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Distribution and lability of land-derived organic matter in the surface sediments of the Rhône prodelta and the adjacent shelf (Mediterranean sea, France): a multi proxy study

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Abstract

The Gulf of Lions is a river-dominated ocean margin (RiOMar) that receives high loads of nutrients, sediments and particulate matter from the Rhône river. Most of the particulate materials from the Rhône settle rapidly on the seafloor, this raises the question of the fate of these large quantities of organic carbon delivered to the benthic boundary layer. Surface sediments (0–0.5 cm) were collected in the Rhône prodelta and its adjacent shelf during a period of low river discharge (April 2007, 16 stations). The sources, distribution and lability of sedimentary organic matter was examined using bulk (organic carbon, total nitrogen, grain size) and molecular-level (pigments, amino acids, fatty acids, δ^{13}C of individual fatty acids) analyses. Our results confirmed previous observations of a southwestward Rhodanian imprint in the nearshore sediments. Fatty acid biomarkers and compound-specific δ^{13}C signatures of most fatty acids clearly indicate that the Rhône inputs consist in a mixture of organic matter (OM) from different sources with a strong contribution from terrestrial plants, and a smaller input from freshwater microalgae, mostly diatoms. The influence of the Rhône River was prominent within the first ten kilometers, but may still be observed in the outer shelf (~21 km) as indicated by the occurrence of long chain fatty acids derived from vascular plants and their δ^{13}C signatures. In the proximal prodelta, bacteria-specific fatty acids were abundant (1.65 mg g^{-1} OC at the mouth site) and were relatively depleted in δ^{13}C confirming that bacteria preferentially utilize terrestrial OM in this area. In the shelf area, the inputs of marine OM and its preferential utilization by the bacteria was confirmed, but the coupling between the pelagic and the benthic compartments appeared limited at this period of the year.

Overall, degradation indexes based on amino acids (Dauwe's degradation index) and pigments (ratio of intact chlorophyll-*a* to the sum of chlorophyll-*a* + phaeopigment-*a*), as well as isotopic enrichment of source-specific fatty acids reveal an offshore gradient of OM decay reflecting the rapid deposition of the terrestrial material in the prodelta, the low mixing with OM deriving from marine sources and the efficient degradation of

the OM once deposited. Terrestrial OM is usually considered as being refractory due to the presence of structural polymers and its advanced stage of degradation. However, the OM delivered by the Rhône is relatively labile as shown by the intermediary value of Dauwe's degradation index (DI = +0.1), the high proportion of bio-available nitrogen and the occurrence of polyunsaturated fatty acids. Deltaic sediments off the Rhône river should thus be of sufficiently high nutritional quality to sustain dense macrofaunal communities.

1 Introduction

River-dominated ocean margins (McKee et al., 2004) have received major attention over the last decades, among many arguments, because of the high loads of sediment and particulate organic matter that rivers deliver to the marine environment. Benthic boundary layer and seabed in land-ocean margins impacted by major rivers are indeed very active zones of biogeochemical transformations (Aller, 1998) and form the most remarkable repository of sediments and organic matter (OM) on Earth (Hedges and Keil, 1995). Within this general framework, one of the goals of the program CHACCRA (Climate and Human-induced Alterations in Carbon Cycling at the River-seA connection) was to characterize the processes that govern the cycling and fate of organic particles in the superficial sediment of the Mediterranean coastal margin dominated by the Rhône river (Rabouille et al., 2011).

The Rhône brings annually 1.2 to $19.4\,10^6\,T$ of suspended matter onto the adjacent continental shelf of the Gulf of Lions margin (Pont et al., 2002) which has been estimated to account for $19 \pm 6\,10^4\,T\,OC\,yr^{-1}$ (Sempere et al., 2000). Most of this matter accumulates rapidly in the delta front area where deposition dynamics are reinforced by flocculation processes (Aloisi et al., 1973). This results in maximum sediment accumulation rates extending from several tens of centimetres per year in the immediate vicinity of the river mouth to only a few millimetres offshore (Radakovitch et al., 1999). This situation raises the question of the fate of these large quantities of organic carbon and

bio-relevant materials delivered to the benthic boundary layer and seabed. If quantity is a crucial parameter for the carbon budget, OM quality as defined by its composition is of critical relevance to appraise the efficiency of biogeochemical transformation kinetics and nutritional relevance of the OM available for benthic organisms (Mayer et al., 1995). Natural organic matter is made of simple monomers and/or biopolymers such as proteins, carbohydrates and lipids, which may be rapidly mineralized. This labile pool of OM rarely exceeds 20% of the total OM (Hedges et al., 2000; Ingalls et al., 2004), but represents the fraction that may undergo early diagenesis in coastal marine sediments.

The large amounts of terrigenous compounds deposited in deltaic systems are generally considered as being refractory to decomposition due to the presence of lignin structures (De Leeuw and Largeau, 1993; in Sanchez-Garcia et al., 2009; for review see: Wakeham and Canuel, 2006). However, recent findings have questioned this paradigm. Several studies demonstrated that river suspended particulate matter is less degraded than coastal sediments (Unger et al., 2005a; Unger et al., 2005b; Gaye et al., 2009; Ingalls et al., 2003) and is highly sensitive to microbial remineralization (Mayer et al., 2008). The lability of the Rhône inputs has been previously discussed with regard to the linkage with benthic community structure and intensity of bacterial remineralization in the sediments (Hermand et al., 2008; Lansard et al., 2008; Goineau et al., 2011; Rosenberg et al., 2003). The distribution and lability of OM sources in the Rhône prodelta and its adjacent shelf have been inferred in these earlier studies from bulk biochemical descriptors (lipids, proteins and carbohydrates) and global geochemical composition (C/N ratios and stable isotopes) (Alliot et al., 2003; Tesi et al., 2007 and references above). These proxies are however difficult to interpret when sediments contain a mixture of different sources of OM at different stages of decomposition as is the case in coastal environments sources (Kim et al., 2006). Molecular-level proxies, such as amino and fatty acids, and specific compound stable isotope composition may shed light on sources, quality and degradation stage of sedimentary OM when C/N ratios and stable isotopes are equivocal. Fatty acids in particular are valuable tools

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to identify OM origin when multiple sources are involved (Canuel, 2001), because the biosynthetic pathways of some fatty acids are species-specific. Moreover, the carbon isotopic composition of individual FAs is another tool for identification of the sources (Canuel et al., 1997; Dai and Sun, 2007). Nutritional quality of sedimentary OM which may be defined as the capability to fulfill the nutritional needs of benthic organisms can also be apprehended using molecular analyses. First, OM digestibility may be assessed using the valuable bio-mimetic approach of Mayer et al. (1995) allowing to quantify the digestibility of the proteinaceous fraction (Grémare et al., 2003). Second, the food must provide sufficient amounts of essential macro and micronutrients because heterotrophic organisms cannot synthesize de novo some of these components. The detailed knowledge of the biochemical composition of sedimentary OM, in particular the amino acid and fatty acid profiles, thus enable to highlight potential nutritional deficiencies (Phillips, 1984). It has to be taken into account that nutritional quality may evolve during OM decay, since compositional changes occurred during early diagenesis (Niggemann and Schubert, 2006). The amino acid-based index of degradation proposed by Dauwe and Middelburg (1998) enable to quantify these changes and allow to scale the state of OM decomposition (Dauwe et al., 1999).

A range of molecular-level proxies were combined in this study in order to describe precisely the origin and quality of sedimentary OM in the surface deposits of the Rhône prodelta and adjacent shelf. This allows for an accurate picture of the distribution of terrestrial versus marine OM while keeping a focus on the lability of these different sources of OM.

2 Material and methods

2.1 Study area

The Gulf of Lions is the largest continental shelf of the Mediterranean Sea with an area of 6700 km^2. Located on the northern part of occidental Mediterranean basin, this area receives considerable freshwater, nutrients and suspended organic matter inputs

from the Rhône river (Raimbault and Durrieu de Madron, 2003). This river is the most important of the Mediterranean sea in terms of discharge ever since the construction of the Aswan high dam on the Nile River (Alliot et al., 2003). The surface of the Rhodanian basin is of 97 800 km^2 and the mean yearly discharge of the Rhône river is 1700 m^2 s^{-1}
⁵ (Pont, 1997). At the river mouth, fluvial sediments settle and form a 40–50 m thick fan-shaped prodeltaic lobe (Rabineau et al., 2005). The description of the study area is more detailed in Cathalot et al. (2010).

2.2 Sample collection

Sediment cores were collected in the prodelta and the adjacent shelf during a period
¹⁰ of low discharge of the river (19–30 April 2007). A total of 16 stations were sampled during the RIOMAR-1 cruise at depth ranging from 25 to 98 m (Table 1 and Fig. 1). The stations were operationally grouped into two regions that will be referred to throughout the text: the prodelta area (A, B, G, K′, L) and the shelf area (C, D, E, F, H, I, J, N, O, M, R2) with stations J and R2 located outside the influence of the Rhône (Fig. 1) (Wright
¹⁵ and Friedrichs, 2006).
    Sediment cores (9.5 cm diameter) were collected with a multicorer MUC 8/100 (Oktopus GmbH) and three cores were selected for further laboratory analyses. The first layer of sediment (0–0.5 cm) of each core was homogenized and conditioned on board. An aliquot of each sample was immediately frozen at −20 °C for bulk and pigment anal-
²⁰ yses. The remaining sediments were rapidly desalted (Pusceddu et al., 2005), stored at −20 °C. All sub-samples were freeze-dried prior to analyses.
    Seven stations (A, B, N, C, D, E and F) distributed along a South West longitudinal transect (Fig. 1) corresponding to the preferential direction of the Rhône river plume (Naudin and Cauwet, 1997) were selected for a detailed description of the biochemical
²⁵ characteristics of the surface sediments. The same analyses were also performed on station (J), a marine reference site located outside the influence of the Rhône river. Amino acid and fatty acid analyses were performed on those 8 stations, while bulk measurements were performed on all of the 16 stations.

Part of the biochemical data has been reported in Pastor et al. (2011), but will be discussed more thoroughly in the present paper.

2.3 Bulk analysis

Sediment granulometry was assessed using a Malvern® Mastersizer 2000 laser micro-granulometer (Pastor et al., 2011). Grain size is given as the d(0.5), which corresponds to the median of the size distribution based on the equivalent spherical volume diameters.

Total nitrogen and organic carbon concentrations (TN and OC, respectively) were measured at each station (3 cores). Homogenized and precisely weighed samples were analysed with an automatic CN-analyzer LECO 2000 after acidification with 2 N HCl (overnight, at 50 °C) in order to remove carbonates prior to the analyses of organic carbon (Cauwet et al., 1990). Precision ranges for OC and TN measurements are about 2%.

2.4 Pigment analysis

Sediments were rapidly thawed and ~100 mg were extracted overnight in 5 ml of acetone at 5 °C in the dark. Adjustment was made for sediment water content to obtain a final acetone degree of 90%. The fluorescence of the sediment extracts was measured on a LS 55 spectrofluorimeter (Perkin Elmer Inc., USA) according to the method developed by Neveux and Lantoine (1993), which allows the quantification of 4 pigments in sediments: chlorophylls-a, b, and c, and degradation products of chlorophyll-a (phaeophytin-a and phaeophorbide-a). 3 cores per station were analysed and extractions were performed in triplicates on each sediment sample (3 extractions × 3 cores × 16 stations). Concentrations were converted in μg g^{-1} DW using water contents. Intra-core variability was generally low with coefficients of variation below 5.5% for 3 fourths of the data set.

2.5 Total hydrolysable and enzymatically hydrolysable amino acids

Protocols for the analysis of total hydrolysable amino acids (THAA) and enzymatically hydrolysable amino acids (EHAA) are given in detail in Pastor et al. (2011).

THAA were extracted by acid hydrolysis and EHAA following the biomimetic approach proposed by Mayer et al. (1995). THAA and EHAA hydrolysates were analysed as isoindole derivatives following reaction with an orthophtaldialdehyde solution and the fluorescent derivatives obtained were separated by reverse-phase high-performance liquid chromatography (HPLC, Gynkotek-Dionex system) using non-linear gradient of methanol-acetate buffer, and detected by fluorescence at 450 nm using an excitation wavelength of 335 nm. The identification was based on retention times within a C18 HPLC column (Lindroth and Mopper, 1979) and the concentration of identified amino acids were calculated on the basis of individual calibration curves obtained from a mixture of 21 amino acids from the amino acid standard solution AA-S-18 (Sigma–Aldrich) to which 6 amino acids were added (asparagine, β-alanine, glutamine, taurine, ornithine, β-glutamic acid). The molar concentration of 15 amino acids was converted as weight per gram of dried sediment (mg g^{-1}DW) for unit homogeneity with the other biochemical proxies. Note that tryptophan and cysteine are not quantified by this method; the former is destroyed during the hydrolysis step and the latter produces derivatives with minimal fluorescence. Moreover, aspartic acid and glutamic acid peaks include the contribution of the corresponding deaminated amino acids, glutamine and asparagine, a typical artefact of the method.

2.6 Fatty acid analysis

Fatty acid analyses were extracted by direct transesterification as previously described in Nahon et al. (2010). 1.5 g of dried sediments were let to react with a solution of methanol, sulfuric acid and chloroform (1.7:0.3:2, v/v/v) in the presence of an antioxidant (buthylhydroxytoluene, Christie, 2003). This procedure enables in one single step to extract the lipid and release the fatty acids that will be transformed in the

corresponding methyl esters (FAMEs). An internal standard (nonadecanoic acid) was added to the extraction vials to account for potential loss or errors during the extraction procedure. The organic phase containing the FAMEs was recovered by three successive rinses and an aliquot of this phase was evaporated to dryness in a rotary evaporator (Savant Speed Vac system) at room temperature. FAMEs were redissolved in hexane prior to analysis by gas chromatography with mass spectrometry detection according to conditions described in Nahon et al. (2010). The instrument was a Varian 3900 coupled to a Saturn 2100T ion trap detector. Fatty acids as methyl esters were separated on a fuse silica capillary factor four VF-23ms column (30 m×0.25 mm ID, 0.25 μm thickness) from Varian. FAMEs in samples were identified by comparison of retention times and mass spectra with authentic commercial standards: Qualmix Fish Synthetic (Ladoran Fine Chemicals, INTERCHIM, France), Supelco 37, PUFA no 1 and no 3 (SUPELCO, France). Qualitatively, the contribution of each individual fatty acid was determined on the basis of the reconstructed integrated chromatogram and expressed as the percentage of the specific compound area to the total peak area (% of total fatty acids). Using a standard containing known amounts of FAMEs (Supelco 37), calibration curves were generated for 37 individual FAMEs by plotting the surface area of the quantifying ion as a function of FAME concentration. Fatty acid concentrations in the sediments were calculated using these calibration curves, corrected with the internal standard and expressed as weight per dry weight (mg g^{-1} DW).

2.7 Compound specific stable isotope analysis

Stable carbon isotopic compositions of individual fatty acids were determined using a GC-C-IRMS system (Agilent 6890 gas chromatograph/on-line combustion/Thermo DELTA plus V isotope ratio mass spectrometer). FAMEs were separated with a 30 m × 0.25 mm i.d. column (DB-5, J&W Scientific) and then combusted to CO_2 over CuO/Pt wires at 850°C. The δ^{13}C values of individual compounds were calculated based on working reference gas (UHP CO_2 for δ^{13}C), which was calibrated to

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international reference materials PDB for δ^{13}C using NIST (National Institute for Standards and Technology) reference materials (measured on Finnigan MAT 252 IRMS) and University of Indiana *n*-alkane reference mixtures (measured on Thermo Delta plus V GC/IRMS). The relative standard deviation of IRMS was less than ±0.5‰ for two internal standard measurements ($n = 38$). The δ^{13}C values of fatty acids were calculated by correcting for the extra carbon atom (its isotopic composition being measured on Finnigan MAT 252 IRMS) in the FAMEs added during extraction/methylation.

2.8 Data treatments

The percentages of OC contained in THAA, EHAA and fatty acids were inferred from individual compound concentrations and number of carbon atoms in each compound. The percentages of N in the form of protein amino acids (THAA-N%) and bioavailable amino acids (EHAA-N%) were determined in the same way.

The amino acid degradation index (DI) proposed by Dauwe and Middelburg (1998) and revised in Dauwe et al. (1999) was calculated for our THAA data set. The calculation of the DI is based on the results of a PCA analysis performed on a suite of samples of varying degradation state from OM sources to sediments. The first axis of the PCA was interpreted to reflect OM degradation. The DI of a sample is defined as its value on the first axis of the PCA, which is the sum of the contributions of each amino acid (in molar %), standardized within the reference data set and weighted by the respective factor coefficient.

$$DI = \sum_i \left[\frac{var_i - AVGvar_i}{STDvar_i} \right] \times fac.coef_i$$

In the equation, var_i is the molar percentage of amino acid i in a given data set, while AVG var_i, STD var_i and fac.coef$_i$ are given by Dauwe et al. (1999) and correspond to the mean, standard deviation and PCA-derived loading of amino acid i.

Positive DI values are indicative of fresh material such as phytoplankton (+1.5) and negative values reveal that the OM has undergone degradation (−2.2 for highly

degraded; Dauwe and Middelburg, 1998). The DI is considered as a robust parameter because it is based on a large number of individual measurements (Meckler et al., 2004) and allows comparing different samples directly and quantitatively (Dittmar et al., 2001).

Caution should be applied when comparing our DI values with data from the literature since we did not include methionine in the calculation of the DI. This has little influence on DI values as they remain unchanged when using methionine molar percentages equivalent to those reported in Dauwe et al. (1999). However, a methionine molar percentage of 0% would entail the deduction of 0.161 to the values reported in the present paper.

All correlation analyses performed in this study are based on Pearson's correlation coefficients. *p*-values below 0.05 were considered to be statistically significant. A Principal Component Analysis (PCA) was performed to test the potential linkage between the origin and the lability of the sedimentary OM. All the statistical procedures were carried out using either R or PAST software (Hammer et al., 2001).

3 Results

3.1 River discharge and environmental conditions

The average daily water discharge rate of the Rhône river during the sampling period was $698 \, \mathrm{m^3 \, s^{-1}}$. This flow rate is characteristic of a period of low discharge since the average annual water discharge is $1700 \, \mathrm{m^3 \, s^{-1}}$ (Pont, 1997). The highest peak of water discharge before the sampling occurred at the beginning of March (3–9) with daily flow rates exceeding $2800 \, \mathrm{m^3 \, s^{-1}}$.

At all sites, bottom oxygen concentrations were well above the level of hypoxia (i.e., $2 \, \mathrm{mg \, l^{-1}} = 123 \, \mathrm{\mu M}$). The depth of the oxygenated sediment layer encompassed the 0–0.5 cm superficial layer at all stations except station A (Cathalot et al., 2010).

3.2 Sediment bulk properties

3.2.1 Grain size

At the exception of station A that exhibited a d(0.5) of 37 µm, grain-size distributions were roughly uniform in the study area with average grain size in the 9–17 µm range (Table 1) and was positively correlated to distance from the river mouth ($p < 0.0001$, 16 stations, $n = 48$). Fine to very-fine muddy material (silt and clay, <63 µm) was dominant in the surface sediments and accounted for between 65 % and 98 %, with the lowest values occurring at the river mouth and highest percentages in the southernmost and easternmost sites (unshown data). Within this fraction, the contribution of clay (<5 µm) ranged from 13 to 33% (data not shown). Stations located at the Rhône mouth (A, B, G and K) were characterized by the occurrence of a coarser fraction (>250 µm) that represented 2 to 6% of the matrix (data not shown).

3.2.2 Total organic carbon and nitrogen contents

Sediment organic carbon (OC) contents ranged from 0.84 ± 0.18 to 1.83 ± 0.18% DW at stations R2 and A, respectively (Table 1 and Fig. 2). Total nitrogen (TN) contents ranged from 0.085 ± 0.004 (station R2) to 0.166 ± 0.004% DW (station A) (Table 1). Stations distributed in the prodelta and adjacent shelf showed a general trend for decreasing OC and TN contents with the distance from the river mouth ($p < 0.0001$ in both cases, 16 stations, $n = 48$).

C/N atomic ratios ranged from 11.2 ± 0.4 to 15.6 ± 1.4 (Table 1). This ratio was correlated with the distance from the river mouth ($p < 0.0001$, 16 stations, $n = 48$), but not with depth ($p = 0.7252$, 16 stations, $n = 48$). Values above 13 were characteristic of sediments located within the first ten km (A, K′, G, N, O, H and I) in agreement with previous data published in Kim et al. (2006) and Goineau et al. (2011). In the offshore area, C/N ratios were higher at stations E and F, located along the SW transect, than at the deeper stations M and R2.

3.3 Pigment concentration and composition

Spatial distribution of chlorophyll-*a* in the study area shows a maximum near the shore $(9.78 \pm 0.82 \, \mu\text{g g}^{-1}$ DW) and a general decrease seawards ($p <0.0001$, 16 stations, $n = 48$, Table 1). Offshore, concentrations in the stations under the Rhône influence remained twice as high as at the marine reference, with values of 1.66 ± 0.13 and $0.81 \pm 0.09 \, \mu\text{g g}^{-1}$DW for stations F and J, respectively (Table 1).

Phaeopigments were constantly predominant over chlorophyll-*a* (Table 1). The proportion of chlorophyll-*a* to the sum of chlorophyll-*a* and phaeopigments was used as a proxy of phytodetritus degradation (Pigment Ratio Index: PRI). This proxy was negatively correlated with distance from the mouth and depth ($p < 0.0001$ in both cases, 16 stations, $n = 48$); values found at the mouth indicate that approximately 68 % of the pigments were degraded (Table 1). Values decreased along the transect and more than 90% of chlorophyll-*a* was degraded 9 km offshore. This trend was more pronounced on either side of the transect. Overall, the degradation status was positively correlated with the chlorophyll-*a* content ($R^2 = 0.95$, $p < 0.0001$, 16 stations, $n = 48$, Fig. 3).

Chlorophyll-*b*, an accessory pigment present in all Chlorophytes (Jeffrey, 1976), was only detected in sediments from stations located in the prodelta (Table 1).

3.4 THAA and EHAA composition

Total hydrolysable amino acid (THAA) concentrations ranged from 2.23 ± 0.06 (station F) to 3.77 ± 0.30 (station A) mg g^{-1}DW and decreased gradually southwestward with distance from the mouth ($p < 0.0001$, 7 stations, $n = 20$) (Table 2). These values are somewhat higher to those found by Grémare et al. (2002) in a larger scale mapping of the sedimentary OM characteristics in the Gulf of Lions. When normalized per gram of organic carbon, THAA values (mg g^{-1}OC) were no longer correlated with the distance from the mouth ($p > 0.05$, unshown data). Sediments from the furthermost stations contained approximately 1.7 times less THAA than at the mouth, and comparable amounts to the marine reference (J). The percentage of carbon contained in

THAA made up 8.6 to 10.7% of the total organic carbon. THAA accounted for a large fraction of the N pool with minimal and maximal values recorded at stations B (32.2%) and N (41.4%), respectively (Table 2).

The acidic amino acids were predominant in the studied area, with a prevalence of aspartic acid (16.8–22.3 mole%) over glutamic acid (11.1–12.0 mole%). Two hydrophobic amino acids, glycine and alanine, were also abundant and accounted on average for 15.5 and 10.5 mole% of the amino acids, respectively. Their contributions to the THAA pool were very consistent among stations with coefficients of variation lower than 4%. Serine, threonine, valine and leucine accounted for between 5 and 10 mole% of the THAA pool, whereas taurine, tyrosine, phenylalanine, isoleucine and the basic amino acids (histidine, arginine, lysine) never exceeded 4 mole% of the amino acids (Table 2).

DI values tended to decrease from the mouth to stations located offshore (Fig. 4) with values of 0.096 ± 0.163 and -0.434 ± 0.235 at stations A and F, respectively ($p = 0.0004$, 7 stations, $n = 20$; Table 2). DI values were positively correlated with OC, TN, pigments and PRI ($p < 0.05$ in all cases, 7 stations, $n = 20$).

Analysis of the contributions of each of the amino acids to the DI reveals that the offshore trend for more a negative index is controlled by a limited number of amino acids including acid aspartic and three non polar essential amino acids (phenylalanine, isoleucine and leucine) that behave in an opposite manner (Fig. 5). While the aspartic acid contribution increased with DI diminution ($p < 0.0001$, 8 stations, $n = 20$), the contributions of the essential amino acids (phenylalanine and leucine) decreased significantly in magnitude ($p < 0.05$ in all cases, 8 stations, $n = 20$). Considering the contribution of the other amino acids, the DI were not correlated with the two non-proteinic amino acids β-alanine and β-glutamic acid ($p > 0.05$, 7 stations, $n = 20$; data not shown).

Enzymatically hydrolysable amino acids (EHAA) ranged from 0.53 ± 0.06 mg g^{-1}DW at the marine reference to 1.17 ± 0.19 mg g^{-1}DW at the mouth (Table 2). They decreased rapidly along the SW transect in the prodelta area, and then remained fairly

constant offshore. They made up 2.5 (station N) to 3.0% (station D) of the OC pool and 8.5 (station B) to 9.8% (station D) of the N pool. Globally, the bioavailable amino acids displayed a similar composition to THAA.

The EHAA/THAA ratio was quite constant in the surface sediments (27.5 ± 1.76 to 28.9 ± 1.99%) except at station N where the ratio fell to 24.5 ± 2.67% (Table 2). These values are in the range of those previously reported for surface sediments in the Gulf of Lions (Grémare et al., 2002). The ratio did not reveal any significant trend with distance from the coast or with depth ($p > 0.05$ in both cases, 7 stations, $n = 20$).

3.5 Distribution of fatty acid biomarkers

Total fatty acid (FA) concentrations ranged from $27.99\,\mu g\,g^{-1}$DW for the marine reference to $160.03\,\mu g\,g^{-1}$DW at the river mouth (i.e. station A) (Table 3). A clear decrease of FA concentrations with increasing distance from the river mouth was observed along the South West transect ($y = 188.41 \cdot x^{-0.5521}$, $R^2 = 0.8972$, $p < 0.0004$, 7 stations, $n = 18$). In contrast to THAA, when normalized per gram of organic carbon, the southwestward decrease of FA was still evident with values falling from 8.74 to $3.75\,mg\,g^{-1}$OC ($y = 9.7519 \cdot x^{-0.3288}$, $R^2 = 0.8427$, $p < 0.0001$, 7 stations, $n = 18$) (Fig. 6). FA accounted for a small fraction of the organic carbon ranging from 0.17 to 0.63% for stations A and J, respectively (data not shown).

Twenty eight individual fatty acids were identified, representing a wide range of OM inputs into the prodelta and adjacent shelf. Identified fatty acids included mid chain saturated fatty acids (C_{10}-C_{20}), long chain saturated fatty acids (C_{22}-C_{28}), monounsaturated fatty acids (MUFAs; e.g. 16:1ω7, 18:1ω9cis and 20:1ω9), polyunsaturated fatty acids (PUFAs; e.g. 16:3ω4, 18:2ω6cis, 18:3ω3, 18:4ω3, 20:4ω6, 20:5ω3 and 22:6ω3), bacterial fatty acids (BAFAs; e.g. 15:0, 17;0, iso- and anteiso-15:0 and 17:0 and 18:1ω7) (Table 3). Source assignment was made according to literature (See below 4.1).

Overall, saturated fatty acids (SAFAs) were the most abundant series (46.65 to 56.50%) of FAs, with the dominance of mid chain SAFAs over long chain compounds

(C$_{22}$-C$_{24}$). The most abundant mid chain SAFAs were 16:0 (>20%) and to a lesser extent 18:0 (5.5–6.7%) (Table 3). Long chain SAFAs were also abundant in stations located near the river mouth, but rapidly decreased with distance from the mouth ($p < 0.0001$, 7 stations, $n = 18$). Nonetheless, these biomarkers of terrestrial inputs were found in the surface sediments at all stations even at the marine reference. The ratio of long chain even numbered fatty acids to short chain even numbered fatty acids (LCFA:SCFA) was comprised in the 0.2–0.5 range. Bacterial FAs were found in all samples with relative contributions ranging from 18.9 to 26.8% of the FAs. Monounsaturated fatty acids (MUFAs) ranged from 15.3 to 17.4% of the FAs with 16:1ω7 accounting for approximately one half of the MUFAs (Table 3). The proportion of polyunsaturated fatty acids (PUFAs) varied from 7.6 to 10.5% of the FAs and was marked by the dominance of PUFAs belonging to the omega 3 series (18:3ω3, 18:4ω3, 20:5ω3, 22:6ω3). 16:3ω4 and 18:2ω6cis were also found in all samples.

3.6 Variations of δ^{13}C of individual fatty acids

Compound-specific stable carbon isotopic compositions of 14 individual fatty acids were determined for sediment samples collected along the transect sites (A, B, C, D, E, and F) and at one reference site (J). Except two measurements of 20:5 at stations E and F, the δ^{13}C values of all fatty acids varied in a range from −23‰ to −34‰ (Fig. 7). For even-number saturated fatty acids, the δ^{13}C values of C$_{14}$-C$_{18}$ compounds were generally 3 to 4‰ higher than those of C$_{20}$-C$_{26}$ compounds at each site. For other groups of fatty acids including monounsaturated (e.g., 16:1 and 18:1), branched (e.g., iso-15:0 and anteiso-15:0), odd-number saturated (e.g., 15:0), and one polyunsaturated (18:2) compound, their δ^{13}C values varied in the same range as those C$_{14}$-C$_{18}$ saturated fatty acids. However, for 20:5 polyunsaturated fatty acid, the δ^{13}C values varied differently from all other compounds and two unusual negative values were observed at stations E and F.

Along the transect from the river mouth to offshore sites, the δ^{13}C values of almost all fatty acids (except 20:5) shifted positively (Fig. 7). In general, approximately 4 to

6‰ enrichments were observed for all compounds but at station D, the δ^{13}C values of these fatty acids became to be equivalent to those found in the reference site (station J). For 20:5 fatty acid, its δ^{13}C values varied little from station A to D but dropped remarkably at station E and F.

3.7 Multivariate analysis of the relationships between descriptors of OM quality, biomarkers of origin and physical characteristics

The first axis of the PCA explains 63.58% of the total variation and is characterized by positive loadings for C/N atomic ratio, Chl-*b*, PRI, OC, FA, DI and terrestrial FA markers; and by negative loadings for algal and bacterial FA markers and EHAA/THAA ratio (Fig. 8). The second axis of the PCA explains another 16.18% of the variation and has positive loadings for EHAA/THAA, algal and bacterial FA markers, FA, PRI, OC, Chl-*b*; and slightly negative loadings for C/N ratio, DI and terrestrial FA markers.

4 Discussion

The main objective of the present study was to provide a picture of the distribution of terrestrial versus marine OM using molecular-level proxies, while keeping a focus on the degradation and bioavailability of these different sources of OM. Since most of the terrestrial particulate matter from the Rhône settles rapidly in the prodelta, this raises the question of the fate of large quantities of organic carbon and bio-relevant materials delivered to the benthic boundary layer. Quantity obviously is a crucial parameter for carbon budget in RiOMar systems, but OM quality as defined by its composition at the molecular level is of critical relevance to appraise the efficiency of OM cycling and its nutritional potential for benthic organisms.

4.1 Spatial distribution of terrestrial and marine derived organic matter in superficial deposits

The influence of the Rhône river in the superficial deposits of the prodelta results in a marked opposition between bulk sediment characteristics (i.e., OC, median grain size) and the distance from the river mouth (Fig. 8a), which is in good agreement with previous observations highlighting the clear southwestward river footprint in the sediments of the prodelta (Alliot et al., 2003; Lansard et al., 2008; Roussiez et al., 2006; Kim et al., 2010). The net diminution of the influence of the river (OC, TN) soutwestward is comforted by molecular-level proxies of origin. Although not completely specific of the origin (marine versus terrestrial), chlorophyll-*b*, an accessory pigment commonly ascribed to the Chlorophytes (Jeffrey, 1976), which include all vascular plants but also green algae, was only found in the prodelta. The contribution of chlorophyll-*b* expressed as percentages of chlorophyll-*a* was comprised in the 10–14% range at the river mouth and decreased seaward. These values are comparable with those reported for suspended particles in the Amazon river system (Saliot et al., 2001). The concomitant presence of high concentrations of chlorophylls-*a* and *b* supports the strong contribution of terrestrial phytodetritus to the muddy deposits in the vicinity of the Rhône mouth. This is in good agreement with previous observations in this area (Lansard et al., 2008; Tesi et al., 2007).

Inputs of chloropigments of marine origin may be intense in coastal margins (Mann, 1982; Day et al., 1989) as marine productivity in deltaic environments tends to be high due to significant nutrient inputs from riverine sources (Hedges and Keil, 1995; Lefevre et al., 1997). However, as the flow near the river mouth resulted in high current velocity and turbidity (Cloern et al., 1983; Cloern, 1987), phytoplankton primary production is rather limited in the close vicinity of the river. This results in a downstream progression of phytoplankton biomass and production along the estuarine coastal plume, like, in the Mississippi river (Lohrenz et al., 1997) and the Yangtze river estuary (Gong et al., 1996). In the Rhône prodelta, the coupling between the pelagic and benthic

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compartments is also probably reduced as suggested by the strong vertical salinity gradient between marine and river waters which limits exchanges between the nutrient-rich freshwater and the potential consumers in the underlying marine water (Naudin et al., 2001). Besides that, carbon fixation by microphytobenthos is certainly of minor im-
5   portance in the Rhône prodelta as confirmed by the absence of oxygen oversaturation at the benthic boundary layer (see O_2 profiles in Cathalot et al., 2010).

To further evaluate the relative importance of autochthonous and allochthonous OM inputs within the superficial sediments of the studied area, the contribution of various individual fatty acids characteristic of known organic matter sources were grouped and
10   used as proxies of origin. The relative proportions of SAFAs, MUFAs and PUFAs were similar to values reported for the Mississippi deltaic system (Waterson and Canuel, 2008).

Long chain even numbered FAs (LCFA) are derived from cuticular waxy leaf coatings of higher plants (Wannigama et al., 1981) and are fairly resistant to degradation
15   (Prahl et al., 1992). They are thus considered as good indicators of vascular plant inputs. In the present study, they were found in all samples even in sediments from the marine reference station. Some marine microalgae might produce small amounts of LCFA, which would constitute a marine source of these fatty acids in open sea sediments (reviewed by Volkman et al., 1998). Nonetheless, the isotopic signature of these
20   fatty acids was consistent with values previously reported for LCFA of terrestrial origin (−35‰ to −30‰, Shi et al., 2001). Because of their abundance in terrestrial plants, the occurrence of 18:2ω6 and 18:3ω3 is commonly considered as another indicator of terrestrial inputs in coastal environments (Dai et al., 2005). Yet, these compounds are rapidly lost when plant tissues are decomposed (Wannigama et al., 1981), which
25   results in low occurrences in the sediments. The contribution of these two fatty acids in the studied area was small (1.3–3.8%), but equivalent to values reported in coastal sediments impacted by river inputs, such as Gilbert Bay in the Labrador (1.2–3.2%, Copeman and Parrish, 2003), Barred Island Cove in Newfoundland (2.5%, Budge et al., 2001), or sites in the Gulf of Mexico located nearby the Mississippi river (e.g. 3.9%

at the level of the SW pass, Waterson, 2005). In good agreement with the dispersion of the river plume, the concentrations of these two FAs decreased seaward and were lowest at the marine reference (station J).

The imprint of autochtonous OM sources was also evident in the surface sediments as indicated by the non negligible amounts of PUFAs (7.6–10.5%). The occurrence of PUFAs in marine sediments is generally considered as an indicator of fresh algal inputs.In the present study, it is however unclear whether the relatively moderate contribution of PUFAs reflects the reduced coupling between the water column and the benthic boundary layer at this period of the year or the enhanced degradation of these labile compounds by pre- and post-depositional processes. The contribution of PUFAs was significantly highest at the inshore and offshore stations (A and F, respectively), and minimal in the inner part of the adjacent shelf (station C located 8.6 km offshore), which also coincides with the limit of detection of chlorophyll-*b*. This pattern of distribution suggests the mixing of two sources of planktonic fatty acids: allochthonous freshwater algae delivered by the Rhône and autochthonous marine phytoplankton whose production was stimulated a little more offshore by riverine inputs of nutrients. Algal PUFAs were dominated by essential fatty acids of the omega 3 series: eicosapentaenoic acid (EPA; 20:5ω3), a typical marker of marine but also freshwater diatoms, and to a lesser extent docosahexaenoic acid (DHA, 22:6ω3), a FA mainly originating from dinoflagellates. In good agreement with the potential inputs of freshwater microalgae, EPA and DHA were found in suspended organic matter from the Rhône river (Pruski, unpublished results, 2010). Arachidonic acid (ARA, 20:4ω6) was found in the sediments with an increased contribution at stations with a stronger marine influence (stations F and J). The presence of this compound, which is the most abundant FA in the freshwater flagellate protist *Euglena gracilis,* is rather unusual in a marine environment and only few marine microalgae are known to produce it: the red algae (e.g. *Porphyridium cruentum*), the green unicellular algae *Nannochloris* spp. and a few species of pennate diatoms (Dunstan et al., 1994; Petkov et al., 1994; Nichols and Appleby, 1969; Hayashi et al., 1994). The abundance of 16:1ω7 (9.3–12.0%), a FA

common in diatoms, together with the presence of some C_{16} and C_{18}PUFA, which dominate in diatoms and flagellates respectively, are another evidence for the input of fresh material derived from microalgae. Albeit the succession of microalgal communities in the Rhône prodelta and adjacent shelf has not been described, the changes in PUFA composition underline the shift of planktonic communities between the stations under the direct influence of the Rhône river and stations more impacted by marine inputs.

Branched fatty acids and odd straight-chain saturated FAs are the dominant FAs of bacteria (Gillan and Hogg, 1984). Other bacterial markers include some MUFAs, like the cis-vaccenic acid ($18:1\omega7$), which is mainly of bacterial origin (Perry et al., 1979), but might also be produced by some microalgae (Nichols et al., 1984; Volkman et al., 1989). In marine environments, heterotrophic bacteria play a key role in the degradation of suspended and settled OM as the main actors of the first steps of early diagenesis (Froelich et al., 1979; Berner, 1980). Hence, sedimentary bacterial FAs have a dual origin: the pelagic bacterioplankton associated with detrital material being deposited on the seafloor as well as microorganisms living in the sediments. A strong bacterial imprint was found in the surface sediments from the Rhône prodelta and adjacent shelf with the FAs derived from bacterial biomass accounting for 18.9 to 26.8% of the FAMEs at the inshore and marine reference stations, respectively. The microbial contribution was quite constant within sediments of a given station (intra-station variability $\leq 6\%$) and was positively correlated with distance from the mouth ($p < 0.0001$, 7 stations, $n = 18$). However, when normalized per gram of organic carbon, FAs derived from bacterial biomass were more abundant in the prodelta area (Fig. 6). This coincides with the higher rates of benthic remineralization measured in situ in this area during the same field work by Cathalot et al. (2010). A close relation between bacterial activity as estimated by bacterial biomarkers and the distribution of labile organic substrates (PUFAs and sterols) has been reported in sediments from the Eastern North Atlantic (Conte et al., 1995) highlighting that the sedimentary microbial community rapidly responds to the pulse of fresh phytodetritus. In the present study, we indeed found a positive

relationship between the bacterial FA and chlorophyll-*a* contents ($p < 0.0001$) suggesting there was a clear coupling between Rhône river organic inputs and the intensity of microbial activity in the sediment.

Only trace amounts of 20:1ω9, a FA that originates from fatty alcohols of copepod wax esters were found in the sediments (Sargent and Falk-Petersen, 1988; Sargent and Henderson, 1986) suggesting a low contribution of material derived from zooplankton.

Compound-specific stable carbon isotopic compositions of most fatty acids (except 20:5) became enriched along the transect from the prodelta to the shelf, which was paralleled with those of bulk OC isotopic compositions (Cathalot et al., 2011). The similar δ^{13}C variations between the total organic matter pool and fatty acids clearly indicate mixed inputs of OM from different sources, but diagenetic processes may have important impacts on distributions of different compounds and their isotopic compositions. For example, non-specific fatty acids (e.g., 14:0 and 16:0) are contributed from all organic matter sources but they have distinct δ^{13}C signatures from source to source (Canuel et al., 1997; Dai et al., 2005). In general, if OM from a terrestrial source is dominated by C3 plants, their δ^{13}C (including compound-specific) values are relatively more negative than those from marine sources. Based on lignin products and their δ^{13}C signatures (−27 to −31‰ across the transect), it was confirmed that terrestrial OC from the Rhône river was mostly from a C3 source (Cathalot et al., 2011). Therefore, the positive shift in δ^{13}C of non-specific fatty acids along the transect reflects a variation in relative proportions of marine vs. terrestrial organic matter, which is consistent with those by other molecular proxies. However, the simple mixing of OM from marine vs. terrestrial sources could not explain the trend of isotopic variations of source-specific fatty acids (e.g., >C20 LCFAs and 18:2 from terrestrial source vs. 16:1 from marine phytoplankton) along the transect. We will discuss the impact of OM degradation on the isotopic variations in the next section.

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4.2 Degradation state of the organic matter in the superficial deposits

THAA concentrations in surface sediments followed the general OC pattern of decreasing values along the SW transect, which resulted in a uniform distribution of % THAA-C and % THAA-N with averaged values of 9% and 35%, respectively. This suggests that there was no preferential degradation of the terrestrial proteinaceous material relative to bulk OC and TN. % THAA-C and % THAA-N values in the Rhône prodelta fall within the range typical for coastal sediments (Lomstein et al., 2006; Unger et al., 2005a; Unger et al., 2005b; Cowie and Hedges, 1992; Buscail et al., 1995). Amino acid composition has been shown to be relatively insensitive to OM sources due to relative constancy of protein composition, but changes in mole percentages are valuable indicators of diagenetic alteration (Cowie and Hedges, 1992; Dauwe et al., 1999; Cowie and Hedges, 1994). Our results show that the % mole of GLU and PHE, generally concentrated in the cell cytoplasm (Hecky et al., 1973) decreased as % mole of GLY and THR, known to be concentrated in the cell walls, increased. These changes in amino acid composition occurring during the first steps of OM degradation may be more easily highlighted (Fig. 5) using the multivariate-based approach i.e. "the degradation index" proposed by Dauwe and Middelburg (1998). The DI showed that material from the Rhône river was rapidly degraded seaward (Fig. 4) with values ranging from +0.1 at station A to −0.4 at station F suggesting that OM delivered by the river was highly sensitive to chemical, physical and biological changes. The analysis of suspended particulate organic matter from the Rhône river indicates that riverine inputs were more enriched in THAA ($234.0\,\mathrm{mg\,gOC^{-1}}$, data not shown) than the superficial deposits off the Rhône river ($148.3\,\mathrm{mg\,gOC^{-1}}$, station A, data not shown). This suggests that riverine suspended material is subjected to intensive processes of degradation in the water column or once deposited at the benthic boundary layer (Mayer et al., 2008). Comparison with data available in the literature suggests that OM from the Rhône prodelta was indeed moderately degraded (Unger et al., 2005a; Unger et al., 2005b; Vandewiele et al., 2009; Lomstein et al., 2006) and this was confirmed by the

fairly low amounts of non proteic amino acids such as β-glutamic acid and β-alanine (less than 0.01 mg g^{-1} DW, Bourgeois, unpublished results, 2010). The general trend described by the DI values was further strengthened by another index of OM degradation, the PRI. Although chlorophyll pigments account for a small fraction of the OM pool, they are among the most labile organic compounds (Lee and Wakeham, 2000; Wakeham et al., 1997). The proportion of undegraded chlorophyll-*a* is thus a valuable indicator of OM freshness. The general covariance of terrestrial biomarkers (FAs, Chl-*b*) with the OM decomposition stage (PRI, DI) along the SW transect (Figure 8a) suggests the continuous degradation of the terrestrial OM during its transport from the river to the seafloor and once deposited. According to Buscail et al. (1990), 89% of OM produced by the source organisms is consumed or degraded before reaching the sediments. Hence, both terrestrial and marine sources of OM would be more degraded offshore, where the water is deeper. Since sediment discharge from the Rhône river plume decreases rapidly offshore, less river-borne particles settle on the seafloor in the adjacent shelf than at the river mouth (Durrieu de Madron et al., 2000). Moreover, river-borne sediments only remain transiently deposited in these highly disturbed environments since they are subjected to intensive reworking processes due to strong winds and currents (Marion et al., 2010). Accordingly, Beaudouin et al. (2005) estimated that two third of the OM initially deposited in the Rhône prodelta may be resuspended. The succession of resuspension and redeposition events increases the time of contact of the OM with oxygen and thus of aerobic degradation. Since labile components of the OM are preferentially degraded in the water column during the phase of resuspension (Raymond and Bauer, 2001), the OM becomes increasingly refractory.

From the prodelta to the shelf, δ^{13}C values of source-specific fatty acids (e.g., LCFAs and 18:2 from terrestrial source and 16:1 from marine phytoplankton) increased, similar to those of non-specific compounds. The isotopic variations of these individual compounds are likely driven by degradation because they are from exclusive sources (no mixing). It was observed (Chikaraishi and Naraoka, 2006) that in a plant-soil system, long-chain (>C24) *n*-alkanes, *n*-alkanoic acids and *n*-alkanols were gradually enriched

in δ^{13}C up to +12.9‰ (average of +4.3‰) from raw leaves to soils (with considerable degradation). Laboratory experiments (Sun et al., 2004) also confirmed that δ^{13}C of phytoplankton-derived fatty acids become enriched (a few ‰) when intensive degradation occurred. As discussed above, OM in this system was largely degraded with distance from the river mouth, along with isotopic enrichment of source-specific fatty acids. Thus, effects of diagenetic processes on molecular isotopic compositions could be important although the mechanism for isotopic alteration has not been well documented.

Another interesting point is the observation of similar variations of bacteria-specific fatty acids along the transect. Bacteria synthesize branched iso- and anteiso-15:0 fatty acids with distinct isotopic compositions, depending on sources of organic materials they used (Boschker et al., 1999) and on environmental conditions (Teece et al., 1999). In this system, OM from a terrestrial source is more important in the prodelta sites than in the shelf sites and they are effectively degraded. Relatively depleted δ^{13}C of these bacteria-specific fatty acids in the nearshore sites indicates a preferential utilization of terrestrial OM by bacteria while in shelf sites, marine-derived OM is a dominant source for microbial synthesis of these compounds. A similar pattern was observed in the Altamaha estuarine system (Dai and Sun, 2007).

4.3 Nutritional quality of the sedimentary organic matter and ecological implications

In contrast to quantity and lability, bioavailability (EHAA) and nutritional quality (PUFA contents) of the sedimentary OM were not correlated with the distance from the Rhône river mouth (Fig. 8a). The index of OM digestibility (EHAA/THAA) remained rather constant (28% on average) in the area under the influence of the Rhône river at the exception of station N. The boundary between the prodelta and the adjacent shelf (i.e., stations N and C) is, moreover, characterized by the lowest PUFA contents. The projection of the 7 stations on the first plan of the PCA shows a boomerang-like distribution

(Fig. 8b). OM from the inner part of the prodelta and from stations of the outer shelf appears to be more digestible and exhibits a higher nutritional quality. Between these two ends, the digestibility and nutritional quality of the sedimentary OM reach minimum values at the boundary between the prodelta area and the adjacent shelf (6 to 9 km from the river mouth). In this area, the land-derived inputs are low, as suggested by mean sediment accumulation estimates (Radakovitch et al., 1999), and are more degraded than in the inner part of the prodelta. The low nutritional quality of this matter is not yet fully compensated by the input of the marine-derived matter as it is probably the case for the shelf stations. Interestingly, stations of the distal prodelta are characterized by low abundance of large macrofaunal species and high densities of *Sternaspis scutata* (Labrune et al., 2011).

PUFAs of the omega 3 series, in particular DHA and EPA, are essential for the growth and the reproduction of animals (see citation in Goedkoop et al., 2000). These two essential nutrients account for nearly 5% of the sediment FAs at the mouth of the river. The DHA:EPA is included in the 0.3–0.5 range reported by Budge et al. (2000) as being adequate for the growth of bivalve juveniles. Thus, it appears that OM delivered by the Rhône river is a well nutritionally balanced source of OM. High EHAA-C:OC ratios indicative of the dominance of labile organic matter (Mayer et al., 2002) are found on the study area. Likewise, the fraction of bioavailable nitrogen (% EHAA-N:TN) in the superficial deposits from the prodelta was in the upper interval of the 2-10% range compiled by Mayer et al. (2008) for data from different coastal regions. Although this labile nitrogen accounts for a small fraction of the nitrogen delivered by the Rhône, it may be easily used by micro and macro biota (Mayer et al., 2008). Moreover, a relationship between the growth rate of benthic invertebrates and the level of essential amino acids has been revealed by Marsh et al. (1989) on *Capitella* sp. I fed on a variety of food types. Accordingly, the relative contributions (% mole) of the essential amino acids in the prodelta were higher than on the shelf (1.59 to 0.82 mg g^{-1}DW, respectively stations A and F, data not shown).

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Thus, although terrestrial inputs are generally considered as being more refractory than marine carbon, the Rhône river supplies large quantities of labile and nutritionally balanced particulate OM that may sustain the diversity, density and biomass of benthic communities. Several studies have shown the importance of terrestrial detritus for the benthic marine food web (Darnaude et al., 2004) and the dynamics of benthic macroinvertebrate communities (Salen-Picard et al., 2003; Rosenberg et al., 2003) on the coastal margin dominated by the Rhône river. Nevertheless, the Rhône prodelta is characterized by rapid and transient deposition of huge amounts of fine particles. Such active deposit centres are rather characterized by adapted (Hermand et al., 2008; Salen-Picard et al., 2003) and stress tolerant (Mojtahid et al., 2009; Goineau et al., 2011) taxa. The biochemical proxies of OM quality from the superficial sediment layer alone cannot explain the composition of benthic communities. Other environmental parameters including physical and chemical factors must also be taken into account in order to explain benthic fauna assemblages.

5 Conclusions

In the classical conception of the functioning of prodelta systems, one generally expects that nutrient riverine inputs stimulate primary production (Day et al., 1989; Mann, 1982) and that terrestrial matter driven seaward by the river is rather refractory to decomposition (Hedges et al., 1994). Regarding the Rhône system, these two paradigms were not observed in the present study. In comparison to other RiOMar systems, primary productivity is low in the shelf adjacent to the Rhône river ($< 1\,\mathrm{g\,C\,m^{-2}\,d^{-1}}$, Rabouille et al., 2008). Moreover, strong vertical salinity gradients between marine and river waters have been shown to limit exchanges between the nutrient-rich freshwater and the potential consumers in the underlying marine water (Naudin et al., 2001). Although the isotopic signatures of specific fatty acids in the shelf sediments unambiguously demonstrate the input of marine OM, the coupling between the pelagic and benthic compartment was limited at this period of the year. As a result, terrestrial

material is the main source of organic matter to the sediment in the Rhône prodelta as well as on the near adjacent shelf. Fatty acid biomarkers and compound-specific δ^{13}C signatures of most fatty acids clearly indicate that the Rhône inputs consist in a mixture of OM from different sources with a strong contribution from terrestrial plants
5 (essentially C3 plants, see data in Cathalot et al., in prep), and a smaller input from freshwater microalgae, mostly diatoms. Visual observations of the sediments confirm that detritus was composed of material at various degrees of decomposition, from decaying woody material to green leaves of duckweeds. This mixing of OM probably explains the intermediary value of Dauwe's degradation index (DI = +0.1 at the mouth
10 site). Apart from being moderately degraded, these inputs are also labile as shown by the high proportion of bioavailable nitrogen and the occurrence of polyunsaturated fatty acids. The correlation between bacteria-specific fatty acids and chlorophyll-*a*, as well as the isotopic signature of the bacterial markers provide convincing evidences that the benthic microbial compartment is able to respond to these inputs of labile terrestrial
15 material. Likewise, remineralization rates measured in situ are high close to the river mouth, but rapidly decrease offshore (Cathalot et al., 2010) following the general trend for decreasing quantity of sedimentary OM from the mouth to the shelf (see Sect. 4.2). Our multi-proxy study has been conducted in spring when phytoplankton blooms are expected and during a period of medium river discharge. It has revealed an offshore
20 gradient of OM decay reflecting the rapid deposition of the relatively labile terrestrial material in the prodelta, the low mixing with fresh OM deriving from marine sources and the efficient degradation of the OM once deposited. In this system where physical forcing controls sediment dynamics (deposition and erosion) (Marion et al., 2010), decomposition of the labile and more refractory fractions are probably enhanced by
25 reexposure to oxic conditions during successive episodes of resuspension (Pastor et al., submitted).

Since 81% of the suspended particulate matter annual flux from the Rhône river are delivered during episodic flood events (Pont, 1997), one might expect the labile fraction of OM delivered by rivers to exhibit seasonal patterns of fluctuations according to river

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regime and the sources of OM (soil-derived OM, vascular plant detritus, freshwater phytoplankton...). Perspectives of this study should take into account the impact of massive discharges of sediments and OM on the sedimentary compartment and the dynamics of system recovery. In particular, efforts should be made to describe how diagenetic processes affect OM delivered during different conditions of river fluxes (low discharge versus flood) once it is deposited.

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Table 1. Locations and sediment bulk characteristics of stations sampled during the RIOMAR-1 cruise (April 2007). Distance refers to the distance from the Rhône River mouth (km). d(0.5) corresponds to the median size distribution of sediment grain; OC for organic carbon; TN for total nitrogen; Chl-*a* for chlorophyll-*a*; Chl-*b* for chlorophyll-*b*; Phaeo-*a* for phaeopigment-*a*; PRI for pigment ratio index. Means ± standard deviation.

	Stations	Lat. (°N)	Long. (°E)	Depth (m)	Distance (km)	d(0.5) (µm)	OC (% DW)	TN (% DW)	C/N ratio	Chl-*a* (µg g^{-1}DW)	Chl-*b* (µg g^{-1}DW)	Phaeo-*a* (µg g^{-1}DW)	PRI (%)
Prodelta area	A	43°18′752	4°51′109	25	1.9	37.40 ± 3.05	1.83 ± 0.18	0.166 ± 0.004	12.90 ± 1.42	9.78 ± 0.82	1.38 ± 0.06	20.51 ± 1.49	32.26 ± 0.52
	B	43°18′175	4°50′135	56	3.0	14.83 ± 0.55	1.53 ± 0.08	0.147 ± 0.003	12.10 ± 0.45	4.99 ± 0.49	0.51 ± 0.06	21.76 ± 1.24	18.62 ± 0.88
	G	43°18′566	4°47′267	48	5.2	17.38 ± 1.04	1.42 ± 0.07	0.118 ± 0.005	14.07 ± 0.26	2.66 ± 0.12	0.15 ± 0.01	14.91 ± 0.17	15.14 ± 0.53
	K'	43°18′075	4°51′467	62	3.3	17.49 ± 1.45	1.79 ± 0.22	0.155 ± 0.016	13.46 ± 0.46	3.70 ± 0.46	0.37 ± 0.04	17.23 ± 0.97	17.63 ± 0.97
	L	43°18′281	4°52′795	62	4.0	13.56 ± 0.79	1.29 ± 0.23	0.131 ± 0.013	11.44 ± 1.61	3.54 ± 0.97	0.32 ± 0.08	18.41 ± 4.00	16.00 ± 0.70
Shelf area	C	43°16′405	4°46′632	76	8.6	11.38 ± 1.12	1.20 ± 0.05	0.109 ± 0.004	12.78 ± 0.63	1.64 ± 0.12	0.06 ± 0.05	12.19 ± 1.19	11.90 ± 0.48
	D	43°14′979	4°43′680	74	13.0	10.45 ± 0.22	1.02 ± 0.03	0.106 ± 0.001	11.23 ± 0.38	1.56 ± 0.29	0.00 ± 0.02	13.76 ± 2.83	10.21 ± 0.43
	E	43°13′302	4°41′974	75	17.0	9.43 ± 0.15	1.10 ± 0.07	0.103 ± 0.002	12.38 ± 1.02	1.51 ± 0.06	0.00 ± 0.02	13.41 ± 0.71	10.11 ± 0.13
	F	43°10′01	4°38′98	78	21.6	9.15 ± 0.94	1.06 ± 0.05	0.098 ± 0.002	12.61 ± 0.87	1.66 ± 0.13	0.00 ± 0.02	14.03 ± 1.14	10.60 ± 0.49
	H	43°15′967	4°49′203	85	7.5	9.99 ± 0.42	1.25 ± 0.07	0.098 ± 0.006	14.89 ± 0.63	1.27 ± 0.16	0.00 ± 0.01	11.58 ± 1.56	9.89 ± 0.30
	I	43°16′050	4°52′943	89	7.7	10.70 ± 0.52	1.14 ± 0.09	0.100 ± 0.001	13.29 ± 1.10	1.15 ± 0.02	0.00 ± 0.01	11.32 ± 0.75	9.26 ± 0.66
	J	43°16′11	4°58′11	86	12.1	11.59 ± 0.31	1.11 ± 0.10	0.097 ± 0.007	13.27 ± 1.08	0.81 ± 0.09	0.00 ± 0.01	9.41 ± 0.58	7.90 ± 0.48
	N	43°17′688	4°47′963	67	5.5	14.01 ± 2.42	1.19 ± 0.21	0.103 ± 0.002	13.46 ± 2.11	2.57 ± 0.60	0.18 ± 0.13	14.31 ± 0.18	15.13 ± 2.95
	O	43°17′006	4°50′170	79	5.2	11.06 ± 0.76	1.28 ± 0.10	0.095 ± 0.002	15.63 ± 1.40	1.82 ± 0.03	0.01 ± 0.02	13.96 ± 0.89	11.54 ± 0.60
	M	43°10′042	4°43′990	91	20.3	9.89 ± 1.53	0.88 ± 0.05	0.091 ± 0.004	11.31 ± 0.80	1.72 ± 0.31	0.00 ± 0.02	16.05 ± 1.17	9.64 ± 1.24
	R2	43°14′465	4°52′921	98	10.3	9.55 ± 0.98	0.84 ± 0.18	0.085 ± 0.004	11.58 ± 2.28	0.71 ± 0.13	0.00 ± 0.01	9.76 ± 1.36	6.78 ± 0.29

Table 2. THAA and EHAA concentrations, contribution of total and enzymatically amino acid to total organic carbon (THAA-C% and EHAA-C%) and total nitrogen (THAA-N% EHAA-N%), EHAA/THAA ratio, amino acid composition as mole% (ASP = aspartic acid, GLU = glutamic acid, SER = serine, HIS = histidine, GLY = glycine, THR = threonine, ARG = arginine, TAU = taurine, ALA = alanine, TYR = tyrosine, VAL = valine, PHE = phenylalanine, ILEU = isoleucine, LEU = leucine, LYS = lysine) and the Degradation Index (DI) in the surface sediments of the longitudinal transect (A, B, N, C, D, E and F) and the marine reference (J). Means ± standard deviation.

Station	A	B	N	C	D	E	F	J
THAA (mg g^{-1} DW)	3.77 ± 0.30	3.14 ± 0.03	2.82 ± 0.35	2.38 ± 0.07	2.54 ± 0.09	2.34 ± 0.01	2.23 ± 0.06	2.25 ± 0.07
THAA-C%	8.94 ± 0.49	9.66 ± 1.82	10.15 ± 0.51	8.49 ± 0.05	10.70 ± 0.24	8.92 ± 0.62	8.82 ± 0.49	8.60 ± 0.74
THAA-N%	34.46 ± 3.63	32.17 ± 1.07	41.36 ± 4.37	32.92 ± 1.22	36.40 ± 1.64	34.81 ± 0.81	34.95 ± 1.83	35.32 ± 1.45
EHAA (mg g^{-1} DW)	1.17 ± 0.19	0.86 ± 0.05	0.68 ± 0.02	0.69 ± 0.03	0.72 ± 0.04	0.65 ± 0.06	0.64 ± 0.03	0.53 ± 0.06
EHAA-C%	2.56 ± 0.24	2.71 ± 0.51	2.53 ± 0.37	2.50 ± 0.21	3.04 ± 0.12	2.54 ± 0.12	2.60 ± 0.11	2.09 ± 0.37
EHAA-N%	9.38 ± 0.59	8.50 ± 0.32	9.54 ± 0.12	9.10 ± 0.43	9.76 ± 0.42	9.07 ± 0.98	9.46 ± 0.67	8.00 ± 0.84
EHAA/THAA	28.21 ± 1.07	27.49 ± 1.76	24.52 ± 2.67	28.91 ± 1.99	28.17 ± 1.85	27.71 ± 2.78	28.65 ± 0.87	23.74 ± 2.33
ASP	16.83 ± 0.04	18.25 ± 0.10	19.34 ± 0.39	20.96 ± 0.65	21.56 ± 0.17	21.64 ± 0.07	22.31 ± 0.70	21.12 ± 0.40
GLU	12.03 ± 0.56	11.76 ± 0.47	11.34 ± 0.19	11.47 ± 0.23	11.57 ± 0.10	11.66 ± 0.14	11.38 ± 0.26	11.06 ± 0.17
SER	8.55 ± 0.03	8.83 ± 0.16	8.77 ± 0.09	8.96 ± 0.17	8.65 ± 0.27	8.52 ± 0.08	8.59 ± 0.33	7.95 ± 0.25
HIS	1.23 ± 0.79	1.23 ± 0.65	1.80 ± 0.39	0.64 ± 0.74	0.99 ± 0.08	2.09 ± 0.40	1.47 ± 1.23	1.26 ± 0.46
GLY	15.03 ± 0.51	15.59 ± 0.54	15.68 ± 0.38	15.91 ± 0.12	15.25 ± 0.26	15.58 ± 0.16	15.35 ± 0.37	15.53 ± 0.22
THR	7.06 ± 0.06	6.96 ± 0.05	6.91 ± 0.05	6.55 ± 0.32	7.13 ± 0.07	7.36 ± 0.30	7.15 ± 0.37	7.30 ± 0.05
ARG	2.80 ± 0.03	2.54 ± 0.14	2.47 ± 0.16	2.54 ± 0.17	2.61 ± 0.09	2.75 ± 0.09	3.00 ± 0.26	3.05 ± 0.10
TAU	0.09 ± 0.00	0.14 ± 0.07	0.16 ± 0.03	0.19 ± 0.02	0.20 ± 0.08	0.23 ± 0.06	0.20 ± 0.08	0.22 ± 0.01
ALA	10.97 ± 0.10	10.95 ± 0.19	10.80 ± 0.15	10.41 ± 0.15	10.58 ± 0.17	10.43 ± 0.21	10.06 ± 0.13	9.77 ± 0.12
TYR	1.70 ± 0.13	1.06 ± 0.09	2.49 ± 0.52	2.30 ± 0.45	2.62 ± 0.09	1.31 ± 0.22	1.58 ± 0.16	1.45 ± 0.35
VAL	6.08 ± 0.08	5.96 ± 0.11	5.22 ± 0.20	5.33 ± 0.14	5.13 ± 0.16	4.70 ± 0.19	4.98 ± 0.08	6.02 ± 0.03
PHE	3.57 ± 0.07	3.54 ± 0.04	3.21 ± 0.12	3.06 ± 0.01	3.11 ± 0.10	2.96 ± 0.09	2.83 ± 0.07	3.09 ± 0.06
ILEU	3.42 ± 0.06	3.13 ± 0.06	2.68 ± 0.14	2.80 ± 0.09	2.55 ± 0.08	2.37 ± 0.05	2.63 ± 0.11	3.18 ± 0.06
LEU	6.89 ± 0.07	6.25 ± 0.16	5.61 ± 0.29	5.49 ± 0.10	5.34 ± 0.09	5.23 ± 0.15	5.24 ± 0.08	5.21 ± 0.06
LYS	3.74 ± 0.17	3.81 ± 0.06	3.54 ± 0.28	3.38 ± 0.04	2.71 ± 0.16	3.17 ± 0.13	3.23 ± 0.04	3.80 ± 0.01
DI	0.10 ± 0.16	−0.17 ± 0.14	−0.04 ± 0.07	−0.33 ± 0.18	−0.33 ± 0.04	−0.38 ± 0.06	−0.44 ± 0.24	−0.39 ± 0.14

Monomeric composition of THAA (mole %)

Table 3. Individual fatty acid composition (% area) and total FA concentrations in the surface sediments along the southwestern longitudinal transect (A, B, N, C, D, E and F) and at the marine reference (J). Means ± standard deviation. nd: non detected.

|	A	B	N	C	D	E	F	J
Saturated FA								
10:0	Trace	0.31 ± 0.13	0.41 ± 0.19	0.65 ± 0.03	0.47 ± 0.11	0.50 ± 0.13	0.28 ± 0.03	0.35 ± 0.04
12:0	1.50 ± 0.25	1.79 ± 0.02	1.78 ± 0.21	1.59 ± 0.06	1.59 ± 0.02	1.44 ± 0.03	1.50 ± 0.07	1.48 ± 0.09
14:0	5.12 ± 0.10	5.37 ± 0.00	6.11 ± 0.23	6.89 ± 0.04	7.52 ± 0.19	7.27 ± 0.06	7.86 ± 0.43	6.74 ± 0.24
16:0	21.69 ± 0.26	20.36 ± 0.60	20.76 ± 0.07	20.75 ± 0.06	21.33 ± 1.01	21.27 ± 0.05	21.62 ± 0.49	22.77 ± 0.94
18:0	6.72 ± 0.35	6.51 ± 0.01	5.86 ± 0.22	5.76 ± 0.10	6.04 ± 0.40	5.74 ± 0.16	5.55 ± 0.00	6.20 ± 0.46
20:0	3.66 ± 0.25	3.54 ± 0.08	3.23 ± 0.42	2.72 ± 0.02	2.39 ± 0.05	2.11 ± 0.02	1.90 ± 0.03	2.39 ± 0.14
21:0	0.67 ± 0.04	0.87 ± 0.14	0.78 ± 0.10	0.80 ± 0.08	1.13 ± 0.12	1.12 ± 0.23	1.00 ± 0.08	1.02 ± 0.10
22:0	6.10 ± 0.29	6.22 ± 0.13	5.21 ± 0.46	4.28 ± 0.04	3.56 ± 0.27	3.23 ± 0.10	2.69 ± 0.11	3.06 ± 0.21
23:0	1.10 ± 0.23	1.06 ± 0.12	1.17 ± 0.12	0.83 ± 0.06	nd	nd	nd	nd
24:0	4.63 ± 0.66	5.72 ± 0.05	5.36 ± 0.11	4.54 ± 0.28	3.91 ± 0.23	3.49 ± 0.09	2.74 ± 0.32	3.32 ± 0.32
26:0	1.95 ± 0.31	2.84 ± 0.19	2.93 ± 0.12	2.34 ± 0.10	1.86 ± 0.10	1.82 ± 0.10	1.51 ± 0.22	2.11 ± 0.43
28:0	1.70 ± 0.16	1.90 ± 0.17	1.68 ± 0.20	nd	nd	nd	nd	nd
% SAFA	54.89 ± 1.73	56.50 ± 0.13	55.27 ± 1.18	51.14 ± 0.48	49.81 ± 1.55	48.00 ± 0.28	46.65 ± 0.05	49.4 ± 2.54
Monounsaturated FA								
16:1ω7	9.35 ± 0.12	9.82 ± 0.30	10.47 ± 0.52	10.69 ± 0.05	11.32 ± 0.36	11.96 ± 0.36	11.66 ± 0.15	11.85 ± 0.34
18:1ω9 cis	6.10 ± 0.57	4.94 ± 0.08	4.60 ± 0.20	4.81 ± 0.50	4.56 ± 0.55	4.44 ± 0.03	5.79 ± 1.52	4.36 ± 0.09
20:1ω9	0.29 ± 0.03	0.19 ± 0.09	0.27 ± 0.04	0.24 ± 0.08	nd	nd	nd	nd
% MUFA	15.74 ± 0.46	14.95 ± 0.31	15.34 ± 0.49	15.75 ± 0.38	15.88 ± 0.76	16.40 ± 0.39	17.45 ± 1.37	16.21 ± 0.41
Polyunsaturated FA								
16:3ω4	0.64 ± 0.06	0.71 ± 0.04	0.72 ± 0.06	0.67 ± 0.07	0.61 ± 0.16	0.62 ± 0.03	0.56 ± 0.06	0.56 ± 0.05
18:2ω6 cis	2.91 ± 0.04	2.18 ± 0.02	1.89 ± 0.07	1.72 ± 0.00	1.62 ± 0.16	1.46 ± 0.15	1.43 ± 0.14	1.35 ± 0.08
18:3ω3	0.89 ± 0.03	0.70 ± 0.02	0.57 ± 0.11	0.36 ± 0.02	0.38 ± 0.01	0.31 ± 0.06	0.26 ± 0.00	nd
18:4ω3	0.41 ± 0.07	0.34 ± 0.01	0.43 ± 0.05	0.42 ± 0.02	0.51 ± 0.11	0.51 ± 0.03	0.64 ± 0.01	nd
20:4ω6	1.05 ± 0.10	0.96 ± 0.13	1.11 ± 0.21	1.79 ± 0.38	1.78 ± 0.15	2.48 ± 0.40	2.78 ± 0.39	2.45 ± 0.57
20:5ω3	2.73 ± 1.11	1.79 ± 0.04	1.62 ± 0.02	2.05 ± 0.20	2.25 ± 0.39	2.83 ± 0.18	3.05 ± 0.28	1.95 ± 0.57
22:6ω3	1.84 ± 1.02	1.46 ± 0.09	1.22 ± 0.03	1.79 ± 0.06	1.39 ± 0.21	1.47 ± 0.10	1.46 ± 0.06	1.33 ± 0.23
%PUFA	10.47 ± 2.01	8.15 ± 0.03	7.56 ± 0.39	8.80 ± 5.10	8.54 ± 0.86	9.68 ± 0.79	10.18 ± 0.53	7.64 ± 1.35
Bacterial FA								
15:0	2.68 ± 0.21	3.18 ± 0.04	3.54 ± 0.06	3.46 ± 0.18	3.77 ± 0.24	3.59 ± 0.09	3.30 ± 0.28	3.26 ± 0.24
17:0	1.19 ± 0.02	1.37 ± 0.01	1.42 ± 0.06	1.44 ± 0.04	1.47 ± 0.13	1.51 ± 0.05	1.49 ± 0.02	1.64 ± 0.12
i-15:0	3.72 ± 0.33	3.78 ± 0.06	4.20 ± 0.17	4.58 ± 0.19	5.16 ± 0.18	5.29 ± 0.12	5.06 ± 0.19	5.46 ± 0.02
ai-15:0	4.37 ± 0.63	5.16 ± 0.17	5.93 ± 0.46	6.83 ± 0.29	7.19 ± 0.71	7.20 ± 0.22	6.57 ± 0.26	7.78 ± 0.33
ai-17:0	0.64 ± 0.01	0.75 ± 0.06	0.83 ± 0.16	1.05 ± 0.11	1.51 ± 0.22	Trace	1.23 ± 0.11	nd
18:1ω7	6.28 ± 0.24	6.15 ± 0.40	5.90 ± 0.46	6.95 ± 0.41	7.17 ± 0.12	7.83 ± 0.40	8.07 ± 0.08	8.63 ± 0.65
%BAFA	18.90 ± 1.14	20.40 ± 0.20	21.83 ± 1.18	24.32 ± 0.24	25.77 ± 1.49	25.42 ± 0.59	25.72 ± 0.79	26.8 ± 0.77
[FA] in µg g DW^{-1}	160.03 ± 13.59	95.64 ± 2.41	57.73 ± 5.43	54.37 ± 2.99	45.53 ± 6.30	41.10 ± 3.31	40.83 ± 0.48	27.99 ± 1.20
[FA] in mg g C org^{-1}	8.74 ± 0.48	6.45 ± 0.06	4.94 ± 0.93	4.65 ± 0.38	4.48 ± 0.66	3.75 ± 0.21	3.85 ± 0.31	2.54 ± 0.23
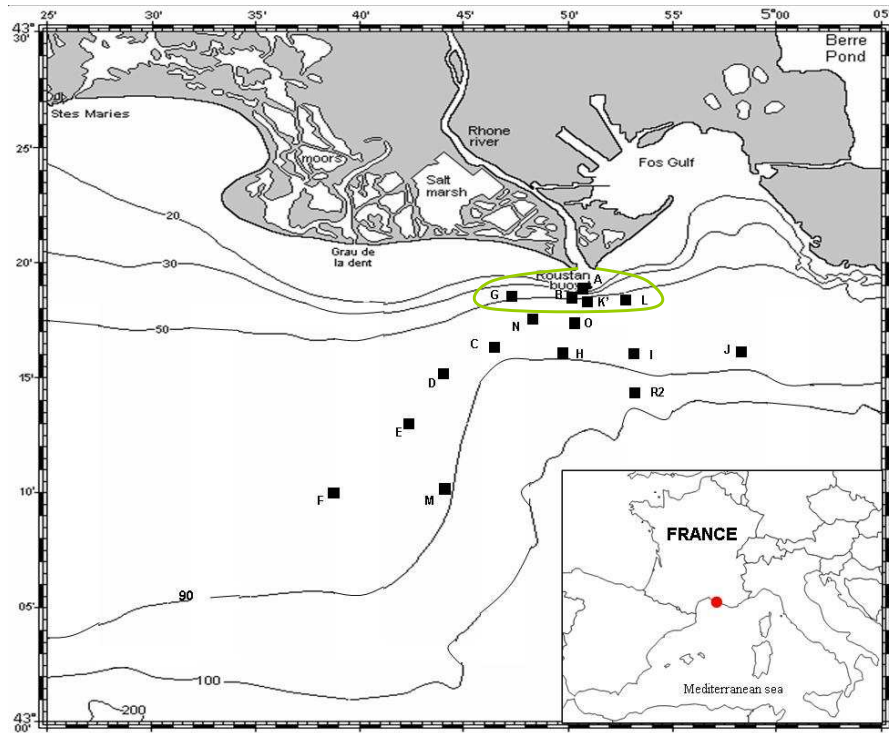
Fig. 1. Map of the Rhône delta including the location of sampling stations during the RIOMAR-1 cruise (April 2007).The green line defines the prodelta area.
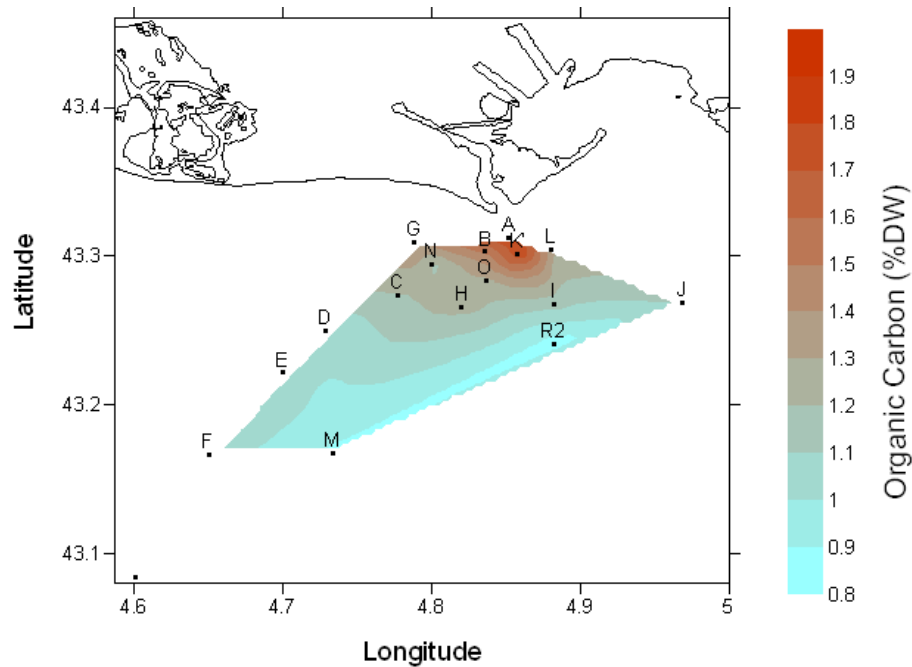
Fig. 2. Organic carbon (% DW) in the surface sediments (16 stations, 48 cores).
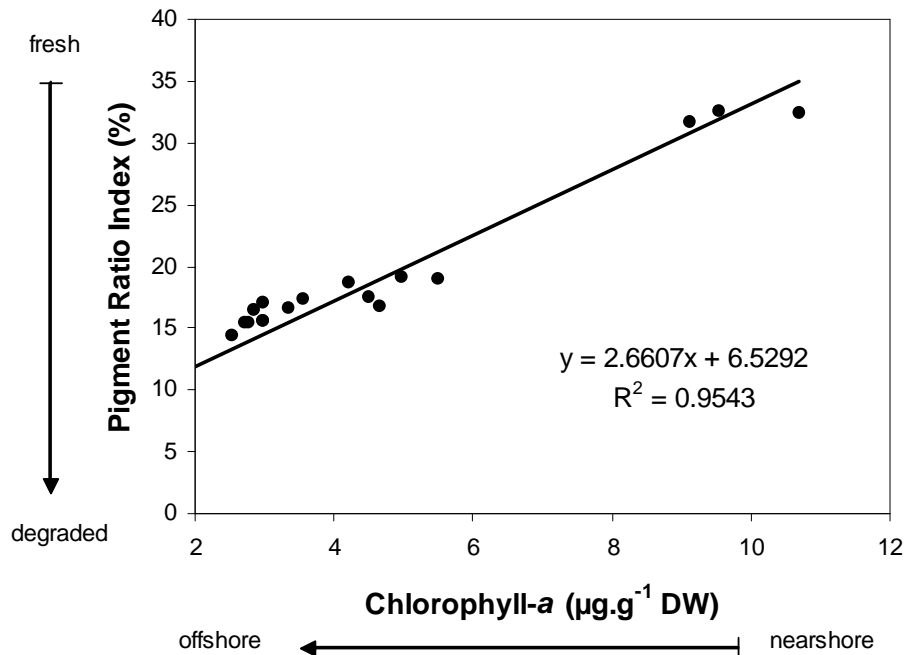
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Fig. 3. Correlation between Pigment Ratio Index (PRI %) values and chlorophyll-*a* concentration in surface sediments off the Rhône river (16 stations, 48 cores).
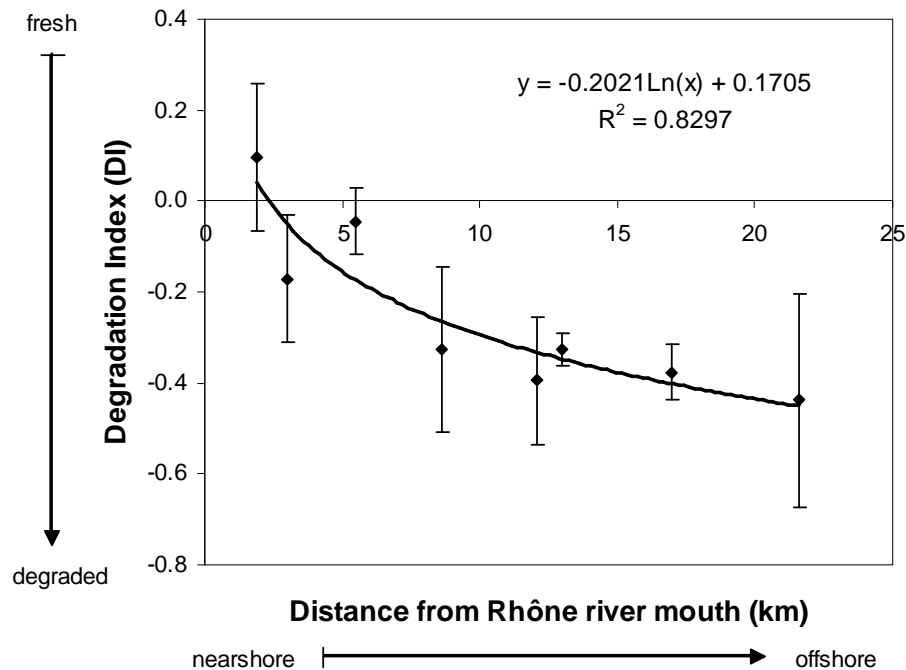
Fig. 4. Correlation between Degradation Index (DI) values and distance from the river mouth in the surface sediments (8 stations, 24 cores).
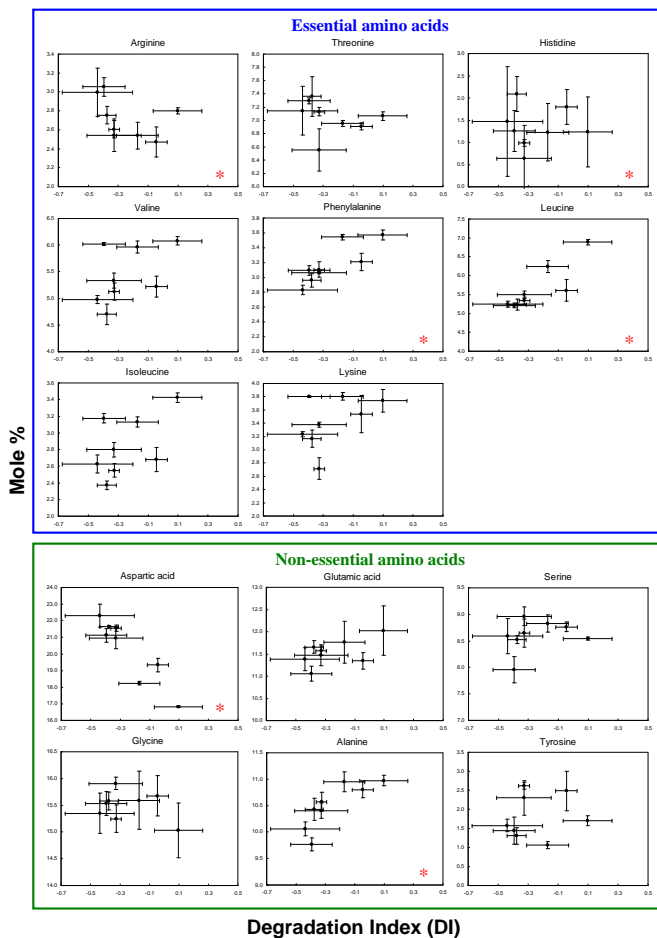
Fig. 5. Correlation between Degradation index (DI) values and amino acid composition (mole%) (8 stations, 24 cores). *: significant correlations ($p < 0.05$).
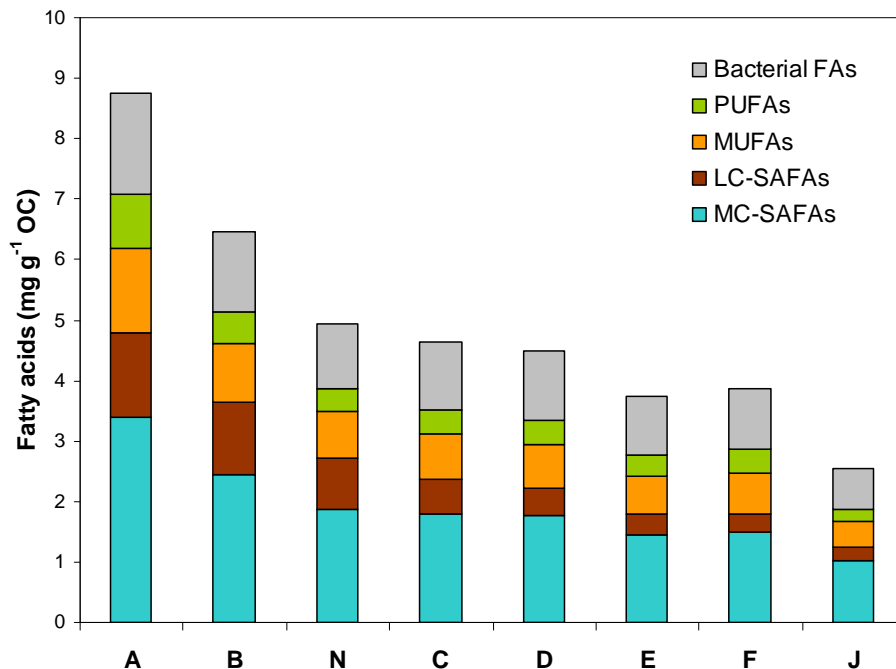
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Fig. 6. Contribution of bacterial, polyunsaturated, monounsaturated, long chain saturated and mid chain saturated fatty acids in the sedimentary organic matter (mg g^{-1} OC). Fatty acids were grouped as follows: Bacterial FAs = odd numbered saturated FAs; iso and anteiso FAs and vaccenic acid; PUFAs = C16 to C22 polyunsaturated FAs; MUFAs = 16:1ω7, 18:1ω9, 20:1ω9; MC-SAFAs $\leq$ C20 even numbered saturated FAs; LC-SAFAs > C20 even numbered saturated FAs.

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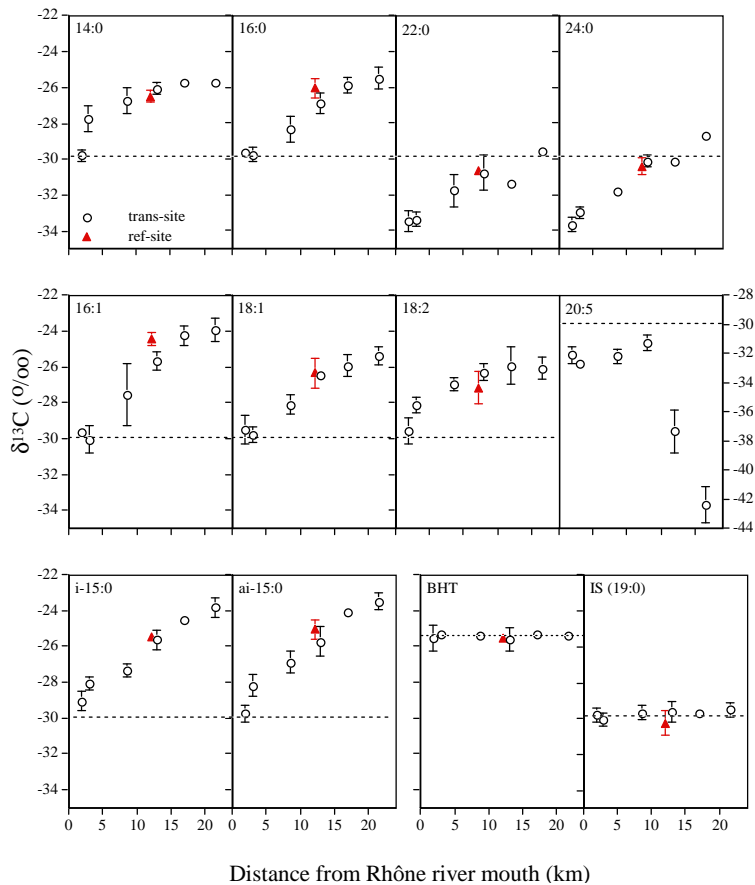
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Fig. 7. Variations of $\delta^{13}C$ of individual fatty acids in sediment samples collected along the prodelta-shelf transect.

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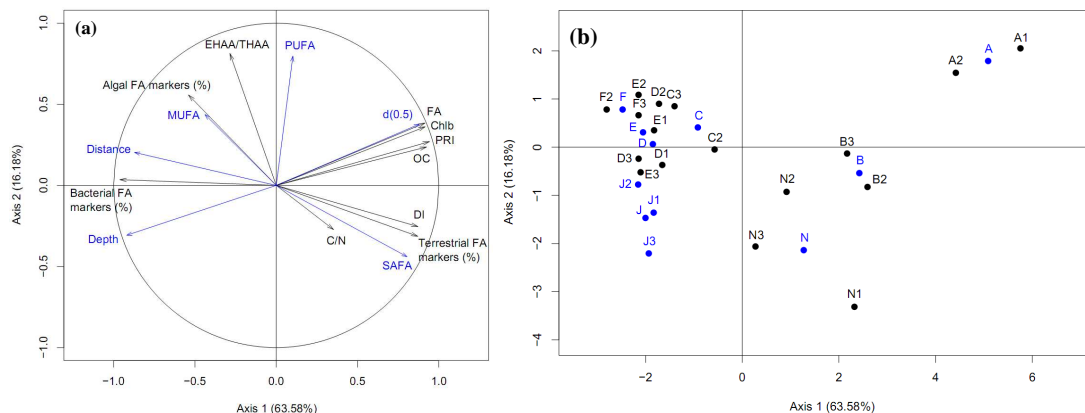Interactive Discussion

Fig. 8. Plot of loadings **(a)** and scores **(b)** for PCA of bulk and molecular-level characteristics of the OM from 7 stations located along a southwestward transect off the Rhône river and a marine reference (station J). Analysis was based on total fatty acid content (FA), terrestrial FA markers, bacterial FA markers, algal FA markers, pigment ratio index (PRI), organic carbon (OC), C/N ratio, chlorophyll-*b* (Chl-*b*), degradation index (DI) and EHAA/THAA ratio (in black). Other scores (average for each station and the marine reference) and loadings (distance, depth, *d*(0.5), %SAFA, %MUFA, %PUFA) were introduced as supplementary parameters (in blue).