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Research papers

Influence of coastal Mediterranean rivers on the organic matter composition and reactivity of continental shelf sediments: The case of the Têt River (Gulf of Lions, France)

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ABSTRACT

River-dominated ocean margins (RiOMars) are areas of high productivity, rapid sediment deposition, and intense recycling. The Gulf of Lions, located in the North occidental Mediterranean Sea, is no exception to this general rule and is under the prevalent influence of the Rhône River. One particularity of this continental shelf is that it is also fed by several small coastal rivers whose inputs actively contribute to the coastal dynamic and export to the deep-sea. Our objective was to gauge the influence of coastal rivers on the quality and reactivity of the organic matter delivered to the continental shelf as these properties control two important functions of coastal areas: benthic productivity and carbon sequestration. We chose for this study, the Têt River, which is typical of coastal Mediterranean rivers with a torrential regime. Sediment cores were sampled five times over a one-year period on four stations located along the dominant trajectory of the Têt River plume. The biogeochemical characteristics of the surface sediments were analysed to highlight spatio-temporal trends in the sedimentary organic matter composition and to identify the major environmental factors controlling its reactivity. Nutrient and dissolved oxygen fluxes at the water-sediment interface were furthermore measured at two stations using *ex-situ* whole core incubations.

Results from this study highlight the seasonal influence of riverine versus autochthonous productions on the quality of sedimentary organic matter in the vicinity of the river mouth. Farther on the mid shelf, a terrestrial imprint is still visible, but the temporal signal is blurred as a consequence of strong mixing during frequent episodes of resuspension/deposition. Organic matter is efficiently remineralised in this system with total oxygen uptake (TOU) rates comparable to those measured off the Rhône River. Finally, organic matter quality and reactivity are also constrained in this system by physical forcings, which promote remineralisation and advection of sediments.

1. Introduction

The Mediterranean Sea is bordered by several large rivers (the Rhône, Nile, Pô and Ebro Rivers) and numerous coastal rivers, which despite the small size of their watershed, have a great significance on the overall inputs to the coastal area (Milliman, 2006). At the scale of the Mediterranean Sea, coastal rivers occupy 38% of the surface drainage area, but contribute to about 58% of the natural suspended particulate matter flux (Sadaoui et al., 2018). The Gulf of Lions is one of the largest and most productive shelves in the Mediterranean Sea, and

is strongly influenced by a series of rivers draining a large variety of watersheds (mountainous, vegetated, rural, urbanised, industrialised...). The Rhône River, nowadays the main source of freshwater and particulate matter to the Mediterranean Sea, accounts for 95% of the whole terrestrial inputs to the gulf of Lions (Sadaoui et al., 2016), but smaller rivers also contribute to the export of dissolved and particulate materials to the coastal area (Higuera et al., 2014). The terrestrial particulate organic matter (POM) delivered by the Rhône River was shown to have a dominantly modern origin (Cathalot et al., 2013) and to represent a labile and biodegradable source of biogenic

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compounds (Bourgeois et al., 2011; Pruski et al., 2015), which promote microbial degradation processes (Cathalot et al., 2010; Pastor et al., 2011) and sustain the benthic food web (Bonifácio et al., 2014; Darnaude et al., 2004; Goineau et al., 2012; Hermand et al., 2008). The suspended particles delivered by smaller coastal rivers are enriched in organic matter by a 2.5–3 factor in comparison to the Rhône River (Higuera et al., 2014) and may thus strongly impact the biogeochemical dynamic on the adjacent marine prodeltas. Due to the Mediterranean climate, small to medium-size rivers furthermore have highly variable regimes with periods of drought and episodes of intense flooding, which affect the quality of the exported material (Higuera et al., 2014). Additionally, coastal rivers are exposed to a long lasting and increasing anthropogenic pressure (UNEP/MAP, 2000), and are predicted to be particularly vulnerable to climatic change (Sánchez-Arcilla et al., 2011). These many reasons stress the need to understand the biogeochemical fate of the POM delivered by coastal rivers to the Gulf of Lions.

The Têt River is typical of coastal Mediterranean rivers with a torrential regime, which was well illustrated by conditions occurring over the 1980–1999 period (Serrat et al., 2001). Annual precipitation for the entire basin was on average 750 mm yr^{-1} and was characterised by extended periods of dry weather interrupted by short, but violent rainfall events (Serrat et al., 2001). If strong enough, the latter can lead within a few hours to flash flood events that are well known in this region. In order to reduce the intensity of these events, a retention dam was built in 1976 at Vinça (55 km upstream the river mouth), at the entrance of its flat alluvial plain. The retention dam has reduced the sediment export from the river drainage basin to the Mediterranean Sea by 80% (Sadaoui et al., 2018) and impaired the natural hydrological regime (Pique et al., 2016). However, the Têt system remains typical of minor Mediterranean rivers, which are characterised by a high seasonal and inter-annual variability of their liquid and solid discharge rates. As with most Mediterranean coastal rivers, sediment transport occurs almost only during episodic runoff events generating a transient prodelta deposit. This sediment is resuspended during storms, transported offshore as near-bottom fluid mud layers, and deposited on the middle shelf where the mud belt is typically located (Traykovski et al., 2000). For this reason, many investigations on the dynamic of sediments and associated particles off the Têt River have targeted episodes of floods or storms (Bourrin et al., 2008; Guillén et al., 2006; Kim et al., 2009; Roussiez et al., 2011). Yet, how inputs from coastal rivers impact the microbial, ecological and biogeochemical processes that transform organic matter on the continental margin of the Gulf of Lions remained poorly known.

Preliminary organic carbon (OC) budgets in the Têt prodelta (28 m depth) suggest efficient degradation of POM at the sediment-water interface (Buscail et al., 1990). Based on fluxes measured by bottom sediment traps and OC accumulation rates, mineralisation rates were estimated to account for 76% of the OC inputs.

The main goals of this study were thus (1) to document the spatio-temporal variability in the composition of surface sediments along the fluvio-deltaic continuum of the Têt River and (2) to provide insights on the environmental factors controlling the sources, quality and fate of POM in this system. Based on previous studies (Bourrin et al., 2008; Buscail et al., 1995, 1990; Kim et al., 2009; Roussiez et al., 2006), four stations located along the dominant trajectory of the Têt River plume were selected (i.e. south eastward transect, Fig. 1) and sampled five times over a one-year period. The biogeochemical properties of the surface sediments were assessed by laser granulometry and the analysis of a suite of complementary biochemical descriptors (OC, total nitrogen, carbohydrates, lipids, amino acids, and fatty acids). Moreover, as a proxy of organic matter reactivity, nutrient and oxygen dynamics at the sediment-water interface were evaluated using *ex-situ* whole core incubations.

2. Material and methods

2.1. Regional settings

The Gulf of Lions, located on the North occidental Mediterranean Sea, is a microtidal, river-dominated continental margin with a crescent-shaped shelf incised by numerous canyons (Fig. 1). It is fed primarily by the Rhône River at the North East, but also receives sediment inputs from several smaller ($< 200 \text{ km}$ in length) and torrential rivers draining small mountainous watersheds along the coast of the Gulf of Lions (Bourrin et al., 2006; Sadaoui et al., 2016). These so-called coastal rivers account for $\sim 5\%$ of the total annual solid discharge to the Mediterranean Sea in this area with increasing contribution in late spring and autumn when flash floods occur (Sadaoui et al., 2016). Fluvial inputs occur mainly during flood events and form ephemeral thick deposits of fine grained sediments in the inner-shelf around 30 m depth, which are swept by storms and rapidly advected toward the middle shelf (Bourrin et al., 2008). These depocenters are commonly named prodeltas and represent active muddy areas, which contrast with the low sedimentation that occurs on the nearby adjacent shelf. A mid-shelf mud belt centred between 50 and 75 m depth is formed by the inputs of the Rhône River and adjacent coastal rivers and narrows towards the south of the shelf and the canyons. The wind-driven general circulation on the shelf is principally North to South and shapes the distribution of surface sediments (Bourrin et al., 2008).

The Têt River can be considered as representative of Mediterranean coastal rivers with a torrential regime (Lespinas et al., 2010). The Têt River takes its source at 2.405 m altitude in the Pyrenees (south-western France) and drains a watershed of about 1.550 km^2 . Its course is barred, in its upstream part, by the hydroelectric dam of the Bouillouses and the dam-reservoir of Vinça (24 hm^3) built in 1976 to protect the alluvial plain from its floods. Damming profoundly affected its natural regime and introduced a time shift between the recharge by precipitation and the releases of the dam (Caballero and Ladouche, 2015). In autumn and early winter, the reservoir is maintained at its lowest level allowing to efficiently curb floods. It then refills with water from the snow melt and sustain irrigation in the Roussillon plain in the summer when the Têt River is at its lowest level.

The watershed of the Têt River is strongly vegetated ($\sim 77\%$ of forests and semi-natural habitats) with a well-developed riparian vegetation in the alluvial plain, but it is also strongly impacted by urban activities in the lowest part of the watershed (Higuera et al., 2014). Subjected to a Mediterranean climate, its regime is characterised by a very low water flow ($10.4 \text{ m}^3 \text{ s}^{-1}$ with minimal and maximal discharge rates of 1 and $471 \text{ m}^3 \text{ s}^{-1}$, respectively, Bourrin et al., 2006) and brief, but intense flash floods ($> 100 \text{ m}^3 \text{ s}^{-1}$) during which the transported solid flows can reach up to 90% of the total annual flux in few days (Serrat et al., 2001). The Têt River flows in the western part of the Gulf of Lions on the Roussillon coast, where sediment deposits form a prodelta (Aloisi and Monaco, 1975). Waves and currents induce strong resuspension (Guillén et al., 2006). As a consequence, only about 20% of the suspended solid discharge is trapped permanently in the Têt prodelta (Bourrin et al., 2006) and most sediments are dispersed along the South and East towards the middle-outer shelf and slope (Guillén et al., 2006).

2.2. Sampling strategy

The collection area is located in the western part of the Gulf of Lions between 20 and 81 m depth off the mouth of the Têt River (Fig. 1).

From January 2008 to January 2009, sediments were sampled on the continental shelf along a south-eastward gradient corresponding to the main dispersal pathway of the Têt River plume (Table 1).

Sediment cores were collected, depending of the depth of the sampling site, by scuba divers or using a Midi multiple corer from Osil (Great-Britain). The cores were stored on the deck in the dark in tanks

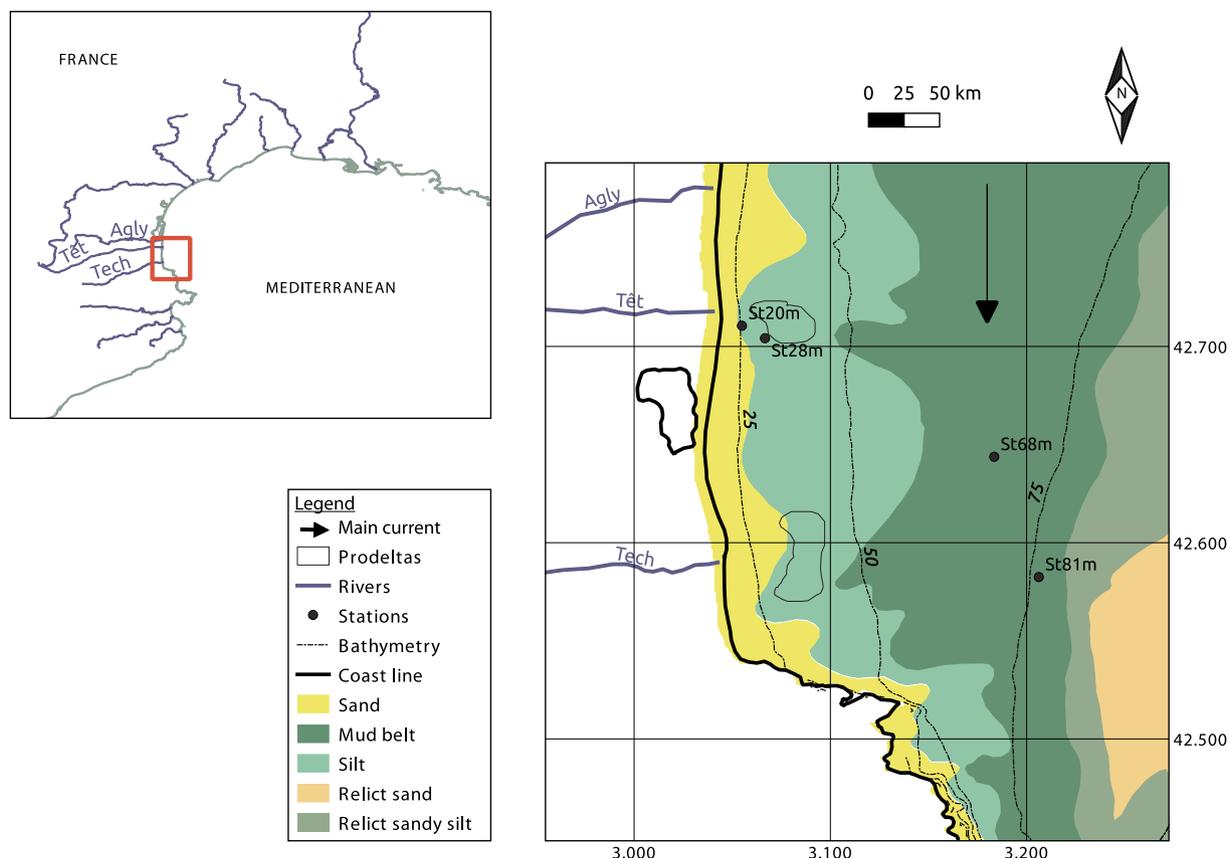


Fig. 1. Sedimentological and bathymetric map of the North occidental Mediterranean Sea showing the sampling locations in the Gulf of Lions (modified from Monaco and Aloisi, 2000). Stations are localised along the preferential dispersal direction of the sediments delivered by the Têt River. The arrow indicates the dominant current.

containing cooled sea water and transported to the laboratory within 3 h. Three undisturbed sediment cores from each station were selected. Cores from stations St20 m and St81 m were immediately sliced into 7 layers (0–0.5 cm; 0.5–1 cm; 1–2 cm; 2–3 cm; 3–5 cm; 5–7 cm; 7–10 cm). The layers were carefully homogenised, conditioned in Falcon® tubes (2 aliquots per sediment layer), and stored at –80 °C. Cores from stations St28 m and St64 m were used for *ex-situ* whole core experiments and the sediment was conditioned at the end of the incubation as described for cores from the two other stations.

2.3. Sedimentological properties

Down-core profiles of porosity (ϕ) and grain size were determined on the triplicate cores of each site. Porosity was calculated from sediment water content (W) and density (ρ) with correction for salt content using the following equation:

$$\phi = W\rho_s / [W\rho_s + (1 - w)\rho_e] \tag{1}$$

where W : water weight/fresh sediment weight of a sediment sample and ρ_s : density of the solid mass (2.63 g cm^{-3}) and ρ_e : density of sea water (1.03 g cm^{-3}).

Sediment granulometry was assessed using a Malvern® Mastersizer

2000 laser diffraction particle size analyser and classified using the Wentworth scale. No pretreatment to remove organic matter or salts was used. D_{50} is the diameter corresponding to the median of particle volumes, assuming that all particles were spherical.

2.4. Bulk biochemical analyses

Total carbon (TC), total nitrogen (N_{tot}) and organic carbon (OC) contents were measured on the freeze-dried, first layer sediment (0–0.5 cm) of each core (3 cores X 4 stations X 5 dates). Homogenised, precisely weighed samples were analysed using an automatic CN-analyser LECO 2000, after acidification with 2N HCl (overnight at 50 °C) in order to remove carbonates prior to the analyses of OC (Cauwet et al., 1990). Precision for OC and N_{tot} measurements are about 2% and 0.3% for TC. Carbonate content was calculated from inorganic carbon (TC-OC) using the molecular mass ratio ($\text{CaCO}_3:\text{C} = 100:12$). Total lipids were measured by a colorimetric method after extraction with a 2/1 (v:v) chloroform-methanol mixture. Absorption of the products of the sulfo-phospho-vanillin reaction was measured at 520 nm with a Beckman spectrophotometer (precision of 10%) (Barnes and Blackstock, 1973). Total carbohydrates were measured by a colorimetric method on the fraction hydrolysed by 3 M H_2SO_4 . Absorption of

Table 1
GPS Coordinates (WGS84/ED50), water depth, distance to the Têt mouth of the sampling sites and type of coring.

Stations	Latitude (N)	Longitude (E)	Depth (m)	Distance to the mouth (km)	Core type
St20 m	42°42.632'	3°03.296'	20	1.7	Scuba diving hand core
St28 m	42°42.250'	3°04.000'	28	3.0	Scuba diving hand core
St64 m	42°38.626'	3°11.010'	64	14.5	Multitube corer
St81 m	42°34.948'	3°12.373'	81	20.5	Multitube corer

the products resulting from the anthrone-sulfuric acid reaction was measured at 625 nm using a Beckman spectrophotometer (precision of 8%) (Brink et al., 1960).

Total hydrolysable amino acids (THAAs) were assayed by a colorimetric method on the fraction hydrolysed by 6 M HCl for 16 h at 110 °C. Absorption of the products resulting from the amino acid-ninhydrin reaction was measured at 570 nm using a UV Beckman spectrophotometer (precision of 15%) (Stevenson and Cheng, 1970). Biopolymeric organic carbon (BPC) was defined as the sum of the carbon equivalents of total carbohydrates (C_{CARB}), proteins (C_{THAA}) and lipids (C_{LIP}) using conversion factors of 0.4, 0.49 and 0.75, respectively (Danovaro et al., 2001).

Organic matter lability was assessed by the measure of the bioavailable or enzymatically hydrolysable amino acids (EHAAs), which represent the fraction of proteins that may be metabolised by marine invertebrates. They were extracted according to the protocol proposed by Mayer et al. (1995). Approximately 200 mg of freeze-dried sediment were poisoned with 1 ml of a solution containing 0.1 M sodium arsenate and 0.1 mM pentachlorophenol within a pH 8 sodium phosphate buffer and were incubated for 1 h at room temperature. This mixture of two inhibitors of bacterial active transport systems prevent the bacterial consumption of the amino acids released after the addition of 100 μl of proteinase K solution (1 mg/mL). This mixture was then incubated for 6 h at 37 °C. After centrifuging to discard the remaining particulate material (10000 g, 30 min, 4 °C), 750 μl of supernatant was recovered. Macromolecules were then precipitated with pure trichloroacetic acid (75 μl) and centrifuged (10000 g, 30 min, 4 °C). The low molecular weight compounds contained in the supernatant were further hydrolysed to monomeric amino acids using strong HCl and quantified fluorimetrically using orthophthalaldehyde on a LS55 luminescence spectrometer from PerkinElmer. The proportions of nitrogen and carbon contained in the EHAAs (EHAA-N and EHAA-C) were calculated assuming nitrogen and carbon account respectively for 16% (Mayer et al., 1986) and 41% (Bourgeois et al., 2011) of the EHAA mass.

2.5. Fatty acid analysis

One gram of freeze-dried surface sediment from each of the triplicate cores were pooled to constitute a new sample. Therefore, although no error bars are provided, concentrations and compositions are average values for the stations at the different dates. Fatty acids were extracted and converted into fatty acid methyl esters (FAMES) by direct acid transmethylation and analysed by GC/MS with a Saturn 2100T ion trap detector (Varian). Details regarding the extraction protocol and analytic procedure are given in Bourgeois et al. (2011) and Pruski et al. (2015). Repeatability of the analysis ranged from 3.2% to 13% for individual fatty acids with a mean value of 5.9%.

Fatty acid concentrations (initially in $\mu\text{g.g}^{-1}$ dry weight) were normalised to total organic content ($\text{mg.g}_{\text{TOC}}^{-1}$) to remove the dilution effect of the mineral matrix. Compounds were grouped as follows: the saturated fatty acids (SAFAs) of mixed origin, the terrestrial long-chain saturated fatty acids (LC-FAs, ≥ 24), the terrestrial C_{18} polyunsaturated fatty acids (C_{18} -PUFAs, 18:2 ω 6 and 18:3 ω 3), the remaining PUFAs attributed to phytoplankton, the monounsaturated fatty acid series (C_{16} and C_{18} MUFAs), and the straight and branched odd-numbered fatty acids of bacterial origin (BAFAs; Pruski et al., 2015). Fatty acids account for one of the most labile fractions of the organic matter; fatty acid yields (OC-normalised concentrations) are thus indicative of inputs or preservation of labile organic matter. In particular, the presence of PUFAs is indicative of fresh organic matter; this information is summarised in the unsaturation index (UI). The terrigenous to aquatic ratio ($\text{TAR}_{\text{FA}} = \text{long-chain fatty acids to short-chain fatty acids}$) was used to evaluate the relative contributions of terrestrial versus algal/microbial sources. A list of the bulk descriptors and biomarkers used in this study is provided in Table 2.

2.6. Benthic fluxes of oxygen and nutrients

Total oxygen uptake (TOU) rates and nutrient fluxes over the sediment-water interface were determined using sediment *ex-situ* whole core incubations (Rabouille et al., 2003). Undisturbed sediment cores from stations St28 m and St64 m (3 cores per station) were brought to the nearby laboratory and left overnight in the dark in a water bath (~ 100 L) filled with running filtered sea water at bottom water temperature. Incubations started early the next morning. Briefly, cores were sealed with gas-tight lids connected to a reserve tank filled with bottom-water and placed in dark, refrigerated cabinets at field temperature. During the 24h-incubation period, the overlying water was continuously homogenised with a magnetic stirrer driving a Teflon-coated magnetic stir bar at 65 rpm to prevent concentration gradients from developing in the water (Cowan and Boynton, 1996). Seawater from the triplicate cores was sampled every 3 h with glass syringes for measurement of dissolved oxygen and nutrients, and a sample was taken from the reserve tank as a blank. Seawater for nutrient analysis was filtered with a 0.45 μm pore-size syringe regenerated cellulose filter (UptiDiscTM, Interchim), and the filtrate was frozen at -20 °C. Nitrate (NO_3^-) + nitrite (NO_2^-) and silicate (Si(OH)_4) were assayed using an automated colorimetric technique (Skalar Auto-Analyser) according to the standard procedures of Armstrong et al. (1967) and Mullin and Riley (1955). Oxygen concentration in the overlying water of each core and the reserve tank was determined by mean of micro Winkler titration (Hansen, 1999). Fluxes were determined by regressing changes in the overlying water concentration over time. A correction for overlying water dilution with bottom-water at each sampling point was applied. Negative signs indicated fluxes directed to the opposite side of the concentration gradient, meaning consumption by the sediments. Non-significant regressions were interpreted as zero flux (i.e., changes over time that were less than the analytical variability, Pearson's correlation, $p < 0.05$).

2.7. Meteorological data and river discharge

Half-hourly wave data were recovered at the Leucate buoy from the CANDHYS database of the CEREMA from November 2007 to April 2010. Significant wave height (H_{sig}) and peak period (T_p) were first used to calculate the orbital wave velocity (u_{br}) at each sampling stations (20 m–81 m depth). Critical shear velocities were estimated at each station using the average bottom sediment grain-size as an input to the Wiberg and Sherwood model (Wiberg and Sherwood, 2008). We then estimated the % of time during which the orbital wave velocities were above the critical shear velocities at each sampling station and thus corresponding to the % of time when resuspension processes can occur.

Discharge data were obtained from the HYDRO database hosted at the French Ministry of Environment.

2.8. Data treatment

Due to the non-normal distribution of most of the variables, non-parametric statistical analyses were used to examine relationships between variables, including the Wilcoxon signed-rank test and the Spearman's rank correlation test (ρ). In all cases, p-values below 0.05 were considered statistically significant. The R package “corrplot” was used to calculate and visualise correlation matrices.

An exploratory principal component analysis (PCA) followed by a hierarchical cluster analysis was performed on the 20 samples (4 stations X 5 dates) and a selection of variables in order to ordinate the samples according to the sedimentological and biochemical (origin/lability) properties of the sediments and to identify the structuring parameters. Since quantitative descriptors of organic matter (N_{tot} , THAA, carbohydrate and lipid concentrations) were all correlated to OC content, we only kept this latter variable to avoid co-correlations in the

Table 2

Summary of biochemical descriptors and indices used in this study with their interpretation. Fatty acids are designated as follows: the number before the colon indicates the number of carbon atoms, the number after the colon indicates the number of carbon-carbon double bonds and the position of the initial unsaturation is indicated by the number of carbon units from the methyl-end of the molecule. Unsaturation index (UI) is calculated as the sum of products of the number of double bonds of each fatty acid multiplied by its percentage of the total fatty acid composition. $TAR_{FA} = (C_{24} + C_{26} + C_{28}) / (C_{12} + C_{14} + C_{16})$. OM = organic matter.

Biochemical descriptors and indices	Main diagnostic information	References
Bulk OM proxies		
C:N		
6–9	Marine derived OM	Moloney and Field (1991)
8–20	Soil derived OM	Hedges and Oades (1997)
> 20	Higher plant derived OM	Meyers (1997)
Biopolymeric Carbon		
Protein to carbohydrate ratio	Fresh and recent material > 1, aged algal material < 1	Dell'Anno et al. (2008)
Lipid to carbohydrate ratio	Increases with OM quality	Isla et al. (2006)
Fatty acid to lipid ratio	Decreases as OM is degraded	This study
Amino acids		
Enzymatically hydrolysable amino acids	OM bioavailability for the benthic fauna	Mayer et al. (1995)
Fatty acids		
Mid-chain even-number (< C ₂₀) SAFA	Non specific, but shorter chains predominate in phytoplankton	Dunstan et al. (1994), Bianchi and Canuel (2011)
Long-chain SAFA (C ≥ 24)	Terrestrial higher plants, macrodetritus	Bianchi and Canuel (2011), Dunstan et al. (1994), Pruski et al. (2015)
C ₁₈ PUFA (C _{18:2ω6} and C _{18:3ω3})	Terrestrial higher plants (> 2.5%)	Budge et al. (2001), Pruski et al. (2015)
PUFA (all except C _{18:2ω6} and C _{18:3ω3})	Phytoplankton (with C _{20:5ω3} specific of diatoms)	Dunstan et al. (1994)
MUFA; in particular C _{16:1ω7}	Common in diatoms and bacteria	Bianchi and Canuel (2011), Dunstan et al. (1994)
Branched iso- and anteiso-, odd-number C ₁₅ and C _{18:1ω7}	Bacterial sources	Bianchi and Canuel (2011)
Unsaturation index (UI)	Degradation (> 70 old detrital matter)	Claustre et al. (1992)
Terrigenous to aquatic acid ratio (TAR _{FA})	Higher values indicative of watershed inputs	Meyers (1997)
C _{16:1ω7} to C _{18:1ω9} ratio	Higher ratios indicative of higher contribution of phytoplankton vs zooplankton	Tolosa et al. (2004)
C _{18:1ω9} to C _{18:1ω7} ratio	< 1 if OM derived from bacteria and faecal pellets	Tolosa et al. (2004)

dataset. Depth, distance to the river mouth, contribution of biopolymeric compounds to total OC content (i.e. C_{CARB}, C_{LIP} and C_{THAA}s expressed as % of total OC), BAFAs and TAR_{FA} were added as supplementary variables, meaning that they do not contribute to the construction of the PCA axes, but are projected on the PCA plot to guide interpretation. Data were log transformed, then auto scaled (variables were scaled by subtracting the variable mean and dividing by the variable standard deviation) prior to analysis. Variables were multinormal (Mardia's test of multinormality) following this standardisation. Multivariate principal component analysis (PCA) was combined to hierarchical clustering of the PCA components (HCPC), which determines clusters of samples that present homogenous characteristics (Husson et al., 2010). The hierarchical cluster analysis was performed on the 5 first components of the PCA (accounting for 95% of the total variance) using Ward's agglomerative method and a Euclidean distance. The PCA and HCPC were performed using R software (3.4.4) with the package Rcmdr – Factominer (Lê et al., 2008) and missing data were handled using the package MissMDA (Josse and Husson, 2013).

3. Results

3.1. Hydrology and climatology

The Têt River is the main input of water and sediment to the studied area. The Têt River water discharge was usually lower than 10 m³ s⁻¹ during the study period with an average daily discharge of 2.5 m³ s⁻¹ (Fig. 2, data provided by DDE Aude/HYDRO-MEDD/DE). Total suspended solid discharge paralleled liquid discharge (data not shown). The Têt River regime in 2007 and 2008 was typical of dry years with no flood event (≥ 100 m³ s⁻¹). However, periods of increased runoff due to major rainfalls were observed in June, November and December 2008 (Fig. 2). Episodes of strong winds were recorded in December 1997 (158 km h⁻¹ at Port Vendres) and January 2008 (119 km h⁻¹ at Port-Vendres). Three annual storms were observed on the shelf of the Gulf of Lions during the study period: two dry storms in November 2007 (Hsig = 4.3 m) and January 2008 (Hsig = 4.6 m) and a small wet

storm in December 2008 (Hsig = 4.8 m), (Fig. 2). On the 26th and 27th of December 2008, in particular, the oceanic storm Britta has affected the Roussillon coastline raising a devastating swell and accompanied by intense rainfalls (10–20 mm h⁻¹) (Sanchez-Vidal et al., 2012).

Sediment erosion showed a marked seasonality and decreased from the inner shelf to the mid-shelf. Sediments can be remobilised over the period studied by the swell 32%, 18%, 4% and 1.6% of the time at 20, 28, 64 and 81 m depth, respectively (Fig. 3). On the mid-shelf mud belt sediment remobilisation was restricted to a few days in the autumn and winter periods. The dashed lines indicate the sampling dates.

3.2. Sedimentological properties

According to their median grain size (D₅₀), sediments can be classified as follows: sand at St20 m, sandy mud at St28 m and muds at 64 and 81 m depth (Table 3). St28 m differed from St20 m by higher proportions of silt (28–35% at St28 m, 8–22% at St20 m), but also by higher proportions (up to 14%) of coarser material in certain layers (Fig. 4), which could be attributed to shell and vegetal debris (Buscaill et al., 1995). The two offshore stations were dominated by fine materials with 84–90% of clay and silt (particles < 63 μm, Fig. 4).

Porosities were constantly lower at the sandy stations than at the muddy stations (Table 3). Generally, there was no significant change of the averaged porosity at a given station during the study period. However, a decrease of the porosity was observed at St28 m in January 2009.

Distinct carbonate contents were associated to the different types of sediments (Table 3). Sandy sediments contained less than 3.5% of CaCO₃, sandy muds 11–14%, whereas muds were characterised by more than 20% of CaCO₃.

3.3. Bulk organic matter composition

Quantity of organic matter in surface sediments (0–0.5 mm) was assessed by measuring organic carbon (OC) and total nitrogen (N_{tot}) contents (Table 3).

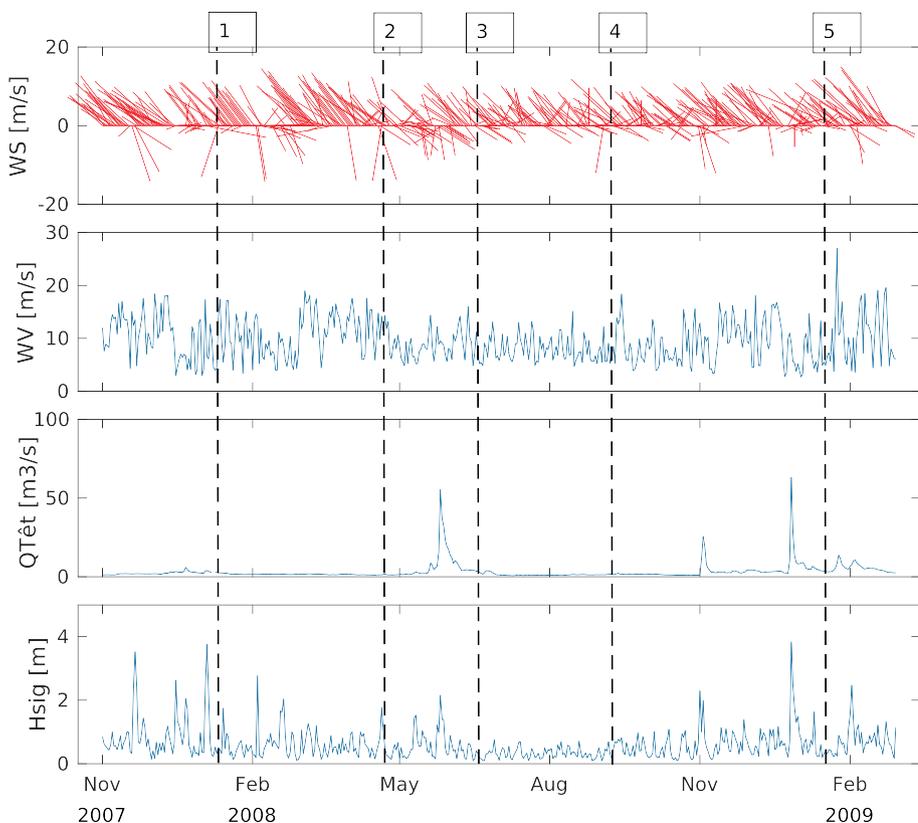


Fig. 2. Time series of wind sticks (WS) and wind field (WV) at the Leucate station, daily river discharge of the Têt River measured at the Bompas station (QTét), and significant wave height (Hsig) at the Leucate buoy. By convention, wind sticks represent the direction from which the wind is blowing (upward = coming from North). The dashed lines indicate the sampling dates.

At 20 m depth, OC contents were low with an annual mean value of $2.4 \pm 0.4 \text{ mg g}^{-1}$. At 28 m depth, OC contents were higher with an annual mean value of $5.7 \pm 0.7 \text{ mg g}^{-1}$. At 64 and 81 m depth, OC contents in sediments were more homogenous with an annual mean

value of 9.8 ± 0.6 and $9.2 \pm 0.4 \text{ mg g}^{-1}$, respectively.

N_{tot} distribution in the surface sediments follows the same pattern as OC content as shown by the significant correlation between these two parameters (Fig. 5).

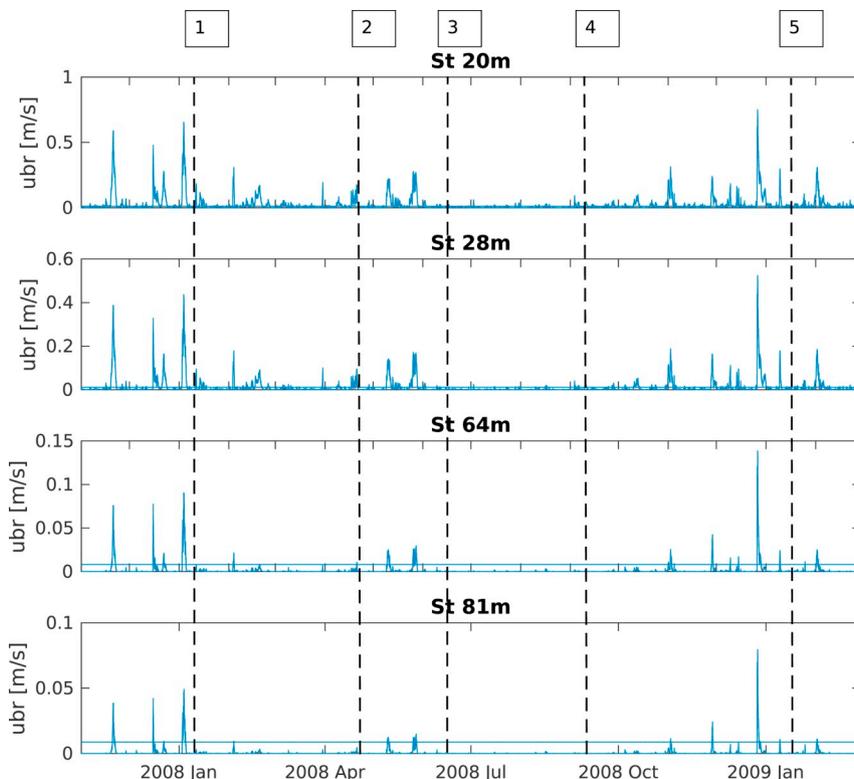


Fig. 3. Time series of bottom wave orbital velocity (ubr) for the four stations. The horizontal lines on the time series correspond to the critical shear velocity for each station. The dashed lines indicate the sampling dates.

Table 3
Sedimentological properties and biochemical organic matter composition (mean \pm standard deviation) of the sediments in the Têt River prodelta and adjacent shelf. Median grain size (D_{50}), porosity (Φ), carbonates (CaCO_3), organic carbon (OC), total nitrogen (Ntot), C/N_a (atomic carbon to nitrogen ratio), total lipids, total carbohydrates, total hydrolyzable amino acids (THAAs), enzymatically hydrolyzable amino acids (EHAAs), percentage of carbon contained in EHAAs (EHAAs-C%), percentage of nitrogen contained in EHAAs (EHAAs-N%), and percentage of biopolymeric carbon (BPC). N = 3, except for porosity where N = 9 (3 replicates per core X 3 cores) and * where N = 2, ND = no data.

Stations	Sampling dates	D_{50} (μm)	Porosity	CaCO_3 (%)	OC ($\text{mg}\cdot\text{g}^{-1}$)	Ntot ($\text{mg}\cdot\text{g}^{-1}$)	C/N_a	Lipids ($\mu\text{g}\cdot\text{g}^{-1}$)	Carbohydrates ($\mu\text{g}\cdot\text{g}^{-1}$)	THAAs ($\mu\text{g}\cdot\text{g}^{-1}$)	EHAAs ($\mu\text{g}\cdot\text{g}^{-1}$)	EHAAs-C%	EHAAs-N%	BPC (%)
Sf20m	January 2008	182 \pm 8	0.43 \pm 0.01	1.7 \pm 0.1	2.1 \pm 0.1	0.2 \pm 0.0	11.0 \pm 1.3	132 \pm 52	300 \pm 77	489 \pm 192	105 \pm 19	2.1 \pm 0.3	7.5 \pm 0.5	23.7 \pm 6.6
	April 2008	147*	0.50 \pm 0.05	3.2 \pm 0.4	3.2 \pm 0.7	0.4 \pm 0.2	11.3 \pm 3.1	175 \pm 64	543 \pm 220	1038 \pm 658	222 \pm 26	3.0 \pm 0.2	10.7 \pm 2.9	26.0 \pm 8.6
	June 2008	174 \pm 7	0.48 \pm 0.01	1.8 \pm 0.1	2.1 \pm 0.1	0.3 \pm 0.0	9.8 \pm 0.4	133 \pm 35	410 \pm 43	685 \pm 235	188 \pm 24	3.7 \pm 0.6	12.0 \pm 2.5	28.5 \pm 3.7
	September 2008	166 \pm 5	0.47 \pm 0.00	1.8 \pm 0.1	2.6 \pm 0.4	0.3 \pm 0.0	11.6 \pm 0.8	246 \pm 27	354 \pm 49	609 \pm 195	194 \pm 60	3.1 \pm 0.6	12.0 \pm 3.1	24.6 \pm 3.1
	January 2009	175 \pm 10	0.52 \pm 0.04	1.4 \pm 0.2	2.3 \pm 0.6	0.2 \pm 0.1	12.4 \pm 2.6	143 \pm 52	1151 \pm 630	455 \pm 192	129 \pm 46	1.7 \pm 0.1	10.7 \pm 6.4	37.7 \pm 13.5
	Annual mean	171 \pm 10	0.47 \pm 0.03	2.0 \pm 0.2	2.4 \pm 0.5	0.3 \pm 0.1	11.5 \pm 1.9	166 \pm 46	552 \pm 204	655 \pm 294	163 \pm 58	2.8 \pm 0.9	10.5 \pm 3.7	27.9 \pm 8.5
Sf25m	January 2008	80 \pm 5	0.57 \pm 0.07	11.4 \pm 0.3	4.6 \pm 0.4	0.4 \pm 0.1	14.1 \pm 0.5	250 \pm 37	563 \pm 184	925 \pm 240	209 \pm 13	1.9 \pm 0.1	9.7 \pm 0.6	18.2 \pm 3.1
	April 2008	76 \pm 13	0.56 \pm 0.01	11.5 \pm 0.4	7.0 \pm 1.2	0.5 \pm 0.1	16.7 \pm 2.9	257 \pm 59	673 \pm 114	1009 \pm 157	202 \pm 5	1.2 \pm 0.2	6.6 \pm 0.8	14.4 \pm 5.7
	June 2008	86 \pm 12	0.56 \pm 0.01	14.2 \pm 0.2	5.9 \pm 0.3	0.5 \pm 0.1	13.3 \pm 1.1	254 \pm 100	1026 \pm 371	1106 \pm 281	296 \pm 57	2.1 \pm 0.3	9.1 \pm 1.1	19.8 \pm 6.1
	September 2008	72 \pm 4	0.60 \pm 0.03	12.0 \pm 0.2	6.0 \pm 0.2	0.5 \pm 0.0	13.5 \pm 0.8	208 \pm 27	1803 \pm 1520	1131 \pm 332	224 \pm 111	2.0 \pm 0.0	9.1 \pm 3.6	23.8 \pm 7.6
	January 2009	78 \pm 5	0.44 \pm 0.07	13.2 \pm 0.4	5.1 \pm 1.4	0.4 \pm 0.1	14.0 \pm 2.5	184 \pm 44	932 \pm 406	631 \pm 27	179 \pm 16	1.5 \pm 0.3	6.9 \pm 1.1	17.3 \pm 7.1
	Annual mean	80 \pm 13	0.56 \pm 0.06	12.4 \pm 0.3	5.5 \pm 1.1	0.5 \pm 0.1	14.3 \pm 2.0	231 \pm 53	999 \pm 519	960 \pm 207	222 \pm 63	1.6 \pm 0.5	7.9 \pm 2.0	18.8 \pm 5.4
Sf64m	January 2008	21 \pm 1	0.80 \pm 0.03	23.1*	9.4 \pm 1.3	0.9 \pm 0.0	11.3 \pm 1.2	655 \pm 78	1970 \pm 967	1645 \pm 177	252 \pm 11	1.2 \pm 0.1	4.2 \pm 0.1	22.4 \pm 1.9
	April 2008	16*	0.76 \pm 0.02	22.6 \pm 0.1	9.8 \pm 0.0	1.0 \pm 0.0	11.7 \pm 0.0	610 \pm 191	2030 \pm 1089	1695 \pm 136	209 \pm 79	0.9 \pm 0.3	3.3 \pm 2.8	21.4 \pm 6.6
	June 2008	22 \pm 2	0.79 \pm 0.01	21.4 \pm 0.3	9.9 \pm 0.8	1.0 \pm 0.0	11.5 \pm 1.0	646 \pm 176	1914 \pm 437	2188 \pm 298	302 \pm 15	1.3 \pm 0.2	4.8 \pm 0.2	23.6 \pm 4.7
	September 2008	14 \pm 2	0.78 \pm 0.03	23.2 \pm 0.1	9.5 \pm 0.1	1.0 \pm 0.0	10.9 \pm 0.3	704 \pm 153	1757 \pm 203	1767 \pm 209	297 \pm 21	1.3 \pm 0.1	4.6 \pm 0.2	22.0 \pm 1.6
	January 2009	18 \pm 2	0.79 \pm 0.01	31.5 \pm 0.7	10.1 \pm 0.8	1.2 \pm 0.1	10.0 \pm 1.4	ND	ND	ND	269 \pm 22	1.1 \pm 0.0	4.4 \pm 0.4	ND
	Annual mean	19 \pm 3	0.78 \pm 0.02	24.4 \pm 0.3	9.7 \pm 0.6	1.0 \pm 0.1	11.1 \pm 1.1	654 \pm 150	1918 \pm 674	1824 \pm 205	265 \pm 50	1.1 \pm 0.2	4.1 \pm 0.8	21.8 \pm 3.1
Sf81m	January 2008	21 \pm 1	0.78 \pm 0.04	20.6*	8.9 \pm 0.1	0.9 \pm 0.1	11.4 \pm 0.9	700 \pm 46	1641 \pm 504	1728 \pm 340	250 \pm 15	1.2 \pm 0.0	4.3 \pm 0.2	22.4 \pm 0.8
	April 2008	17 \pm 1	0.79 \pm 0.02	20.7 \pm 0.1	8.8 \pm 0.3	1.0 \pm 0.0	10.1 \pm 0.4	503 \pm 121	1919 \pm 756	2234 \pm 206	249*	1.1 \pm 0.0	3.9 \pm 0.1	25.5 \pm 3.2
	June 2008	20 \pm 3	0.80 \pm 0.00	20.4 \pm 0.1	8.8 \pm 0.6	1.0 \pm 0.0	10.4 \pm 0.6	596 \pm 58	1438 \pm 154	1950 \pm 201	292 \pm 32	1.4 \pm 0.1	4.7 \pm 0.5	22.5 \pm 1.4
	September 2008	18 \pm 2	0.80 \pm 0.00	20.0 \pm 0.2	10.1 \pm 0.2	1.1 \pm 0.0	10.8 \pm 0.2	751 \pm 195	1929 \pm 750	2103 \pm 207	281 \pm 32	1.1 \pm 0.1	4.1 \pm 0.4	23.5 \pm 2.6
	January 2009	18 \pm 2	0.80 \pm 0.00	21.0 \pm 0.1	9.4 \pm 0.7	1.1 \pm 0.0	10.5 \pm 0.6	602 \pm 153	1473 \pm 134	1965 \pm 97	312 \pm 54	1.4 \pm 0.3	4.3 \pm 0.8	20.2 \pm 0.9
	Annual mean	19 \pm 3	0.80 \pm 0.02	20.5 \pm 0.1	9.2 \pm 0.6	1.0 \pm 0.1	10.7 \pm 0.6	630 \pm 115	1680 \pm 460	1996 \pm 210	282 \pm 37	1.3 \pm 0.2	4.3 \pm 0.4	22.9 \pm 2.4

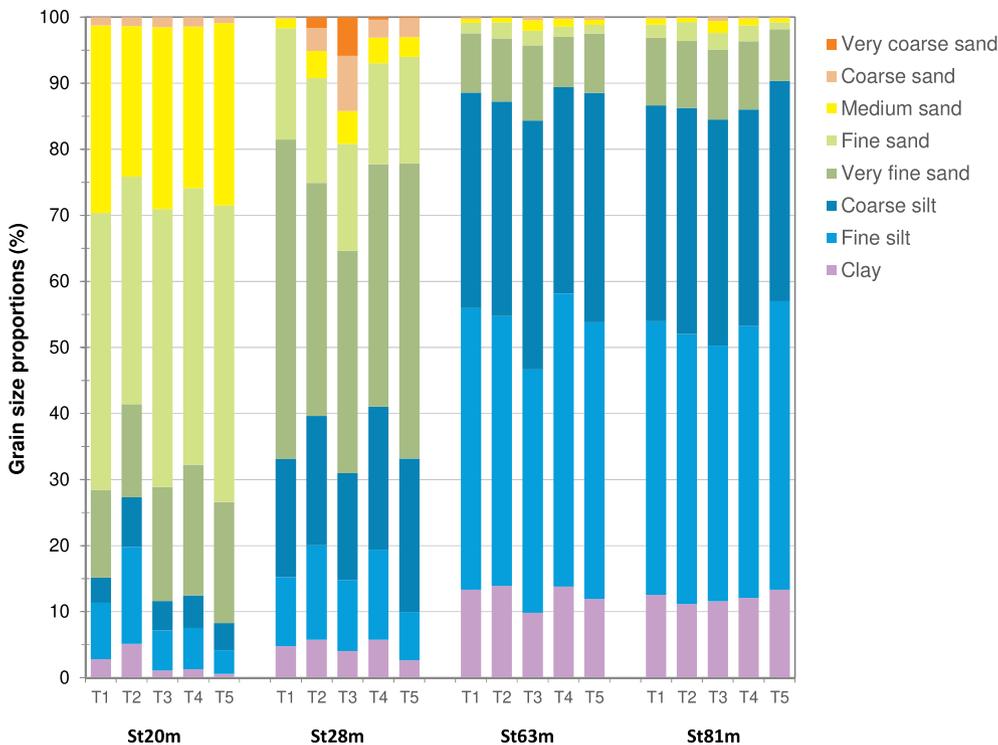


Fig. 4. Grain size distribution in surface sediments from the Têt prodelta and adjacent shelf. Values are averaged proportions from 3 cores. T1 = January 2008, T2 = April 2008, T3 = June 2008, T4 = September 2008 and T5 = January 2009. Sediments are classified as follows: Clay < 4 μm , fine silt = 4–20 μm , coarse silt = 20–63 μm , very fine sand = 63–125 μm , fine sand = 125–250 μm , medium sand = 250–500 μm , coarse sand = 0.5–1 mm, and very coarse sand = 1–2 mm.

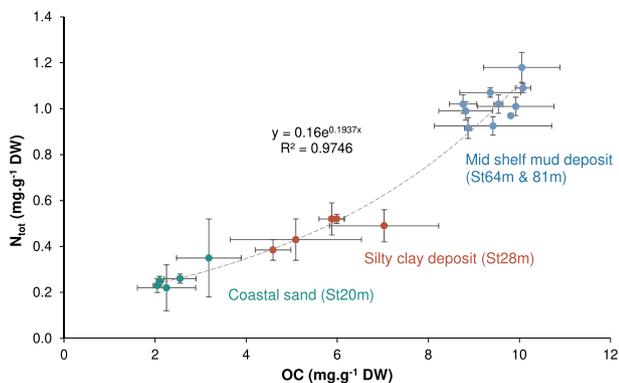


Fig. 5. Relationship between total organic carbon (OC) and total nitrogen (N_{tot}) contents (mg.g^{-1} dry weight) in surface sediments from the Têt prodelta and its adjacent shelf.

The intercept of the linear regression is close to zero, indicating that nearly all the nitrogen was associated to organic matter. At 20 m depth, N_{tot} contents were low with an annual mean value of $0.26 \pm 0.07 \text{ mg.g}^{-1}$. At 28 m depth, N_{tot} contents were two times higher, with an annual mean value of $0.47 \pm 0.06 \text{ mg.g}^{-1}$. At 64 m and 81 m depth, N_{tot} contents increased, with annual mean values of $1.02 \pm 0.04 \text{ mg.g}^{-1}$ and $1.02 \pm 0.03 \text{ mg.g}^{-1}$, respectively.

These results show that the OC and N_{tot} contents in surface sediments tended to increase regularly from the station located at the inlet of the Têt River (20 m depth) to the adjacent shelf with no obvious difference between the two stations located offshore on the shelf.

C:N atomic ratios ($C:N_a$) fluctuated between 9.8 and 16.7 with the highest values in the Têt prodelta and an annual mean value of 14.3 ± 2.0 . Lower $C:N_a$ ratios characterised both sandy coastal deposits with an annual mean value of 11.2 ± 1.7 and the offshore muddy sediments with annual mean values of 11.1 ± 1.1 and 10.7 ± 0.6 for stations at 64 m and 81 m depth, respectively (Table 3).

Quality of organic matter was assessed by the measure of total lipids, total carbohydrates, total and enzymatically hydrolysable amino acids (THAAs and EHAAs). Among the three biopolymeric classes of

compounds, carbohydrates and THAAs (accounting for proteins) contributed more to the sedimentary organic matter than lipids (Table 3). The three classes of biopolymeric compounds were positively correlated to OC content (Spearman's rank correlations, $p < 0.0001$, Fig. S1) and thus globally followed similar trends. The average annual concentrations of these three classes of compounds increased moderately between coastal sands at 20 m depth and silty muds in the prodelta at 28 m depth (Table 3). Then, the average annual concentrations increased by a factor of 3 for total lipids and doubled for total carbohydrates and THAAs in the muddy deposits of both stations at 64 m and 81 m depth in the continental shelf (Table 3). BPC accounted on average for 14–38% of the total OC content (Table 3). THAAs were usually the most abundant biopolymeric compounds ($129\text{--}405 \text{ mg.g}_{\text{TOC}}^{-1}$, ~5–22% of the OC pool) with a trend for higher values at 20 m depth and decreasing values at 28 m depth (Fig. 6). Carbohydrates were the second most abundant polymeric compounds ($104\text{--}565 \text{ mg.g}_{\text{TOC}}^{-1}$) and contributed to 3–33% of the OC pool. The highest values were observed in January 2009 at 20 m depth and in September 2008 at 28 m depth with surficial deposits remarkably enriched in carbohydrates (on average about 565 and $298 \text{ mg.g}_{\text{TOC}}^{-1}$ for these two dates). Lipid contribution was lower ($35\text{--}97 \text{ mg.g}_{\text{TOC}}^{-1}$, ~2–9% of the OC pool) with a remarkably higher input of lipids at 20 m depth in September 2008.

The bioavailable amino acids (EHAAs) ranged from 105.3 to $312.5 \mu\text{g.g}^{-1}$ with minimal and maximal values at 20 m depth in January 2008 and at 81 m depth in January 2009 (Table 3). EHAAs were best correlated to proxies of labile organic matter - total nitrogen and lipids - than to OC content (Spearman's rank correlations, Fig. S1). They accounted for ~7–51% of the THAAs, the lowest percentages being found in muddy sediments and the highest at the inlet of the Têt River. Throughout our survey, higher EHAA yields were recorded at the inlet of the Têt River ($50\text{--}90 \text{ mg.g}_{\text{TOC}}^{-1}$, Fig. 7), indicating higher bioavailability of the protein fraction, especially in the summer where yields are ~3 times higher at 20 m depth than further offshore. EHAA yields ranged in the prodelta from $29 \text{ mg.g}_{\text{TOC}}^{-1}$ in spring to $50 \text{ mg.g}_{\text{TOC}}^{-1}$ in summer. EHAA yields were lower (on average 27 and $30 \text{ mg.g}_{\text{TOC}}^{-1}$ at St64 m and St81 m, respectively) and more constant offshore with the exception of April 2008, when a sudden decrease was observed at 68 m depth. EHAAs made up less than 5% of the total

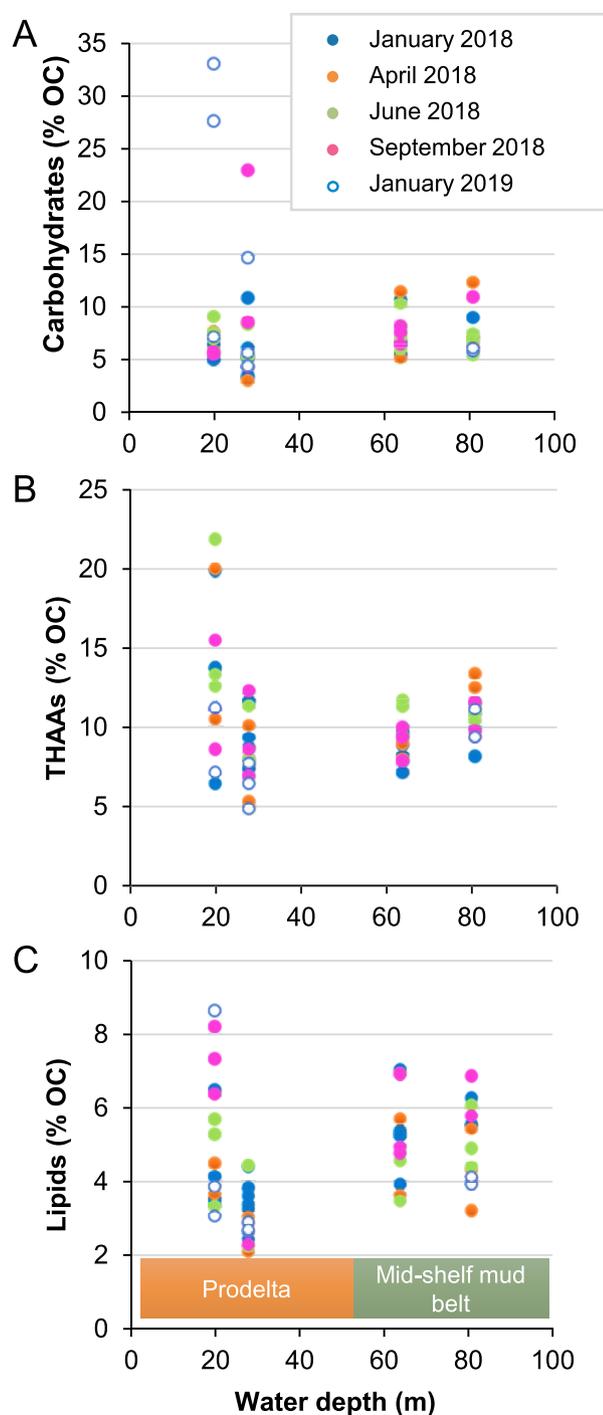


Fig. 6. Biopolymeric carbon (BPC) in surface sediments from the Têt prodelta and adjacent shelf. Contribution of carbohydrates (A), total hydrolysable amino acids (B), and lipids (C) to the total organic carbon.

nitrogen in muddy sediments, while they accounted for up to 12% in coarse-grained sediments (Table 3). At 20 m depth, the EHAA-N percentage remained high from April 2008 for the whole spring and summer period. At 28 m depth, lower percentages were found in April 2008 and January 2009. Offshore, the proportion of bioavailable proteinaceous nitrogen was relatively constant over the study period with the exception of April 2008 when a net decrease of the EHAA-N percentage was observed. In contrast, EHAAs accounted for a small fraction of the OC (< 0.5% for muddy sediments and 0.5–1.5% for the sands and sandy muds, Table 3).

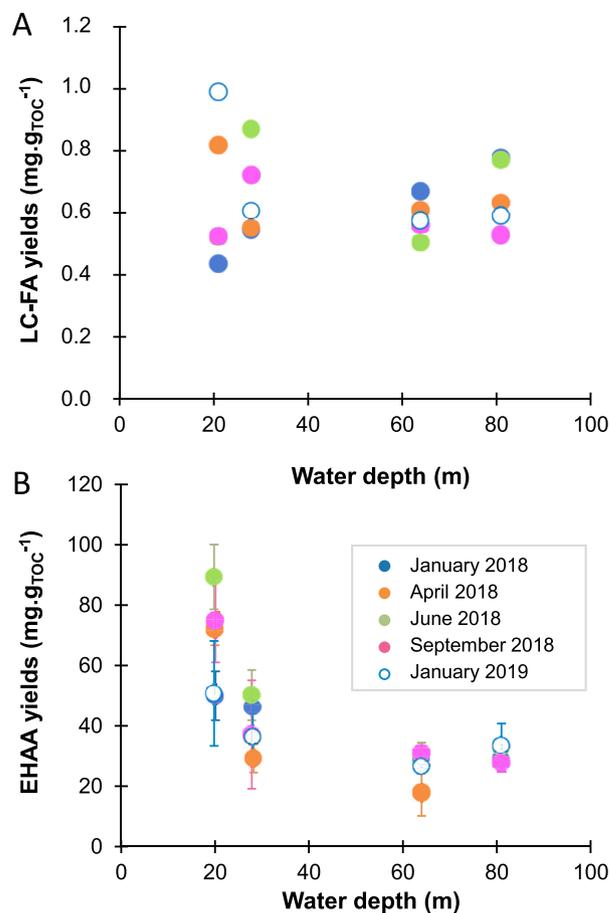


Fig. 7. Yields of higher plant biomarkers (A) and enzymatically hydrolysable amino acids (B) in surface sediments from the Têt prodelta and adjacent shelf. $n = 3$ for EHAAs (mean \pm standard deviation).

3.4. Fatty acid biomarkers

Fatty acid yields ranged from 3.7 to 15.4 $\text{mg.g}_{\text{TOC}}^{-1}$ at St20 m and St28 m, and 4.0–6.4 $\text{mg.g}_{\text{TOC}}^{-1}$ in the two offshore stations (Table S1). Fatty acid composition was dominated by SAFAs (40.6–59.6%) with the preponderance of short chain SAFAs over long chain compounds (Fig. 8).

Biomarkers of higher plants (LC-FAs) were highly variable (3.4–19.3%) with no clear spatial or temporal trend. The lowest LC-FA contribution was observed at 20 m depth in spring (< 5%) and the highest contribution was observed in January 2008 at 81 m depth. MUFAs were the second class of fatty acids in abundance with contribution ranging from 21.8 to 26.2%. They were dominated by $\text{C}_{16:1\omega7}$ and to a lesser extent $\text{C}_{18:1\omega7}$ and $\text{C}_{18:1\omega9}$. Specific fatty acid biomarkers used for bacteria (BAFA) tended to be less abundant at the two shallowest sites (11.8–19.3%) than at the deepest sites (14.9–27.2%). A wide range of bacterial fatty acids was found. Among the odd number saturated SAFAs, $\text{C}_{15:0}$ dominated (up to 13% of the total fatty acids). Branched *iso*- and *anteiso*-fatty acids were also found with the preponderance of branched $\text{C}_{15:0}$ (*iso* and *anteiso*) while hydroxylated fatty acids were generally low ($\leq 1\%$). The contribution of cyclopropanoic acid (ΔC_{17}) showed strong variations among the surface samples (from 0 to 6%). PUFA contribution ranged from 4.1 to 14.1% and was more variable nearshore. The highest contributions of PUFAs were recorded at 20 m depth in June and September. PUFAs were diversified with a predominance of $\text{C}_{20:5\omega3}$, $\text{C}_{22:6\omega3}$, $\text{C}_{18:2\omega6}$ *cis*, $\text{C}_{16:3\omega4}$, and $\text{C}_{18:4\omega3}$ (14 PUFAs identified, see Table S1). The index of unsaturation (UI) varied from 41 to 85 revealing marked differences in the degree of unsaturation of the organic matter and thus differences in organic matter quality

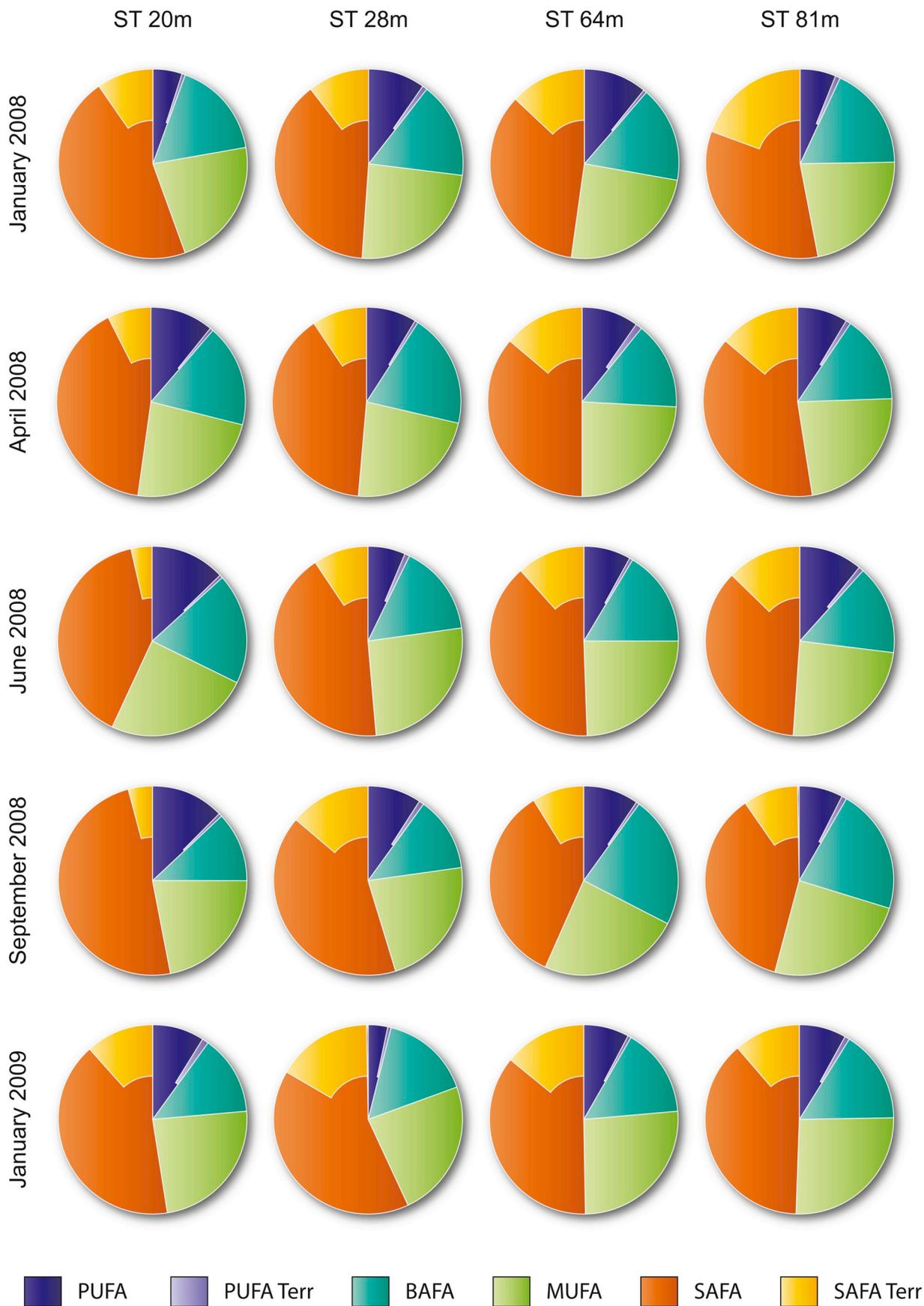


Fig. 8. Pie charts showing the fatty acid composition of the surface sediments collected along the Têt prodelta-shelf transect during the 2008–2009 survey (4 stations X 5 dates). PUFA Terr: PUFA of terrestrial origin ($C_{18:2\omega6}$ and $C_{18:3\omega3}$), SAFA Terr = long chain SAFA of terrestrial origin ($\geq 24C$, LC-FAs).

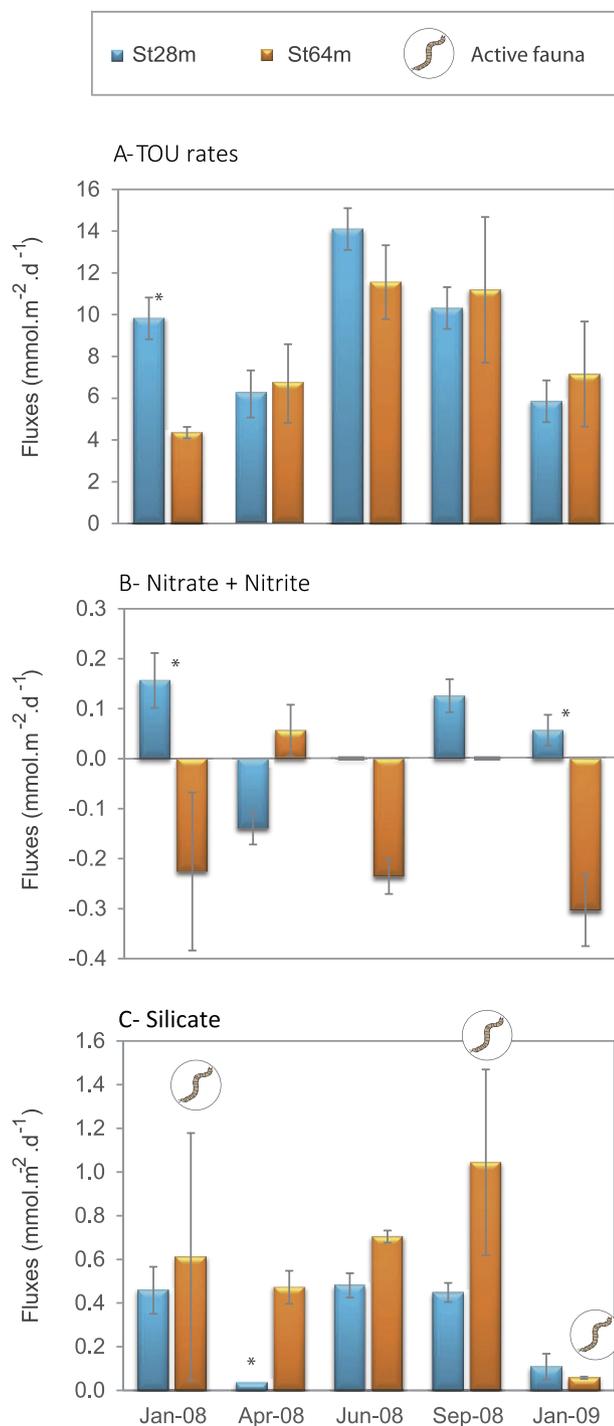


Fig. 9. Dissolved oxygen and nutrient fluxes at the sediment-water interface measured using *ex-situ* whole core incubation: (A) Total oxygen uptake (TOU) rates, (B) Nitrate + nitrite fluxes, and (C) Silicate fluxes. $N = 3$, * indicate significant differences between stations ($p < 0.05$). For nitrate + nitrite and silicate fluxes, positive fluxes indicate release in the water column and negative fluxes indicate consumption by the sediments. Living endofauna was found at the end of the incubation in cores collected at station St64 m in January 2008, September 2008 and December 2009.

(Table S1). The TAR_{FA} varied from 0.10 to 0.59 indicating variable influences of terrigenous organic matter (Table S1).

3.5. Benthic fluxes of oxygen and nutrients

Benthic fluxes exhibited a high spatial and temporal variability

(Fig. 9). Sharp differences in $NO_3^- + NO_2^-$ fluxes were observed between the sandy and muddy stations, and over sampling dates ranging from high negative flux in January 2009 at 64 m depth ($-303 \pm 72 \mu\text{mol m}^{-2} \cdot \text{d}^{-1}$) to positive flux in January 2008 at 28 m depth ($157 \pm 55 \mu\text{mol m}^{-2} \cdot \text{d}^{-1}$). However, we did not observe any clear pattern for the dynamic of these nutrients at the sediment-water interface. At the sandy station, $NO_3^- + NO_2^-$ fluxes were generally directed towards the water column except for the sediment cores collected in April 2008. At the muddy station, high influxes of $NO_3^- + NO_2^-$ were revealed in January 2008 and 2009, as well as in September 2008. Silicate fluxes were directed towards the water column and ranged from $37 \pm 42 \mu\text{mol m}^{-2} \cdot \text{d}^{-1}$ in April 2008 at the sandy station to $1044 \pm 426 \mu\text{mol m}^{-2} \cdot \text{d}^{-1}$ in September 2008 at the muddy station. Differences between stations were observed, with a tendency for higher fluxes at the muddy station except in January 2009. TOU rates ranged from $4.35 \pm 0.28 \text{ mmol m}^{-2} \cdot \text{d}^{-1}$ in January 2008 at 64 m depth to $14.10 \pm 3.51 \text{ mmol m}^{-2} \cdot \text{d}^{-1}$ in June 2008 at 28 m depth. TOU rates exhibited a strong seasonality with higher fluxes during the warmer months (June and September), but no significant difference between sites (except in January 2008).

4. Discussion

4.1. Bulk characteristics of sediments from a typical Mediterranean prodelta, the Têt River system

Due to the climatic conditions of its watershed, its hydrological regime, the nature of the particulate inputs, and shelf sedimentary dynamic, the Têt prodelta system is typical of the muddy deposits that form at the mouth of small mountainous rivers draining the Mediterranean basin (Bourrin et al., 2006; Guillén et al., 2006; Higuera et al., 2014; Lespinas et al., 2010; Ludwig et al., 2004). Grain size distribution in the sediments of the four stations was consistent with the different sedimentological facies described by Monaco and Aloisi (2000) for the continental shelf of the Gulf of Lions (Fig. 1). A decrease in grain size is observed from the inner shelf to the outer shelf (Fig. 4): at 20 m depth, the coastal sand, at 28 m depth in the prodelta, the silty clay deposit corresponding to the sand-mud transition, which overlaps the average wave action limit at around 30 m water depth (Jago and Barousseau, 1981); the two stations located offshore (64 and 81 m) belong to the mid-shelf mud deposit, which follows the mean shelf circulation pattern from north to south (Millot, 1990).

Organic matter distribution is strongly influenced by the grain size composition of the sediment, which in turn is controlled by the nature of the river inputs and the hydrodynamic conditions. Consequently, the lowest organic matter contents were recorded in the coarse sand of the coastal sand-bar (station St20 m) with OC and N_{tot} contents of 2.1–3.2 and 0.22–0.35 mg g^{-1} , respectively. In front of the Têt River mouth, the prodelta silty-muds (station St28 m) were relatively poor in organic matter with OC and N_{tot} contents of 4.6–7 and 0.39–0.52 mg g^{-1} , respectively (Fig. 5). Such low organic matter contents are a common feature in the Têt prodelta, although enriched flood deposits are occasionally observed during the autumnal period (Buscaill et al., 1995; Kim et al., 2006). No autumnal flood event occurred during our study as indicated by the low runoff of the Têt River in 2008 (Fig. 2). As organic compounds are preferentially associated with fine particles, the mid-shelf mud deposit (stations St64 m and St81 m) shows an increase in OC (9–10.1 mg g^{-1}) and N_{tot} (0.92–1.20 mg g^{-1}) contents (Fig. 5).

River prodeltas are areas where sedimentary organics are typically fuelled by organic matter of terrestrial and marine origins (Goñi et al., 2003; Alt-Epping et al., 2007). The $C:N_a$ ratio can be used to assess the relative contributions of these two sources (Table 2). Moloney and Field (1991) proposed a $C:N_a$ of 6 for marine organic matter because of the high protein content of organisms such as phytoplankton and zooplankton. By contrast, terrestrial organic matter deriving from higher plants typically have higher $C:N_a$ ratios (> 20) because of higher

contributions of non-protein components (Meyers, 1997). C:N_a ratios in marine sediments are usually higher than in marine organisms such as plankton. C:N_a comprised between 6 and 12 in sediments is considered as representing degraded organic detritus implying a breakdown of the more labile nitrogenous compounds (Table 2). Furthermore, a C:N_a ratio higher than 13 indicates a significant participation of terrestrial organic matter (Buscaill et al., 1990; Buscaill and Germain, 1997; Goñi et al., 2003; Kim et al., 2006). C:N_a ratios measured during this one-year survey are consistent with those of previous investigations (Buscaill et al., 1995; Kim et al., 2006). The highest values characterised the Têt prodelta (St28 m) with an annual mean value of 14.3 ± 2.0 . In a previous study at the same depth (26 m) in the Têt prodelta, Buscaill et al. (1995) described the OC fraction incorporated to the sandy fraction. Named coarse organic carbon (COC), this material made of undegraded plant debris or charcoal remains from summer fires on the land, represented 30–90% of total OC depending on the season. The highest values (COC = 60–90% of total OC) resulted from the floods of the Têt River or from the hydrodynamical sorting by active currents, which eliminated the finest material from the deposit and induced a relative enrichment with coarse organic remains (plant detritus). Lower C:N_a ratios characterised the offshore muddy sediments with annual mean values of 11.1 ± 1.1 and 10.7 ± 0.6 at 64 m and 81 m depth, respectively. In this context, C/N_a ratio of 11 is suggestive of the predominance of degraded marine organic matter and reflects the preferential degradation of nitrogen containing compounds during early diagenesis (e.g., Hedges et al., 1988; Cowie and Hedges, 1996).

4.2. Origin and quality of sedimentary organic matter in Mediterranean prodeltas

A time survey investigation in the Gulf of Lions has shown that terrestrial organic matter contribution accounted for 40–86% (median value = 48%) in the Têt prodelta and was strongly influenced by meteorological and hydrological drivers (i.e. wet and dry storms, rainfall, snow melt) (Kim et al., 2006). In the mid-shelf, OC inputs were somewhat higher than in the prodelta with no obvious decrease of the terrestrial organic matter contribution (48% at St81 m, Kim et al., 2006). A similar trend is observed on the shelf adjacent to the Rhône prodelta, where sedimentary organic matter contains marine and terrestrial organic matter in equal amounts (Bourgeois et al., 2011). Long chain fatty acids (LC-FAs) deriving from epicuticular waxes of vascular plants are tracers of terrestrial inputs. Off the Rhône River mouth, LC-FA yields higher than $1 \text{ mg.g}_{\text{TOC}}^{-1}$ correspond to sediments with a marked predominance of terrestrial organic matter (i.e. prodelta ~100% terrestrial organic matter; Bourgeois et al., 2011). Similar high yields of LC-FAs are observed in the Têt prodelta, clearly enabling to trace the riverine imprint on the inner and mid-shelf (Fig. 7). The high temporal variability of these biomarkers confirms the dynamic nature of the inputs of plant detritus, which are controlled by river runoff, organic matter source seasonality and hydrodynamic conditions. In good consistency with our results, lignin degradation products were shown to vary by a ten-fold factor in the Têt prodelta (Buscaill et al., 1990). This temporal variability in the coastal sands is also apparent from the contents of microalgal biomarkers, whose contribution increases in spring and summer (Fig. 8). These markers are usually attributed to marine phytoplankton, but could as well derive from a recent input of freshwater phytoplankton or more likely to the development of micro-phytobenthos. During the summer, the stability of the water mass and the strong insolation on the coastal area enable the development of a benthic diatom biofilm (Riaux-Gobin et al., 1998). Farther on the shelf, temporal trends are less clear highlighting the stronger mixing and reprocessing of the different sources of organic matter.

The quality of sedimentary organic matter may be defined by the proportion of biodegradable and nutritious organic matter (i.e. the labile organic matter). Naturally occurring macromolecules such as proteins, carbohydrates and lipids form the bulk of living matter and fresh

detritus. However, these labile compounds are remineralised by microorganisms and assimilated by animals, so that only a minor fraction is preserved in marine sediments. Concentrations in THAAs, carbohydrates and lipids were of the same order of magnitude (Table 3) as those reported for other larger river-dominated systems in the Mediterranean Sea (Dell'Anno et al., 2008; Fabiano and Danovaro, 1994; Goineau et al., 2012; Pastor et al., 2011). In particular, sediments from the Têt transect had a composition similar to those collected in the Rhône River system (Goineau et al., 2012; Pastor et al., 2011), with a dominance of THAAs over carbohydrates and lipids (Fig. 6). A strong contribution of proteins is considered as an indication of the inputs of recent and labile material (Dell'Anno et al., 2008), whose provenance in Mediterranean prodeltas is certainly the particulate organic matter delivered by rivers. Biomarker and isotopic analyses have indeed revealed that inputs from the Rhône River predominantly consist of modern vascular C3 plant detritus (Bourgeois et al., 2011; Cathalot et al., 2013; Tesi et al., 2007). These terrestrial inputs can be regarded as fresh and labile in comparison to the organic matter deriving from marine phytoplankton, which is already degraded when it settles on the seafloor (Bourgeois et al., 2011; Cathalot et al., 2013; Tesi et al., 2007). In the Têt prodelta, suspended organic matter has been shown to be fresher than in the Rhône prodelta (Gadel et al., 1990). Accordingly, high BPC contents were found in sediments from the Têt transect. The strong coverage by riparian vegetation in the alluvial plain, the accumulation of plant remains during periods of drought and the reduced length of the Têt River are factors that contribute to the export of fresh plant detritus to the coastal area. Moreover, during our survey no flood event has occurred. Such events bring soil-derived organic matter depleted in labile organic components that are deposited in the prodeltaic area (Cathalot et al., 2010). At the outlet of the Têt River, coastal sands displayed elevated BPC contents (range 21–47% OC) and a strong heterogeneity between cores revealing the patchy distribution of the labile detritus. Coastal sands are also remarkably enriched in EHAAAs, which correspond to the fraction of amino acids that can be assimilated by benthic deposit-feeders (Mayer et al., 1995). Despite the better quality of the organic matter at this site, macrofauna abundance was low (382 individuals m^{-2} in January 2008; pers. Com. J.M. Amouroux). The highest density was reached a little farther in sediments from the sand-mud transition (3004 individuals m^{-2} in January 2008; pers. Com. J.M. Amouroux), which despite a slightly lower quality retain more organic substrates and are more stable due to lower remobilisation. Overall, sediments in the Têt prodelta and adjacent shelf exhibit a good trophic status indicating that they can sustain macrofaunal assemblages. This is consistent with biotic indexes, which assigned a high to good ecological quality status to this area (Romero-Ramirez et al., 2016) despite its exposure to river-borne contaminants (Reoyo-Prats et al., 2017).

4.3. Linking proxies of organic matter quality and origins to spatio-temporal patterns

This one-year study highlights that organic matter composition, in terms of quantity, quality and provenance, varies both spatially and temporally on the shelf off the Têt River. The drivers that determine this variability are however unclear. We thus performed an exploratory PCA to look for relationships between geochemical properties of the sediments, proxies of organic matter quantity, quality and origin, bathymetry and season (Fig. 10).

The first two principal component axes account for 71.8% of the variance of the dataset. The first component axis (PC1) accounts for most of the variance (48.1%) and is explained by two groups of variables: on one hand EHAA-N, fatty acid to lipid ratio and medium sand (125–500 μm) with positive loadings and on the other hand CaCO_3 , OC content, porosity and fine sediment (< 63 μm) with negative loadings. The first component reflects the general relationship between marine sediment characteristics and bathymetry as confirmed by the strong correlation between the supplementary variables depth and distance to

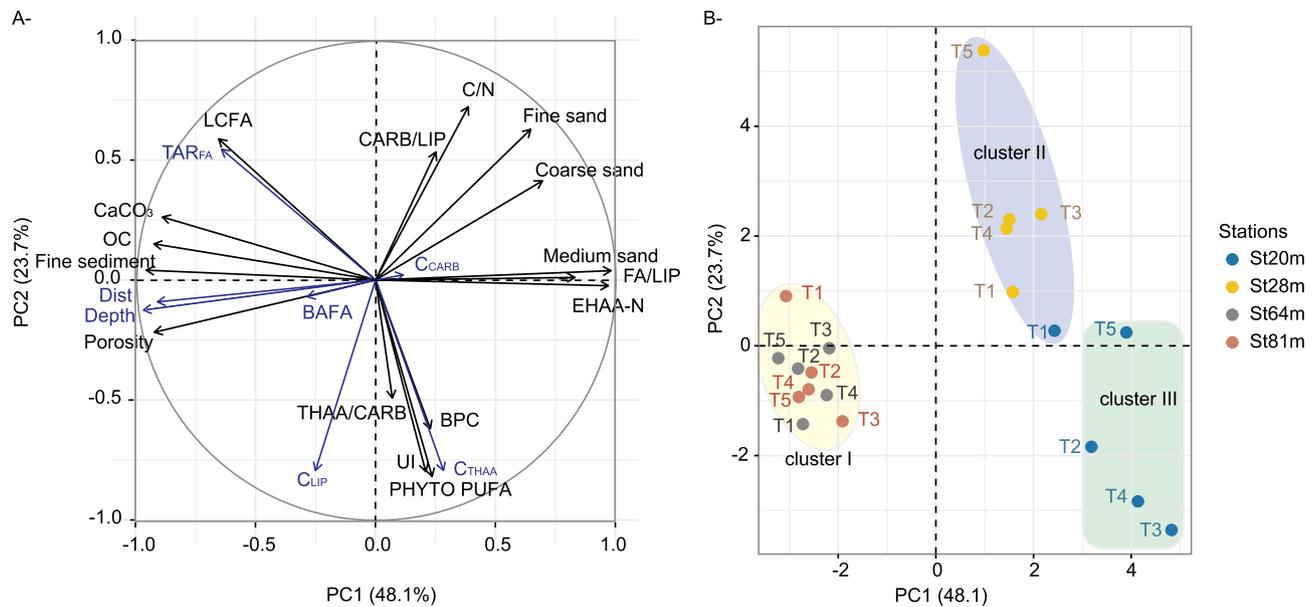


Fig. 10. Principal component analysis (PCA) of surface sediments collected off the Têt River: (A) loading plots for the first and second principal components, and (B) score plot for the first and second principal components (4 stations * 5 dates). Black arrows indicate active variables and blue arrows supplementary variables. Samples were clustered in 3 groups according to a hierarchical clustering analysis performed on the 5 first principal components of the PCA. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

the river mouth with PC1, as well as the opposition between fine sediment and medium sand (120–500 μm) on the first axis. At greater depths, sediments are composed of clay and silt and are characterised by a higher porosity. The general trend for higher organic matter content in muddy sediments is explained by the increased adsorption of organic compounds to fine grained particles (Mayer, 1994). In contrast, shallow stations are characterised by coarser sediments with a lower porosity and OC content. Moreover, strong negative relationships between proxies of organic matter lability (EHAAs-N and fatty acid to lipid ratio) and depth were found, confirming that sandy sediments are poorer, but contain organic matter of higher nutritional quality. This relationship has been related to the fact that fragmentation increases humification (Schaeztl and Thompson, 2015). Coarse sediments contain larger plant residues, which are less prone to humification, and are thus more labile. The second component axis (PC2) representing 23.7% of the variance is mainly explained by the opposition between indicators of labile organic matter (UI, phytoplankton PUFAs) with negative loadings and proxies of more refractory organic matter (C/N_a and carbohydrate to lipid ratio) with positive loadings. It discriminates the nearshore sediments in two clusters. Sediments from the river mouth were characterised in spring and summer by descriptors of labile organic matter (high EHAAs-N, BPC, fatty acid to lipid ratio, C_{THAA}, Phytoplankton PUFAs and UI), indicative of fresh phytodetritic inputs (cluster III). In the western Mediterranean Sea, phytoplankton blooms occur generally early in the year at the end of the winter (Long term series provided by the network SOMLIT “Service d’Observation en Milieu Littoral”, INSU-CNRS, station SOLA), whereas enhanced production of freshwater algae are recorded in rivers when snow melts in early spring. Phytoplankton contains high amounts of fatty acids, which are rapidly degraded in the water column and in the sediments (Harvey et al., 1995; Meyers, 1997). Higher UI and contribution of phytoplankton markers (in particular C_{20:5 ω 3}) in spring and summer are thus consistent with recent inputs of fresh organic matter. Consistent with this, we also found higher amounts of total fatty acids in the nearshore stations in the summer. At this period of the year, the development of a microphytobenthic film could contribute to the seabed enrichment in labile organic matter (Buscaill et al., 1995). Sediments from the river mouth deviate in winter from those collected on the other dates, with the January 2008 sample being clustered with sediments collected in

the prodelta depositional area (cluster II). Organic matter was less labile in winter (lower UI and contribution of phytoplankton PUFAs, Table S1) and contained higher amounts of higher plant biomarkers (both dates) and carbohydrates (January 2009). This distinct biochemical signature can be explained by the inputs of litter in autumn and the limited primary productivity in coastal waters at this period of the year (Buscaill et al., 1995, 1990).

At 28 m depth, sediments mainly differ from coastal sands by higher C:N_a ratios (> 13), which in conjunction with more LC-FAs confirms that detritus of terrestrial origin are deposited in the prodelta area. Although OC content increased in spring and summer, there was no evidence of a concomitant increase of organic matter bioavailability. At the end of May, a minor flood event was surveyed during three days (Fig. 2). Although the influence of this event on surface sediments from the Têt prodelta is more than probable, its imprint is hardly seen along the coast-shelf transect. Even so, an increase of carbohydrates was observed after the May event at 28 m depth, which could be explained by the export of vegetal detritus enriched in cellulose and hemicellulose in periods of higher runoff. Sediments in the prodelta displayed distinct characteristics in January 2008 and 2009 as shown by their distance on the PCA score plot (Fig. 10). The oceanic storm of December 2008 triggered rainfalls and increased runoff in the Pyrenees resulting in the erosion of riverbanks and resuspension of riverbed sediments (Higuera et al., 2014). This event considerably enhanced the export of terrestrial organic matter (plant remains and soils) to the sea on the Catalan coast (Sanchez-Vidal et al., 2013). The impact of the wet storm on the Têt prodelta is confirmed by the lower porosity and the loss of fine particles on the 3 first centimetres of the cores collected at 28 m depth. This effect is less obvious at 20 m depth as the sediment was coarser. The surface deposit was depleted in labile components (lipids, THAAs, phytoplankton PUFAs) and enriched in vascular plant remains, consistent with the export of soils and plant debris accumulated on the ground throughout the autumn. This signal was not found in January 2008 in good agreement with the fact that meteorological conditions in the months before the sampling were different, with strong winds but no major rainfall event.

Sediments from the stations on the mid-shelf exhibited similar bulk and molecular composition, and thus were clustered together (cluster I). Temporal changes of the sediment characteristics were more limited

at those depths and no obvious seasonal effect could be highlighted from the suite of descriptors analysed. The influence of the river on the sediment characteristics was clear with on average 12.7% of higher plant biomarkers (LC-FAs) in the surface sediments. These high contributions highlight the preservation of terrestrial organic matter on the shelf as previously demonstrated by isotopic analyses (terrestrial organic matter ~48% at 81 m depth, Kim et al., 2006). Terrestrial organic matter on the mid-shelf certainly does not only originate from the Têt River; other rivers located further North on the coastline and especially the Rhône River provide substantial amounts of terrestrial organic matter during flood events, which can be advected along the shelf and exported at the south-western end of the Gulf of Lions (Palanques et al., 2006). Overall, shelf sediments were enriched in OC and nitrogen in comparison to nearshore sediments throughout the year, with no obvious imprint of the spring bloom. The only modification that could be attributed to the sedimentation of the marine primary production is an enrichment in labile organic matter proxies in June 2008 at the deepest station (higher phytoplankton marker contribution, $C_{16:1\omega7}$ to $C_{18:1\omega9}$ ratio, UI and EHAA-N) and low TAR_{FA} values over the productive season, consistent with a lower contribution of terrestrial inputs. Using sediment traps deployed further on the slope, Monaco et al. (1990) evidenced the strong decrease of POC fluxes between 50 and 100 m depth, which could be explained by intense recycling of the organic rich particles in the surface waters or hydrodynamic decoupling with the underlying waters. Overall, our results agree with these early findings and confirm that the coupling between the marine pelagic productivity and the benthic compartment is rather limited on the shelf.

In contrast to what was observed in nearshore sediments, at our deeper station (81 m), enrichment in OC and total nitrogen was observed at the end of the summer. This sediment layer was enriched in carbohydrates and was more degraded (higher contribution of bacterial fatty acids, lower UI, lower EHAA-N) than on the other dates (Tables 3 and S1). It was further characterised by the decrease of the $C_{16:1\omega7}$ to $C_{18:1\omega9}$ ratio and a higher $C_{18:1\omega9}$ to $C_{18:1\omega7}$ ratio (see Table 2 for the interpretation of biomarker indices), which points to faecal pellets as a likely source of organic matter inputs. In good consistency with these trends, faecal pellets have been shown to dominate POC fluxes in the summer at 50 m water depth farther on the shelf (Monaco et al., 1990).

4.4. Organic matter reactivity at the sediment-water interface

Biochemical quality exerts a strong control on the processes leading to the degradation or preservation of POM in coastal sediments (Blair and Aller, 2012). A higher quality, defined here by higher proportions of labile components (pigments, amino acids, fatty acids), classically enables higher degradation rates through enhanced microbial remineralisation. This assertion must be modulated to take into account biotic (fauna abundance and diversity) and abiotic parameters (accumulation rates, hydrodynamism, redox conditions, interactions with minerals), which are key drivers of organic matter degradation. Organic matter recycling in the Rhône prodelta has been the focus on many studies, which provided deep insights on the degradation rates, microbial processes and environmental drivers that constrained benthic mineralisation (Cathalot et al., 2010; Lansard et al., 2009, 2008; Pastor et al., 2011; Pruski et al., 2015). So far, the influence of smaller coastal rivers on organic matter cycling is poorly constrained.

Despite some possible artefacts, sediment core incubations provide a useful tool to measure benthic fluxes of oxygen and nutrients and provide rates that converge with those obtained from benthic chambers (Grenz et al., 2003; Rabouille et al., 2003). They are widely used to study spatial and temporal trends in organic matter remineralisation (Belley et al., 2016; Grenz et al., 2000) or to apprehend the response of the benthic compartment to enhance organic matter inputs (for example in link with shellfish farming, Black et al., 2012). Off the Têt River, clear temporal trends were observed over the study period with each site showing distinct oxygen and nutrient dynamics (Fig. 9). A

high variability of benthic fluxes was recorded within replicates. Part of this variability may be explained by the abundance of hidden endofauna (annelids, crustaceans) that reworked intensively the sediments during the 24 h of incubation (A. Pruski, Pers. Obs.). Benthic dwelling organisms have been shown to increase TOU rates in sediments (François et al., 2002; Pischedda et al., 2008). Part of the oxygen consumption is directly linked to faunal metabolism, but solute exchange and mineralisation processes are also significantly influenced by organisms (Kristensen, 2001; Pischedda et al., 2008; Shang et al., 2014). Indeed, strong coefficients of variation were always linked to the presence of invertebrates actively bioturbating and bioirrigating the sediments (Fig. 9). At a small spatial scale, variability in solute fluxes may also be linked to patchiness in the distribution of sedimentary organic matter (Cathalot et al., 2010; Rabouille et al., 2003). In Mediterranean deltaic shelves, particle dynamic is strongly affected by flood and resuspension events, which can affect organic matter deposition, and create local areas of enrichment (Cathalot et al., 2010; Guillén et al., 2006; Kim et al., 2010). Organic inputs off the Têt River were indeed heterogeneously distributed as confirmed by high coefficients of variation (see carbohydrate, lipid and THAA concentrations in Table 3).

Total benthic O_2 uptake (TOU) is considered as a good proxy of the total benthic carbon mineralisation (Canfield et al., 1993) although most of the organic matter is degraded by anaerobic pathways in coastal sediments. This measure takes into account the respiration of aerobic heterotrophic bacteria and fauna, as well as the reoxidation of the reduced end-products released when organic matter is degraded anaerobically (Glud, 2008). TOU rates found in the Têt prodelta ($4\text{--}14 \mu\text{mol } O_2 \text{ m}^{-2} \cdot \text{d}^{-1}$) are within the range of values reported in other coastal marine sediments (Hicks et al., 2017; Serpetti et al., 2016). In particular, they are comparable to values previously measured in other Mediterranean systems, the Rhône prodelta (Cathalot et al., 2010; Lansard et al., 2009, 2008; Pastor et al., 2011) and the Medjerda River delta (Helali et al., 2015) (Table 4). The fluxes of O_2 in the sandy muds (St28 m) are comparable to those measured in the muddy sediments (St64 m) despite the two-fold lower OC content (Table 3). Organic matter remineralisation dynamic in sandy sediments has been somewhat neglected because they retain low amounts of OC and fewer bacteria. However, the permeability of sandy sediments allows pore water advection of solutes, which may sustain high remineralisation rates (Boudreau et al., 2001; Glud, 2008; Shum and Sundby, 1996). The Têt prodelta is a hydrodynamically energetic environment; resuspension events and/or subtidal pumping could thereby increase penetration depth and O_2 consumption at our shallow station (Moriarty et al., 2017). Furthermore, it has been hypothesised that such dynamic conditions select a few, but abundant resident microbes that could fulfil most of the main microbial functions (heterotrophic degradation) (Gobet et al., 2012).

Higher TOU rates were observed at the end of spring (June), when temperature and lability of organic matter were both higher (Spearman's rank correlations, $p < 0.05$, Fig. S2). Temperature is an important abiotic factor influencing benthic microbial and faunal activity, as well as the diffusion of oxygen in the sediments. Investigations in the Thau lagoon (French Mediterranean coast) have shown that temperature was a key driver of oxygen dynamic (Dedieu et al., 2007). In this shallow enclosed system, most of the seasonal variation of the dissolved oxygen fluxes were explained by the strong seasonal temperature variation (10°C) (Dedieu et al., 2007). Off the Têt River, the temperature range during the study period was much lower (3°C) and is less likely to explain alone the observed variability. In addition, TOU rates in the Têt prodelta were remarkably higher in January 2008 than in January 2009, which suggests that other drivers, such as organic matter bioavailability, could control oxygen consumption. In good consistency with this hypothesis, higher TOU rates and EHAA concentration were recorded in June with a concomitant high yield of bacterial biomarkers, which may be explained by the rapid response of the microbial compartment to this input of labile organic matter.

Table 4
Comparison of Total Oxygen Uptake (TOU) rates measured in sediments from different locations in the Mediterranean Sea.

Sites	TOU rates (mmol O ₂ m ⁻² d ⁻¹)	References
Têt prodelta, France — 28 m depth	4.4–11.6	This study
Shelf adjacent to Têt prodelta, France — 64 m depth	5.9–14.1	This study
Gulf of Fos, France — 8 m depth	12.8–31.4	Rabouille et al. (2003)
	18.6 ± 4.0	Lansard et al. (2009)
Medjerda River delta, Tunisia — 10–40 m depth	2.3–10.4	Helali et al. (2015)
Fish farm, Gulf of Eilat, Israel — 22–25 m depth	45–154	Black et al. (2012)
Rhône prodelta, France		
20 m depth	26.2 ± 2.1	Lansard et al. (2009)
24 m depth	15.6 ± 5.0	Cathalot et al. (2010)
24 m depth (post flood)	9.8 ± 1.4	Cathalot et al. (2010)
Shelf adjacent to Rhône prodelta, France		
74 m depth	10.0 ± 1.3	Cathalot et al. (2010)
74 m depth (post flood)	4.4 ± 0.4	Cathalot et al. (2010)
83 m depth	9.9 ± 3.6	Lansard et al. (2009)
98 m depth	8.8 ± 2.0	Lansard et al. (2008)
Shelf of the NW Gulf of Lions, France — 64–162 m depth	3.1–11.2	Denis and Grenz (2003)

Similarly, benthic fluxes of oxygen and nutrients were shown to respond to the spring bloom and the settling of fresh phytoplankton detritus in the bay of San Francisco (Grenz et al., 2000). Nutrient fluxes provide further indications on the processes involved in the decomposition of organic matter and its remineralisation off the Têt prodelta. Nitrate/nitrite fluxes can be directed into or out the sediments depending on the relative importance of N-producing and N-consuming processes (Lehmann et al., 2004). Nitrate/nitrite fluxes were significantly correlated to the parameters that best describe the two stations (depth, distance to the river mouth, N_{tot} , OC, porosity, lipids, THAAs, and C:N_a), reflecting different dynamics at the two stations (Fig. S2). A trend for positive fluxes of nitrate/nitrite was observed at the sandy mud station (except in April). The release of nitrate from the sediments is indicative of nitrification, a process by which the ammonium produced from organic nitrogen is oxidised to nitrate. In permeable sediments, advection appears to favour this conversion (Huettel et al., 1998; Janssen et al., 2005), consistent with our results. In contrast, influxes of nitrate/nitrite (negative fluxes) at the shelf station indicate that these sediments primarily act as a sink for nitrate/nitrite. In cohesive sediments, exchanges across the interface are driven by molecular diffusion and the oxidised layer is limited to a few millimetres (Aller, 1982). The reduction of the O₂ penetration depth restricts nitrification to the first top millimetres. Below, in the suboxic transition zone, nitrate can be reduced (Eh values indicate that this transition zone reaches the depth of 3–5 cm, R. Buscail, unpublished results). Microbial reduction of nitrate in cohesive sediments may thus counterbalance or exceed the production of nitrate by nitrification, resulting in net denitrification (Barnes and Owens, 1999; Cheng et al., 2015; Mortimer et al., 1999). Our results suggest that nitrate respiration might play an important role in the decomposition of organic matter in muddy sediments from the distal sedimentation area. In April, however, this pattern of net denitrification was not observed on the shelf, whilst to the contrary no efflux of nitrate/nitrate was recorded in the Têt prodelta. Furthermore, at two occasions (June 2008 at St28 m and September 2008 at St64 m), nitrate/nitrite fluxes at the sediment-water interface were insignificant, suggesting a tight coupling between nitrification and nitrate reduction. Many factors can affect nitrogen processes in the sediments, such as nitrate concentration in the overlying seawater, temperature, macrofauna density, resuspension/erosion events, or organic matter content (Barnes and Owens, 1999; Moriarty et al., 2017). Any of these factors may have affected benthic fluxes during the study period. For instance, nitrate concentration in the water column dropped in April at the nearby SOLA monitoring station (27 m depth in the bay of Banyuls-sur-mer) as a consequence of the onset of the spring bloom (data provided by “Service d’Observation en Milieu Littoral”, INSU-CNRS, station SOLA). Concomitantly, the characteristics of the sediments in the Têt prodelta changed remarkably between

January and April 2008, with increased concentrations in OC, fatty acids, and chlorophyll a (F. Lantoine, Pers. Com.), in good consistency with phytoplankton inputs and/or microphytobenthic production in these coastal waters. Lower nutrient concentrations in the water column, enhanced consumption by photosynthetic residents and heterotrophic bacteria, combined to a low hydrodynamism may have contributed to deplete the pore water in nutrients, which in turns would lead to an influx of nitrate/nitrite. Following the increased runoff that occurred in June, sediments in the prodelta had a distinctive smell indicative of sulphate reduction. The decomposition of the plant debris brought by the Têt River during this event may have depleted the pore water in O₂ and enable sulphate reduction to occur at a lower depth as observed by Buscail et al. (1995) following an autumnal flood.

Silicate efflux was extremely variable, with periods of limited exchange across the sediment-water interface (< 0.2 mmol m⁻².d⁻¹, April 2008 for station St28 m and January 2009 for both stations) and higher exchange on the other dates (> 0.4 mmol m⁻².d⁻¹). These values are in the lower range of those reported in eutrophic environments such as the Southern North Sea (Oehler et al., 2015), but consistent with values reported off the Rhône and Ebro Rivers in the North Occidental Mediterranean Sea (Denis and Grenz, 2003; Tahey et al., 1994). In contrast to nitrate/nitrite, silicate release is not directly linked to organic matter degradation. Benthic fluxes of silicate are mainly due to the dissolution of biogenic silica. They are controlled by the amount of biogenic silica (diatom frustules), the degradation of the organic matrix by bacteria, the temperature, which affects dissolution and solubilisation, and bioirrigation, which favours solute exchange. Higher phytodetritic inputs from the water column certainly account for the overall higher silicate flux recorded for the offshore muddy sediments. Effluxes were furthermore more elevated at the end of the summer, when both inputs of phytodetritus from the water column and macrofauna density are at their highest levels. Silicate flux at the sediment-water interface is an important component of the benthic-pelagic coupling as it may sustain some new production of diatoms at the end of the summer (Arndt and Regnier, 2007). In the prodelta, the silicate efflux did not show any obvious seasonal pattern. Low efflux of silicate in April could be linked to the development of benthic diatoms, which by their biomineralisation activity, alter dissolved silicate fluxes at the sediment-water interface (Sigmon and Cahoon, 1997).

5. Conclusions

The temporal variability of organic matter source, quality and reactivity has been investigated in sediments from the Têt prodelta and its adjacent shelf using bulk geochemical proxies, molecular descriptors, and *ex-situ* whole core incubations. Organic carbon accumulation in this small prodeltaic unit is low, but the composition of the organic matter

temporally trapped in the Têt prodelta is surprisingly very similar to that accumulated in the Rhône prodelta despite major differences between these two systems in terms of watersheds, river regimes, solid flows and accumulation rates. In contrast to the Rhône River shelf, which is controlled by the contributions and dynamics of the river flow, the Têt River shelf is mainly controlled by marine dynamics. Temporal compositional trends in the prodelta are related to the nature of the riverine inputs and the autochthonous production in the summer when the river flow is at its lowest level. However, these shallow deposits are subjected to frequent episodes of resuspension as evidenced by the strong spatio-temporal heterogeneity observed during our survey. The strong mixing and recycling induced by storms further explain the homogenous composition of the sedimentary organic matter on the mid-shelf.

This study provides insights on the biogeochemical fate of the POM delivered by coastal rivers in the gulf of Lions. Inputs of labile organic matter and hydrodynamic conditions support high benthic remineralisation rates with distinct microbial dynamics in the sandy mud of the prodelta and the muddy deposit of the mid-shelf. This efficient degradation affects the reactivity of the organic matter that is exported on the outer shelf and to the deep-sea ecosystems.

In summary, sedimentary organic matter quality in front of small coastal Mediterranean rivers is constrained by changes in the biochemical composition of the river and autochthonous inputs, the degradation of the bioavailable organic matter, and physical forcing, which promote remineralisation of organic matter and advection of sediments.

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Appendix A. Supplementary data

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