflats, the natural OM sources include terrestrial plants, freshwater

460 algae, marine phytoplankton, microphytobenthos, as well as *Ulva* sp., a green macroalgae highly present on the

Brittany coast. The contribution of these primary producers in SOM was assessed via elemental, isotopic and biomarkers analysis.

The increasing gradient of $\delta^{13}C$ along the estuary-coastal zone continuum generally illustrates the mixture of OM from continental to marine origin (e.g. Cook et al., 2004; Li et al., 2016; Ogrinc et al., 2005), which was observed here at both the regional and local (mudflat) scale (Fig. 3). In the Lorient Bay, for example, the upstream sites were characterized by the lowest $\delta^{13}C$ values ($\approx$ -23 ‰), dominated by the largest inputs of terrestrial plants (Fig. S1), resulting in elevated sedimentary C:N ratios (>12) (Fig. 2a). In this Bay, downstream sediments show an enrichment of OM from green macroalgae with high concentrations and proportions of these biomarkers in the lipidic pool (Fig. 4). The presence of macroalgae resulted in an increase in $\delta^{13}C$ seaward of Lorient Bay (up to -19 ‰; Fig. 3). This is in line with the $\delta^{13}C$ signature of Ulva sp. of around -15.8 ± 4.4 ‰ (Berto et al., 2013; Dubois et al., 2012; Riera et al., 1996), which is significantly higher than the $\delta^{13}C$ associated to C_3 terrestrial plants ($\delta^{13}C$ = -28.7 ± 0.5 ‰; Davoult et al., 2017; Meyers, 1994). In these downstream sites, the C:N ratio of sediments still remains high (mean = 11.5 ± 1.4), in accordance with the C:N ratio of Ulva sp. around a value of 13 (Dubois et al., 2012; Liénart et al., 2013).

A large contribution of ^{13}C enriched marine OM sources in the sediment composition was typically observed in the samples collected directly in a bay, e.g. in the Gulf of Morbihan and the Morlaix Bay (Fig. 3). In the Morlaix Bay, the higher proportions of phytoplankton biomarkers could explain the $\delta^{13}C$ values of -20.6 ± 0.4 ‰ in the sediments, close to the isotopic signature associated to marine phytoplankton (-21.3 ± 1.2 ‰; Liénart et al., 2017). Sediments collected in the Gulf of Morbihan were characterized by the highest $\delta^{13}C$ values observed at the regional scale (mean = - 17.0 ± 0.6 ‰) (Fig. 3) and a significant contribution of microalgae in SOM composition (Fig. S2). Here, we assume that the major source of OM is microphytobenthos, for which $\delta^{13}C$ is around – 18.2 ± 1.7 ‰ (Dubois et al., 2012; Riera et al., 1996) instead of marine phytoplankton. Over all sediments of the Gulf of Morbihan, the mean C:N ratio was 11.1 ± 1.6, which is slightly higher than the C:N ratio widely used as signature of microphytobenthos (mean = 9.6 ± 1.0) (Dubois et al., 2012; Liénart et al., 2013).

4.1.2. Anthropogenic sources

In addition to the natural sources of OM, eutrophicated coastal systems receive anthropogenic matter from urban discharges, agricultural and industrial activities impacting the SOM composition. The analysis of oil and by-products markers in the sediments allowed to discriminate the pollutions between the north and the south of the Brittany coast (Fig. 4). The north sites seem to have been impacted by oil spills leading to the enrichment of crude oil markers in the sediments. For the south sites, the sediments were characterized by an enrichment of petroleum products, particularly those collected in sites classified in the group "bay". No significant difference in $\delta^{15}N$ was observed between northern and southern Brittany, despite the contrasting isotopic signature of crude oil ($\delta^{15}N < 2$ ‰) and petroleum products ($\delta^{15}N > 9$ ‰) (Rumolo et al., 2011 and references therein). While the crude oil and by-products are largely depleted in ^{13}C ($\delta^{13}C < -28$ ‰) (Rumolo et al., 2011 and references therein), the ^{13}C-enriched sediments collected in the present study were associated to higher proportions of petroleum products markers (Table 3). This can be explained by the fact that the composition of sediments collected directly in the bay in the southern Brittany was also impacted by the ^{13}C-enriched marine OM inputs as discussed earlier (section 1.1). The petroleum inputs seem to have a minor impact on the isotopic signature of sediments.

In addition to oil pollution, urban discharge from sewage treatment plants are widely detected by a large increase
500   in $\delta^{15}N$ in the bulk sediment ($\delta^{15}N \approx$ 8-10 ‰) (e.g. Rumolo et al., 2011; Savage, 2005). The current study shows
the impact of sewage discharges on the isotopic composition of the sediment at the local scale. For example, the
highest $\delta^{15}N$ values were measured in the sediments collected downstream of a wastewater treatment plant
(WWTP) (for ~ 60.000 person equivalent) in the Vannes estuary (site #41). The sediments of this site were also
characterized by an enrichment of fecal matter through, in particular, higher concentrations (208 ± 107 ng.g^{-1} dry
505   sediment) and proportions (0.9 ± 0.2 of the lipid pool) of coprostanol. This marker represents around 60 % of the
total sterols in human faeces (Leeming et al., 1996, Harrault et al., 2019). The effect of sewage effluent on the
SOM composition was gradually diluted through a decrease in $\delta^{15}N$ of $\approx$ 1.7 ‰ measured around 2-3 km from the
site #41 (sites #40 and #42; Fig. 1). This is more pronounced than the 1 ‰ decrease reported by Savage (2005)
within 10 km of the outfall of a WWTP (for ~ 250.000 person equivalent) in a bay of Sweden. In contrast, a high
510    $\delta^{15}N$ gradient was exhibited by Rumolo et al. (2011) in the harbor of Naples ($\approx$ 10 ‰) within 1.5 km of the outfall
of a WWTP. As the authors claimed, the spatial effect of sewage effluents on sediment composition would be
under the control of the hydrodynamics of the coastal system which itself determine the sedimentation rate of OM-
rich fine particles. Consistent with the dilution of the $\delta^{15}N$ value between the sites #40 and #42 in the present study,
the concentrations and proportions of fecal markers in the SOM declined by $\approx$ 60 % between these two sites.

515   High values of $\delta^{15}N$ in the sediment were also observed in the mid estuary of the Rance (from 7.7 to 9.2 ‰). The
proportions of fecal markers were significantly higher than those measured on the regional scale (Wilcoxon test,
$p < 0.005$), while larger concentrations of these markers were not observed. Previous studies showed an increase
in $\delta^{15}N$ in aquatic systems impacted by agricultural activities, where animal waste is often used as a fertilizer
(Finlay and Kendall, 2007 and references therein). Since the watersheds in Brittany are particularly impacted by
520   intensive agricultural activities (e.g. Morand and Briand, 1996), it is assumed that the high $\delta^{15}N$ values measured
in the sediment of the Rance estuary are due to the high proportion of cultivated areas in the watershed. The
TN:Org-P ratio, a second sedimentary characteristic confirms this hypothesis. The sediments collected in the
Rance Estuary presented the lowest TN:Org-P ratios (Fig. 2b), with a mean value of 16.0 ± 7.6 against 23.1 ± 6.9
overall sediments. We suggest that a low TN:Org-P ratio could result from the agricultural runoff. Indeed, animal
525   manure such as pig slurry, used for crop growth, tend to decrease the TN:Org-P ratio of soil through a high retention
of P in soil and a rapid leaching of N into groundwater and rivers (Penuelas et al., 2009; Toth et al., 2006). This
could thus lead to a decrease in the TN:Org-P ratio of OM inputs from watersheds in the estuary-coastal zone
continuum.

4.2. The role of the SOM origin on the sediment biodegradability

530

After characterizing the SOM composition at the regional scale, the objective of this work was to quantify the
relative significance of the SOM origin on the sediment reactivity, as well as to identify the SOM sources enabling
the sediment to act as a nutrient source for the overlying water.

4.2.1. Mineralization rates under oxic conditions

535   In the present study, the role of the SOM origin and sediment physico-chemical composition on the sediment
biodegradability was assessed by determining potential mineralization reactions under oxic conditions and
continuous mixing of the sediment at 19°C. According to the variance partitioning, 39 % and 3 % of the variation

of these mineralization rates was explained respectively by the independent effect of "physico-chemical composition" and "SOM origin" variables (Fig. 8). The potential sediment mineralization rates were assessed
540   under oxic conditions; it is widely accepted that the presence of O_2 would enhance the organic carbon reactivity in many marine sediments (LaRowe et al., 2020 and references therein). Indeed, the presence of O_2 would allow both the aerobic respiration and the cleaving of the non-hydrolysable bonds in the more refractory organic compounds (Burdige et al., 2007). The mineralization process would thus be slightly affected by the OM quality regardless its quantity. This is line with our results highlighting that the spatial variability of OM sources would
545   have a weak independent impact on the mineralization rate of the sediment when it is not constrained by the anoxic conditions. To a lesser extent, the variables "SOM origin" and "physico-chemical composition" shared 16 % of the variance partitioning of the mineralization rates. Considering that this effect reflected the coupled OM quantity-origin, it means that a large deposition of OM from specific sources would enhance the SOM biodegradability. According to the positive association between the proportion of fecal matter markers and the mineralization rate
550   determined by the RDA, we suggest that the coastal sediment composition impacted by human or animal waste would have a greater potential biodegradability.

The sediment reactivity k, calculated from the mineralization rate and the TOC content, ranged from 0.8 to 11 y^{-1} for 75 % of data (Fig. 7b). Since the SOM biodegradability seems to be only weakly impacted by its origin as discussed above, we suggest that the spatial variability of k is likely explained by the residual part of the variance
555   partitioning of the mineralization rate reaching 42%. This can include the biological parameters not measured in this work, such as the microbial abundance and diversity.

4.2.2. Nutrient fluxes at the sediment-water interface

The benthic nutrient fluxes are driven by chemical (e.g. precipitation/dissolution; adsorption/desorption), biological (e.g. bacterial respiration) and physical (e.g. diffusion) processes (e.g. Capone et al., 2008; Ekholm and
560   Lehtoranta, 2012; Santschi et al., 1990). The SOM mineralization is involved in the nutrient fluxes through the regeneration of NH_4^+ and PO_4 in the porewater of sediment. Therefore, in addition to the measurements of mineralization rates, the sediment biodegradability was also assessed through its capacity to act as a nutrient source to the overlying water. The NH_4^+ and PO_4 fluxes at the sediment-water interface were measured from the sediment core incubations in the dark and under controlled temperature (19°C). The realistic redox conditions of the
565   sediment were preserved during the core incubations. In the eutrophicated coastal areas, as is the case in Brittany coast, the sediments are often constrained by the hypoxia, and thus the SOM mineralization is limited by a low O_2 penetration in the sediment of few millimeters (Middelburg and Levin, 2009). Under these redox conditions, we expect that the mineralization process is more driven by the lability of the SOM rather than by its quantity/accessibility. The OM sources control the SOM composition and likely its lability. We thus suggest that
570   the SOM origin could significantly drive the regeneration of NH_4^+ and PO_4 in the sediment and consequently their effluxes. The variance partitioning of NH_4^+ and PO_4 fluxes confirms this hypothesis (Fig. 8). The percentage of the variance of NH_4^+ and PO_4 fluxes only explained by the variables "SOM origin" reached 15 and 14 % respectively, against 3 and 9 % for the "physico-chemical composition". All parameters measured and selected in the present study explained 34 and 33 % of the variation of PO_4 and NH_4^+ fluxes. The RDA allowed to determine
575   the relationships between these parameters and the benthic nutrient fluxes, and particularly to assess which SOM sources can enhance the PO_4 and NH_4^+ fluxes. (Fig. 9a and b). The PO_4 fluxes were positively linked to the

proportion of fecal markers in the sediment. This suggests that anthropogenic inputs, such as sewage discharges or agricultural runoff, rich in fecal matter would be positively impacting the PO_4 fluxes from the sediment. The RDA also showed a positive relationship between the PO_4 flux and the Org-P and Fe-P contents, as previously

580   observed for the same sediments (Louis et al., 2021). This may highlight the concomitance of Org-P mineralization and Fe-P dissolution on the PO_4 effluxes under specific anoxic conditions enhanced by anthropogenic pressures (Lehtoranta et al., 2009). This is in line with a work carried out in the Bay of Brest (Brittany), showing both larger mineralization rate and a larger dissolution rate of Fe-P, as well as a larger PO_4 flux, where the sediment was influenced by higher urban and farming activities in the watershed (Ait Ballagh et al., 2020).

585   The NH_4^+ fluxes were positively related to both the isotopic signature of the bulk sediment ($\delta^{15}N$ and $\delta^{13}C$) and the proportions of microalgae and petroleum markers. The NH_4^+ fluxes seem to increase when the SOM composition is influenced by ^{13}C-enriched OM marine inputs, and particularly from microalgae. In addition, high NH_4^+ fluxes would characterize the sediments collected in coastal areas under anthropogenic pressures. The positive relationship with the proportion of petroleum product markers means that this would correspond to the

590   sediments with a composition particularly impacted by industrial, shipping/docking activities, such as in the bays in the southern Brittany (Fig. 5). The second positive association with the $\delta^{15}N$ of bulk sediment highlights, in general terms, a stimulation of benthic NH_4^+ flux fueled by anthropogenic nitrogen emissions (e.g. Savage, 2005; Finlay and Kendall, 2007; Rumolo et al., 2011). As discussed above (see section 4.1.2), the highest values of $\delta^{15}N$ measured overall sediment samples likely resulted from domestic wastes or agricultural activities. In summary,

595   whether for the PO_4 or NH_4^+ fluxes, human activities seem to stimulate the nutrient dynamics at the sediment-water interface, assuming that this results from an increase in sediment biodegradability. This can be illustrated by the sediment collected both in the Rance Estuary and Vannes Estuary. In the Rance Estuary, the intensive agricultural activities in the watershed, likely affect the sediment composition as previously discussed (see section 4.1.2). Except for the sediments collected at the mouth of the estuary (site #36), high PO_4 fluxes (mean = 34 ± 26

600    $\mu mol.m^{-2}.h^{-1}$) were measured overall sampling sites of the Rance. The erosion and/or runoff events of agricultural soils could stimulate the PO_4 fluxes at the sediment-water interface on a large-scale estuary. In the Vannes Estuary, the sewage discharges appeared to impact the sediment composition, showing a gradient with the distance from the WWTP outfall (see discussion section 4.1.2). In this area, no significant stimulation of PO_4 fluxes was observed, but high NH_4^+ fluxes were measured for the sediments collected at proximity of the WWTP (site #41,

605   mean 410 ± 58 $\mu mol.m^{-2}.h^{-1}$), highlighting an effect of sewage effluent at the local-scale.

In Brittany, a main symptom of the coastal eutrophication, fueled by anthropogenic pressures, is the proliferation of green macroalgae (*Ulva* sp.). Previous studies highlighted the stimulation of the mineralization rate and nutrient effluxes during the decomposition of green macroalgae in the surface coastal sediment (Corzo et al., 2009; Garcia-Robledo et al., 2013; Lomstein et al., 2006; Trimmer et al., 2000). An increase in NH_4^+ and PO_4 fluxes for the

610   sediments characterized by a high contribution of these algae in their composition might thus have been expected. However, in the present study, no significant link was shown between the lipid markers specific to green macroalgae and the benthic nutrient fluxes. Only the sediments collected seaward of the Lorient Bay (sites #10 and #11) showing a green macroalgae enrichment (see discussion section 4.1.1) presented, in parallel, NH_4^+ and PO_4 fluxes significantly higher than that measured on the regional scale (Wilcoxon test, $p < 0.005$).

615   In the present study, we focused on the link between the benthic nutrient fluxes and the sediment composition, with a comparison of significant effect of SOM origin *vs* quantity. Nevertheless, we must keep in mind that a large part of the variance of benthic NH_4^+ and PO_4 fluxes on the regional scale remains unexplained here (66-67 %) (Fig. 8). As mentioned earlier, the microbial abundance and diversity were not assessed in the current study, and the abundance and/or diversity may very well play an additional role in the degradation of the OM. In addition,

620   the bioturbation, mediated by the macrofauna activities, was likely preserved in the sediment core incubations and therefore may be involved in the spatial variability of NH_4^+ and PO_4 fluxes (Graf and Rosenberg, 1997; Welsh, 2003; Kristensen et al., 2012).

5. Conclusion

     This is the first study to our knowledge that has described the variability in SOM composition through a broad

625   sampling campaign of marine mudflats at the regional scale, and made the link with sediment potential biodegradability and nutrient release. The sediment slurry incubations allowed to determine the spatial variability of potential mineralization rates under oxic conditions. The physical and chemical sedimentary characteristics explained 58% of the variability of mineralization rates, with a negligible effect of the SOM origin. The sediment core incubations allowed to assess the spatial variability of sediment biodegradability under realistic redox

630   conditions of the sediment through the measurements of NH_4^+ and PO_4 fluxes at the sediment-water interface. The physical and chemical sedimentary characteristics explained 34 and 33 % of the variation of PO_4 and NH_4^+ fluxes. The sediment core incubations showed the prevalent role of SOM origin over quantity on the benthic nutrient fluxes, with a significant effect 5 and 1.5 fold higher on the PO_4 and NH_4^+ fluxes respectively. The present study also highlighted the potential impact of human activities on the nutrient dynamics at the sediment-water interface,

635   through agricultural runoff and/or sewages discharges.

     A significant fraction of the spatial variability of benthic nutrient fluxes could not be explained here by the sedimentary characteristics, suggesting that the spatial variability of benthic microbial diversity/abundance should be considered for further investigations. It would be interesting to link the chemical composition to genetic information of sediment in the aim to understand the variability of benthic microbial function of coastal areas

640   under anthropogenic pressures.

     In this work, all mudflats were under a macro-tidal regime, and therefore another recommendation would be to determine to what extend the tidal forcing can change the sediment composition and thus its biodegradability.

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645   AML, FA, FC, EJ, ER, NL participated in the field campaign, collected and prepared the samples. JL, EJ, ML, NL, FA, FC and ER performed the measurements. JL analyzed the data, with the help of AP.

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