The fate of river organic carbon in coastal areas: A study in the Rhône River delta using multiple isotopic (δ\(^{13}\)C, Δ\(^{14}\)C) and organic tracers

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Abstract:

A significant fraction of the global carbon flux to the ocean occurs in River-dominated Ocean Margins (RiOMar) although large uncertainties remain in the cycle of organic matter (OM) in these systems. In particular, the OM sources and residence time have not been well clarified. Surface (0–1 cm) and sub-surface (3–4 cm) sediments and water column particles (bottom and intermediate depth) from the Rhône River delta system were collected in June 2005 and in April 2007 for a multi-proxy study. Lignin phenols, black carbon (BC), proto-kerogen/BC mixture, polycyclic aromatic hydrocarbons (PAHs), carbon stable isotope (δ\(^{13}\)C\(_{OC}\)), and radiocarbon measurements (Δ\(^{14}\)C\(_{OC}\)) were carried out to characterize the source of sedimentary organic material and to address degradation and transport processes. The bulk OM in the prodelta sediment appears to have a predominantly modern terrigenous origin with a significant contribution of modern vascular C\(_3\) plant detritus (Δ\(^{14}\)C\(_{OC}\) = 27.9‰, δ\(^{13}\)C\(_{OC}\) = −27.4‰). In contrast, the adjacent continental shelf, below the river plume, seems to be dominated by aged OM (Δ\(^{14}\)C\(_{OC}\) = −400‰, δ\(^{13}\)C\(_{OC}\) = −24.2‰), and shows no evidence of dilution and/or replacement by freshly produced marine carbon. Our data suggest an important contribution of black carbon (50% of OC) in the continental shelf sediments. Selective degradation processes occur along the main dispersal sediment system, promoting the loss of a modern terrestrial OM but also proto-kerogen-like OM. In addition, we hypothesize that during the transport across the shelf, a long term resuspension/deposition loop induces efficient long term degradation processes able to rework such refractory-like material until the OC is protected by the mineral matrix of particles.
River-dominated Ocean Margins (RiOMar) play a critically-important role in the biogeochemical cycles of carbon, as they receive large amounts of riverine inputs of carbon and nutrients, sustaining large biological activity (Bianchi and Allison, 2009; Dagg et al., 2004; McKee et al., 2004). High rates of organic carbon (OC) burial and mineralization represent substantial sink and source terms in the carbon budget for the coastal ocean, providing insights on the underlying processes (Borges, 2005; Hedges, 1992). For instance, OC burial is the second largest atmospheric CO$_2$ sink and plays a major role in long-term climate regulation (Berner, 1990). Terrestrial OC (OC$_{\text{terr}}$) originating from both continental erosion and river autochthonous production can be selectively degraded, deposited and buried in continental margins. The fraction of organic matter that escape either mineralization or burial in the shelf is then exported to the open ocean. OC burial efficiency in RiOMar areas is directly linked to the nature of terrestrial OC delivered to the coastal ocean because different origins and residence time ensure a wide range of reactivity (Hartnett et al., 1998; Hedges and Keil, 1995). Studying the structure, distributions and quantities of terrestrial organic matter, as well as processes governing its fate in the coastal ocean is a key for assessing global biogeochemical cycles (Galy et al., 2007; Raymond and Bauer, 2001a).

The Rhône River is the largest river input to the Mediterranean, both in term of water and particulate discharge rates (Ludwig et al., 2003), since the Nile River has been dammed. The Rhône River constitutes 80% of the total riverine inputs into the Gulf of Lions, the Northwestern Mediterranean continental margin, and provides $1.6 \pm 0.5 \times 10^{10}$ mol C y$^{-1}$ to the Mediterranean Sea (Sempéré et al., 2000). In this context, the export and the fate of this terrestrial material from the Rhône River have been the subject of many intensive physical, biogeochemical and oceanographic studies (Estournel et al., 2001; Radakovitch et al., 1999b;
Roussiez et al., 2006; Tesi et al., 2007a; Ulses et al., 2008). These studies used radionuclide-based tracers that provided new insights into particle transfer processes although questions about the fate of river-borne organic matter still need to be addressed. Until recently, studies of particulate organic carbon cycling were mainly focused on off-shelf and canyon transfers rather than continental shelf distribution and margin processes (Tesi et al., 2010b). Thus, although the organic composition of the exported material was fairly well constrained in these studies, little insight is known about the chemical changes along the sediment transport in the shelf. Based on the results from Tesi et al. (2007), Lansard et al. (2009) made a first quantification of the terrigeneous OC fractions of the Rhône River particles using stable carbon isotopes ($\delta^{13}C$), C/N ratios and lignin-derived biomarkers. Their estimation relies on a two end-member mixing model between terrestrial and marine OC, and it is constrained by a narrow range of $\delta^{13}C$ values. However, an approach like this can yield only a few information on the reactivity of the sedimentary OC.

To better understand the OM cycles in RiOMar systems and provide new insight about residence time and reactivity of sedimentary OC, additional tracers are required to estimate the contribution of terrestrial organic matter to continental margins and its fate. Radiocarbon values ($\Delta^{14}C$), measured by accelerator mass spectrometry, have proven to be a powerful tool to investigate the dynamics of OC in river systems and marine environments (Druffel et al., 2005; Hedges et al., 1986a; Megens et al., 2001; Raymond and Bauer, 2001b). Radiocarbon can provide useful information on the sources and residence times of particulate organic matter (POM). Organic matter in river suspended particles presents a wide range of $\Delta^{14}C$ signatures from -980 to +75‰ (Blair et al., 2003; Druffel and Williams, 1991; Galy et al., 2007; Hedges et al., 1986b; Nagao et al., 2005; Raymond and Bauer, 2001a) whereas plankton and marine particulate organic carbon (POC) usually display enriched values from -45 to +110‰ (Wang et al., 1998; Williams et al., 1992). Nevertheless, each river system
exhibits a contrasting range of $\Delta^{14}C$ values of organic matter, reflecting both sediment transport processes within the watershed and local autochthonous production (Goni et al., 2006). This varying range of $\Delta^{14}C$ values has been applied to distinguish sources of the deposited material (Blair et al., 2003; Goni et al., 1997). Furthermore, the combined use of $\Delta^{14}C$ and $\delta^{13}C$ adds a second dimension to assess the carbon cycling in river-dominated margins, especially to determine the fate and reactivity of particulate OC (Drenzek et al., 2007).

In this study, we used a multi-proxy approach on both sediments and suspended particles, combining $\Delta^{14}C$ and $\delta^{13}C$ of bulk OC, lignin-derived biomarkers and their compound-specific $\delta^{13}C$, and polycyclic aromatic hydrocarbons (PAHs), black carbon (BC) and proto-kerogen/BC mixture, to elucidate the fate of terrestrial particulate organic matter released from the Rhône River to the Gulf of Lions continental margin. The chemical and isotopic analyses for these samples were modelled based on a four end-members model. The relative contributions of organic matter from various sources were quantitatively examined and the importance of pre-aged OC from continental shelf particles was demonstrated.

2. BACKGROUND

The Rhône River is the major source of freshwater, nutrients and organic carbon to the Gulf of Lions, a large continental shelf located in the NW Mediterranean Sea (De Madron et al., 2000; Pont et al., 2002; Sempéré et al., 2000). The Rhône River flows from the mountain range of the Alps to the Mediterranean Sea, where a delta is formed at its mouth. The catchment area of the Rhône River displays a strong climatic and geological heterogeneity since it drains oceanic, mountainous and Mediterranean weather systems over an area of 97800 km$^2$. As an example of the catchment heterogeneity, part of the Durance River’s basin (14 000 km$^2$) is very rich in clay, devoid of vegetation and subjected to intense erosion.
when an important part of the Rhône River watershed consists of carbonate rocks (Pont et al., 2002). A consequence of such heterogeneity is a great variability in the hydrological regime of the Rhône River in terms of precipitation and solid transport capacity, with large differences between low (<700 m$^3$ s$^{-1}$) and high (>3000 m$^3$ s$^{-1}$) water discharge rates (Pont et al., 2002). Most of the solid discharge is transported during Mediterranean floods but the mineralogical composition of the suspended matter reaching the river mouth is highly related to the flood origin (Ollivier et al., 2010; Pont et al., 2002). Similarly, the organic material exported at the Rhône River mouth derives from various allochthonous sources (vascular plants, bacteria and soils) and varies with flood events (Panagiotopoulos et al., 2012).

Large amount of terrestrial material is deposited in the sediments off the Rhône River mouth between 0 and 20 m water depth (Maillet et al., 2006). In fact, most of the material delivered by the Rhône River accumulates in the prograding prodelta (Fig.1) which extends from the shoreline to 60 m depth with a significant slope (Maillet et al., 2006; Wright and Friedrichs, 2006). Net sedimentation rates in the prodelta range from 20 to 50 cm y$^{-1}$ at shallow stations (20 m) near the river mouth (Charmasson et al., 1998; Radakovitch et al., 1999a) down to ≈1 cm y$^{-1}$ at 60 m water depth where the prodelta ends. The remainder of the Rhône River sediment delivered to the sea is transported and deposited onto the continental shelf at a mean rate < 0.3 cm yr$^{-1}$ (Miralles et al., 2005; Radakovitch et al., 1999a; Zuo et al., 1997).

The Northwestern Mediterranean current flowing southwestward along the slope imposes a general cyclonic circulation on the continental shelf of the Gulf of Lions (Fig. 1; Millot, 1990). Episodic southeasterly storms may cause the resuspension of Rhône River prodeltaic deposits that are then transported to the southwestern end of the shelf (Roussiez et al., 2005; Ulses et al., 2008). The Gulf of Lions is oligotrophic and the water column is seasonally
stratified. Intense vertical mixing events occur in winter and early spring due to strong regional winds and induce major nutrient export, through cascading and dense water formation (de Madron et al., 2003; Millot, 1990).

This study investigates the transition zone between the Rhône River prodelta and the Gulf of Lions continental shelf. Most of the changes in sedimentation rates happen within this zone subjected to resuspension (Fig. 1). We expect therefore significant changes in organic matter composition and new insights into the sediment transport system off the Rhône River mouth.

3. MATERIAL AND METHODS

3.1. Sampling

3.1.1. River sampling

Suspended particulate matter (SPM) from the Rhône River were sampled monthly from 2006-2009 at the Arles monitoring station (Maillet et al., 2006). The automatic sampler (CALYPSO 2000S) is located 50 cm from the surface and 3 m from the bank, and the sampling is assumed to be representative of the entire water column due to the homogeneous SPM distribution along the cross and bottom-up section at moderate flow conditions (Pont et al., 2002). Four 250-ml water samples were pumped per day into the same bottle, providing an integrated daily sample. For more details about the design and functioning of the monitoring station, see Pont et al (2002). River samples were collected every month over the course of the three years and covered a broad range of riverine discharge rates (Fig.1) including flood events. Water sub-samples were filtered in the laboratory on Whatman GF/F precombusted quartz filters in an all-glass filter holder and then dried for 24 h at 65°C and weighted to evaluate the total suspended particulate matter before further analysis (organic carbon and D\textsuperscript{14}C\textsubscript{POC}). Further analysis (organic carbon, δ\textsuperscript{13}C\textsubscript{POC} and Δ\textsuperscript{14}C\textsubscript{POC}) were performed on freeze-dried
particulate material concentrated after a decantation step (24 h in a 5°C dark room) of the remaining water sample, following by a centrifugation (2000 rpm, 5°C, 5 min).

3.1.2. Sediment and SPM Sampling

Two scientific cruises (Minercot 2 and RiOMar 1) were conducted off the Rhône River mouth in June 2005 and April 2007, respectively. The network of sampling stations (Fig. 1) is described by Lansard et al. (2009) and the locations and water depths are displayed in Tables 1 and 2. The sampling strategy focused on the Rhône River prodelta, with a grid of closely spaced stations (A, B, K). The connection of the Rhône River prodelta with the continental shelf was studied through South-West, South and South-East onshore–offshore transects. The 2 cruises took place during period of average discharge rates of the Rhône River (Cathalot et al., 2010; Lansard et al., 2009).

Sediment samples were collected with a multicorer MUC 8/100 (Oktopus GmbH) deployed from the R.V. Téthys II. Eight cores (internal diameter: 9.5 cm) were simultaneously collected and sliced at 1 cm depth intervals. The subsampled sediments were then stored at -20°C until analysis. Sediment samples were freeze-dried and then ground using an agate mortar.

In addition, intermediate and bottom waters were collected using Niskin bottles in April 2007 (Table 1). Water samples were filtered on Whatman GF/F precombusted quartz filters in an all-glass filter holder. Filters were washed with distilled water to eliminate the remaining salt and immediately frozen on board at -20°C. They were then dried at the laboratory for 24 h at 65°C and weighted to evaluate the total suspended particulate matter.

3.2. Organic Carbon Content
Organic Carbon (OC) content was measured in surface sediment (0–1 cm) after inorganic carbon removal by dissolution with a 1% HCl solution. The OC content for the sediments collected in June 2005 were determined at LSCE, using an automatic Fisons Instrument NA 1500 Element Analyzer, whereas OC measurements for the sediments sampled in April 2007 were performed at CEFREM, by an automatic CHN-analyser LECO® 2000. Precisions for OC by both types of analyses were 2% (relative standard deviation).

Measurements of POC in bottom and intermediate waters (April 2007) were performed at LSCE using a different decarbonation treatment: filters were acidified with H$_3$PO$_4$ (1%) during 24 hours at room temperature (Druffel et al., 1992). The remaining acid was removed by percolating through the filters, which were then dried at 65°C during two days. The precision for OC by this procedure was 3%.

### 3.3. Stable Isotopic Composition of Organic Carbon

Stable carbon isotope ratios of OC were determined in surface sediment ($\delta^{13}$C$_{OC}$) and SPM ($\delta^{13}$C$_{POC}$) after carbonate removal by acidification. Analysis of the June 2005 samples were performed using a continuous flow ThermoFinigan Delta Plus XP Isotopic-Ratio Mass Spectrometer (IR-MS). Isotopic signatures of April 2007 sediments were measured at CEFREM on an Isoprime (GVI) IR-MS. An intercomparison between the two IRMSs was performed with 3 decarbonated samples from April 2007. Results showed no significant difference between the $\delta^{13}$C$_{OC}$ values obtained (p<0.01, non parametric Mann-Whitney test).

The isotopic compositions were reported using the standard δ-notation (‰) with respect to the Vienna Pee Dee Belemnite (PDB) standard. Isotopic results were obtained with uncertainties of ± 0.15‰.
3.4. **Proto-kerogen and Black Carbon fractionation:**
Two operationally defined pools of OC were chemically and physically isolated from bulk sediments. The wet procedure described by Song et al. (2002) was used to obtain a proto-kerogen/ black carbon (BC) mixture via acid demineralization, solvent extraction, and base hydrolysis. The procedure described by Gustafsson et al. (2001) was used to obtain pyrogenic BC through thermal oxidation and HCl treatment. Description of the methods used to isolate and quantify the Proto-kerogen/BC mixture, and pyrogenic-graphitic BC are provided as Supplementary material.

3.5. **Polycyclic Aromatic Hydrocarbons (PAH) Analysis in the Rhône River Delta Sediments**
The analysis of the Rhône River delta sediments included different suites of PAHs such as unsubstituted parent compounds, alkyl-substituted homologues (C-PAH) and unsubstituted sulfur heterocycle and their alkyl-substituted compounds (SPAH and C-SPAH). The concentrations were determined for more than 40 individual compounds and also group of their alkyl-substituted homologues (Tronczynski et al., 2004). A description of the method is provided as Supplementary material.

Quantitative PAH source apportionment was carried on the Rhône River samples together with PAH data determined in surface sediments from the bay of Biscay and the Northwestern Mediterranean Sea (Tronczynski et al., 2004). The source analysis in these sediment samples was constrained to two sources of PAH: i) pyrogenic/combustion, and ii) petroleum /oil residue. Two common mixture analysis approaches were adopted using Alternating Least Squares (ALS) and Multivariate Curve Resolution (MCR) calculation techniques (Larsen and Baker, 2003). Both methods give similar results ($r^2 = 0.98$, $n = 95$) and only ALS results are
Mixture analysis calculation provides PAH source amounts apportionment in each sample as well as PAH source profiles (compositions) estimates (Tauler et al., 1993).

### 3.6. Lignin-Phenol Analysis

A detailed description of the method is provided in the Supplementary Material. Briefly, freeze-dried sediment samples (transect from station A to F) were analyzed for lignin-phenols using the cupric-oxide method (Hedges and Ertel, 1982). Lignin oxidation products were quantified by GC-FID.

We quantified eight lignin-derived phenols, unique to vascular plants, and produced during alkaline CuO oxidation. The vanillyl phenol (V) group, consisting of vanillin (Vl), vanillic acid (Vd) and acetovanillone (Vn), is present in all vascular plants. The syringyl group (S), consisting of syringaldehyde (Sl), syringic acid (Sd), and acetosyringone (Sn), are only found in woody and non-woody angiosperms. The cinnamyl phenols, ferulic acid (Fd) and \( p \)-coumaric acid (\( p \)-Cd), are only present in non-woody tissues of gymnosperms and angiosperms. In addition, CuO oxidation yields \( p \)-hydroxybenzenes (P) that are derived from both lignin and non-lignin sources (Goni and Hedges, 1995). Lignin parameters of total syringyl to vanillyl (S/V) and total cinnamyl to vanillyl (C/V) phenols were used to distinguish the relative contributions of plant types (gymnosperm vs. angiosperm) and tissue types (woody vs. non-woody) respectively. Cinnamyl phenols were found to be readily released from herbaceous tissues with a mild-base hydrolysis and exhibit a marked increase in lability relative to the lignin pool, during decomposition (Opsahl and Benner, 1994); therefore, to avoid the large variability in cinnamyl phenol pools and reactivity, the contribution of lignin to the organic matter pool was estimated using the carbon-normalized sum of syringyl and vanillyl phenols, \( \Lambda_6 (\Lambda_6 = S + V) \).

### 3.7. Compound-specific Isotope Analysis of Lignin-Phenols
The compound-specific δ^{13}C values of lignin-derived phenols were measured by isotope ratio monitoring-gas chromatography-mass spectrometry (irm-GC-MS). Please see description in Supplementary Material. The δ^{13}C value of the lignin pool was estimated by isotopic mass balance of syringyl and vanillyl phenols (equation 1):

$$\delta^{13}C_{S,V} = \Sigma f_i \delta_i$$

where $i$ represents individual lignin phenols (vanillin, vanillic acid, acetovanillone, syringaldehyde, syringic acid and acetosyringone); $f_i$ represents the fraction of each phenol, and $\delta_i$ indicates the δ^{13}C value of the corresponding lignin phenol. Errors were calculated following the classical error propagation formula for the linear combination of each phenols contribution (equation 2):

$$\text{std} \delta^{13}C_{S,V} = (\Sigma f_i^2 \text{std} \delta_i)^{1/2}$$

with std designating the error on the δ^{13}C value considered.

3.8. Radiocarbon Organic Carbon Content

Radiocarbon measurements (\(^{14}C\)) were performed either by the Artémis accelerator mass spectrometer (AMS) at the Laboratoire de Mesure du Carbone 14, Gif-sur-Yvette (for sediment samples) or by the NSF - Arizona AMS facility, Tucson (for suspended particles samples). Measurements were performed at two different sediment depths: 0-1 cm and 3-4 cm depth. After the decarbonation, the entire sample was combusted in a sealed quartz tube at 850°C with copper oxide and silver wool. The released CO\(_2\) was dried, volumetrically measured, and collected in a glass ampoule. Then, the CO\(_2\) sample was converted to graphite target in an atmosphere of H\(_2\) over an iron powder catalyst at 600°C (Arnold et al., 1989) and
the sample $^{14}$C/$^{12}$C ratio was then measured. The $^{14}$C activities are determined with respect to the international standard of oxalic acid and are reported in $\Delta^{14}$C (Stuiver and Polach, 1977). The $\Delta^{14}$C is defined as the deviation in parts per mil from the modern standard. All $\Delta^{14}$C values were corrected from 1950, and from the delay between sampling and measurement years (Mook and van der Plicht, 1999). Ages were calculated from the $\Delta^{14}$C values using the conventional $^{14}$C half-life. The precisions of $\Delta^{14}$C measurements were ± 3‰ for the sediment samples (Artemis AMS) and ± 0.2‰ for the suspended particles (Arizona AMS facility). Total uncertainties in $\Delta^{14}$C$_{OC}$ are listed in Tables 1 and 2 for each samples.

4. RESULTS:

4.1. River samples:

The suspended particulate matter (SPM) sampled monthly from 2006 to 2009 in the Rhône River displayed a mean OC content of 1.9 ± 0.5 %, and a $\delta^{13}$C$_{POC}$ mean value of -27.4‰ ± 0.7‰ (Table 1). This $\delta^{13}$C$_{POC}$ composition is in agreement with a previous survey on the SPM from the Rhône River, which gave a mean $\delta^{13}$C$_{POC}$ of -26.8‰ ± 0.2‰ over 2004-2005 (Harmelin-Vivien et al., 2010; Harmelin-Vivien et al., 2008) and reflects the dominance of the C$_3$ photosynthetic pathway within the Rhône River watershed throughout the seasons (Table 1).

Over the three years survey, SPM displayed $\Delta^{14}$C$_{POC}$ signatures between 148 and -90‰, including period of flood events. Black carbon (BC) contents in the Rhône River SPM were 0.34 ± 0.12% (d.w.).

4.2. Background Data: Organic Carbon Content

In April 2007, temperatures in bottom and intermediate waters were homogeneous over the entire study area (prodelta and continental shelf), ranging between 14.1 and 15.3°C at depths
of 13 to 98 m (Table 1). The SPM contents varied between 0.8 and 5.4 mg L\(^{-1}\), with no significant spatial pattern.

The highest POC concentrations were observed near the Rhône River mouth with values ranging between 150 and 266 µgC l\(^{-1}\) (Stations A, K, B, L and N). The POC contents of SPM samples were around 10% at the river mouth and decreased offshore to values around 3% (Table 1). Surface and intermediate waters presented slightly higher POC contents than bottom waters, but given the variability, they were not significantly different (p>0.05).

The distribution and values of OC in surface sediment were stable over the two cruises and ranged between 2% at the vicinity of the river mouth and 1% offshore. The OC contents were slightly lower offshore during the June 2005 cruise but the overall prodelta distribution was not significantly different from April 2007 (p>0.05, Table 2, for data in June 2005 see Lansard et al., 2009).

### 4.3. Stable Carbon Isotopic Composition

The \(\delta^{13}\)C\(_{OC}\) values for surface sediments collected in June 2005 are those reported by Lansard et al. (2009). The \(\delta^{13}\)C\(_{OC}\) signatures did not show any significant changes between June 2005 and April 2007 in surface sediment (p>0.05): values of \(\delta^{13}\)C\(_{OC}\) ranged from -27.2‰ at station A (outlet of the river) to -23.9‰ at station J (south-eastward) (Table 2). All \(\delta^{13}\)C\(_{OC}\) values increased with distance from the Rhône River mouth (\(r^2 = 0.845, n = 27, p<0.01\), see Lansard et al., 2009). Stations A, B and K are located within a 2 km radius off the Rhône River mouth and presented strongly depleted \(\delta^{13}\)C\(_{OC}\) values around -27 and -26‰, associated with high OC contents (~2%). Proceeding offshore, stable carbon isotope ratios rose up to -24‰ at the far most end of the South-West transect and eastern stations, corresponding to the lowest OC contents (~0.8 - 1%).
Contrary to surface sediment values, stable carbon isotope ratios of suspended POC ($\delta^{13}C_{\text{POC}}$) in bottom and intermediate waters were homogeneous in the whole prodelta, with values of $-24.0 \pm 0.3\%$ in bottom waters and $-23.2 \pm 0.8\%$ in intermediate waters, respectively (Table 1). There was no specific trend in spatial $\delta^{13}C_{\text{POC}}$ distribution in the prodelta or the continental shelf.

4.4. Distribution of $\Delta^{14}C_{\text{OC}}$ and $\Delta^{14}C_{\text{POC}}$

$\Delta^{14}C_{\text{POC}}$ signatures were measured in SPM from the Rhône River. Samples collected in April 2006, March 2007, September and November 2008 and February 2009 displayed $\Delta^{14}C_{\text{POC}}$ values between $-90\%$ and $148\%$ (Table 1).

The $\Delta^{14}C_{\text{OC}}$ signature of surface sediments in the prodelta presented a wide range of values from $+143\%$ to $-400\%$ (Table 2). A clear trend was observed with $\Delta^{14}C_{\text{OC}}$ values decreasing with distance from the Rhône river mouth ($r^2 = 0.942$, $n = 14$, $p<0.01$, see Fig. 2). Surface sediments in the immediate vicinity of the Rhône River mouth (station A) presented a modern $\Delta^{14}C_{\text{OC}}$ signature ranging between $59\%$ and $143\%$, slightly higher than the current atmospheric $\Delta^{14}C_{\text{CO}_2}$ level ($-70\%$, (Levin and Kromer, 2004)), and around $0\%$ at B and K (Fig. 2, Table 2). Moving offshore, the $\Delta^{14}C_{\text{OC}}$ signatures of sediments decreased rapidly with distance from the Rhône River mouth, down to values around $-400\%$ in the most distal area, corresponding to an age of about 4000 years BP (Fig. 2; Table 2).

Except station A, which was markedly enriched with POC values in SPM of intermediate waters reaching modern carbon values, all stations showed SPM in bottom waters with $\Delta^{14}C_{\text{POC}}$ lower than $-100\%$. Offshore, the $\Delta^{14}C_{\text{POC}}$ values of SPM decreased very quickly, down to values around $-300\%$ (Table 1). At the station E, on the continental shelf, the radiocarbon signature of SPM ($\Delta^{14}C_{\text{POC}}$) was similar to surface sediments $\Delta^{14}C_{\text{OC}}$ (Table 1).
Nevertheless, our results show no correlation between sediment and overlying suspended POC radiocarbon signatures (p>0.05, Table 1 and 2).

4.5. Black Carbon (BC) and Proto-kerogen/BC mixture:  
Sediment in the prodelta and the continental shelf display similar Black Carbon (BC) contents, ranging from 0.21 to 0.47% d.w. with a mean $\delta^{13}$C value of -24.6 ± 0.6‰ (Fig. 6). Since OC content in the sediment decrease from the river mouth to the continental shelf (from 1.8% to 0.8%), such constant BC values correspond to an increase from 12 to 50% of BC content in OC.

On the contrary, the proto-kerogen/BC mixture shows a clear decrease within the transition zone: sediment in the prodelta (stations A, B, K) displayed contents of 0.69 ± 0.12% d.w. significantly higher than the stations on the continental shelf with values of 0.47 ± 0.02%. In addition, the stable carbon isotopic signature of the proto-kerogen/BC mixture in the prodelta was -27.5 ± 0.6‰ whereas it was -25.3 ± 0.4‰ in the continental shelf. The proto-kerogen/BC mixture contribution to OC did not show any clear pattern over the area and was around 40-50% OC.

Please note that both fractions were obtained through different technique (chemical or thermal procedure) and the respective contribution of BC and proto-kerogen/BC mixture to OC content should not be compared among one another (Elmquist et al., 2004; Gelinas et al., 2001).

4.6. Lignin-Derived Phenols And Their Stable Carbon Signatures  
The average carbon-normalized lignin contents ($\Lambda_e$) were similar in the 1-2 cm and the 3-4 cm depths and decreased with distance from the river mouth (Table 3). Syringyl and vanillyl phenol contributions were fairly equal (around 50%, Table 3) near the river mouth (station A) but the vanillyl phenol yield increased with offshore transport (Table 3), suggesting a greater
The contribution of angiosperm tissues in near-shore sediments (Hedges and Mann, 1979b). The relative cinnamyl phenol yields were the lowest, ranging from 4.6% to 11.8% in upper 1-2 cm sediments and 5.6 to 7.2% at 3-4 cm depth. The S/V and C/V ratios at both depths generally decreased with an increased distance from the river mouth (Table 3, Fig. 3). The (Ad/Al)v ratio of sediments from the Rhône River transect did not significantly vary with offshore distance but nearly a doubling in (P/V+S) was observed (Table 3).

δ\(^{13}\)C values of the syringyl and vanillyl pool (δ\(^{13}\)C\(_{S,V}\)) were consistently lower in sediments at 1-2 cm relative to those at 3-4 cm depth. However, there was an increase in the δ\(^{13}\)C value along the transect at both depths (Table 3). From station A to station E, the δ\(^{13}\)C value of lignin in surface sediments (1-2 cm) increased by 4.3%, while those of sediments at 3-4 cm increased by 7.3% (Table 3). Despite its rather weak significance level (probably as a result of the low amount of data available), this increase in δ\(^{13}\)C\(_{S,V}\) along the transect was statistically relevant (p ≤ 0.1, Kruskal-Wallis).

**4.7. PAH in the Rhône Prodelta And Adjacent Continental Shelf.**

Summed concentration of total PAHs in the sediment from the Rhône River prodelta and adjacent continental shelf ranged from about 2000 to 2400 µg kg\(^{-1}\) (d.w.) and showed no gradient along the dispersal system (Table 4). Results from the Rhosos cruise performed in 2008 (Tronczynski, unpublished results) were added as additional PAHs data in surface sediments of the continental shelf. The concentrations of total PAHs normalized to organic carbon ranged from about 110 to 330 mg kg\(^{-1}\) OC and were higher at station C (75 m) than at the station A. The levels of summed sedimentary concentrations of six indicators ΣPAH\(_6\) ranged from 450 to 600 µg kg\(^{-1}\) d.w. (Table 4).

The petroleum component is estimated to be 30% (mean ± 1 % n = 4) of total PAH in the Rhône delta sediments (Table 4) using mixture analysis calculation by ALS (Grande and
Manne, 2000). The remaining 70% originates from fossil fuel and biomass combustion (pyrogenic origin).

The total PAH content of the sediment was estimated by using a multiplying factor of 5 on our PAH estimates (Table 4) to account for all sulfur, oxygen and not quantified compounds, as previously used in coastal sediments (Tolosa et al., 1996; Tronczynski et al., 2004). The total PAH concentration in the Rhône River prodelta is thus about 10 mg kg\(^{-1}\) dry weight (dw) (2000 µg kg\(^{-1}\) from Table 4 multiplied by 5).

Petroleum PAH fraction represents 30% of the total PAH (Table 4) which leads to a concentration of petroleum residues-PAH of 3 mg kg\(^{-1}\) dw. To calculate the petroleum carbon content, we used a conservative value of 20% of PAH in petroleum, since aromatic hydrocarbons significantly vary from one oil (and its refinery products) to another, ranging from 20 to 50% of different oils and refinery products (Lee et al., 1986). The total concentration of oil residue-derived OC in the sediment was therefore estimated to be 15 mg kg\(^{-1}\) dw (3 mg kg\(^{-1}\)/20%).

The pyrogenic fraction of PAH is derived from combustion of fossil fuel or biomass and represents 70% of PAH: hence 7 mg kg\(^{-1}\) of PAH out of the total of 10 mg kg\(^{-1}\) was of pyrogenic origin (i.e. wood chars and soot). The predominance of fossil fuel combustion over residential wood combustion as the major source of pyrogenic BC and associated PAHs was examined by using ratios of 1.7-dimethylphenanthrene to 2.6-dimethylphenanthrene. Expressed as 1,7/(1,7+2.6)-DMP, this ratio is known to be less than 0.42 for diesel particles and urban dust, whereas it reaches 0.70-0.90 in emissions from wood combustion (Benner et al., 1995). In sediment from our study area, we found this PAH ratio to be 0.45 implying that about 95% of the pyrolytic PAHs were derived from fossil fuel combustion (Yunker et al., 2012). Neglecting the wood/biomass combustion fraction, we can therefore consider that 7
mg kg\(^{-1}\) of PAH out of the total of 10 mg kg\(^{-1}\) originate from fossil fuel combustion (i.e. diesel soot, vehicle emission). In addition, assuming that PAHs represent 5% of the total combustion carbon (White et al., 2005), we can calculate a concentration of pyrogenic BC of 140 mg kg\(^{-1}\).

5. DISCUSSION

The radiocarbon signatures, stable carbon isotopic compositions and BC contents presented above indicate that different OC sources contribute to the organic matter in the river and shelf samples (Fig. 5). Additionally, lignin phenols” yields and isotopic signature suggest that a significant fraction of the organic matter exported by the Rhône River is lost during its introduction into the shelf environment. In the following sections, we investigate the sources of the OC pools exported by the Rhône River and the processes affecting their export in the sediments of the Gulf of Lions continental shelf.

5.1. River input of organic matter: variability and signature

The largest source of organic matter to the delta is the Rhône River which is characterized by large variations of discharge (Fig. 1). Flood periods, defined as water discharge rates exceeding 3000 m\(^3\) s\(^{-1}\) at Arles gauging station, occur in early spring and late fall and lasts from a few days to a week. These high discharge episodes are known to carry most of the material (about 80%) to the coastal ocean (Antonelli et al., 2004; Roussiez et al., 2005).

In this study, six periods characterized by high river discharge (with four floods) were investigated for \(\Delta^{14}C_{POC}\) whereas \(\delta^{13}C_{POC}\) was measured every month over the three-year study (January 2006 to February 2009). The time-series shows that the \(\delta^{13}C_{POC}\) signature of the suspended particles in the Rhône River is relatively stable (-27.4 ± 0.7‰) during both low
discharge and flood events (2006-2008). The Rhône River SPM displayed a variable $\Delta^{14}C_{\text{POC}}$ signature between 147 and -90‰ (average 29 ± 93‰, n=5, Table 1) which likely reflected the mixing of different terrigenous materials in the River, i.e. fresh plant debris mixed with a low proportion of older soil organic matter. The $\Delta^{14}C_{\text{POC}}$ signature of the Rhône River could also be influenced by the adjacent nuclear power plants: they can potentially increase the $\Delta^{14}C_{\text{POC}}$ signature in the river (Faurescu et al., 2008). This is contrasting with other RiOMar systems in temperate settings, where $^{14}C$ signatures of POC are relatively older with $\Delta^{14}C_{\text{POC}}$ signature ranging from -175‰ down to -550‰ (Raymond and Bauer, 2001a; Wakeham et al., 2009). The $\Delta^{14}C_{\text{POC}}$ decreased to a low value of -495‰ only one time over the three years of monitoring, in May-June 2008, due to an exceptional flood of the Durance River located in the south-western Alps. This flood was linked to a water release by a dam. Therefore it is likely that during the event the flood wave carried a large amount of fine organic-poor sediments originating from bank erosion. This distinct source of organic matter was also obvious based on the $\delta^{13}C_{\text{POC}}$ signature (-25.8‰), a value never reached during the 3-year monitoring period. On average, the organic matter supplied to the Rhône River prodelta corresponds to a modern terrestrial material similar to the one observed in the sediment of the shallowest station A located just off the river mouth (24 m water depth).

5.2. The River-Shelf transition zone: major changes in particle signature

The input of Rhône River exerts first order control on the composition of sedimentary organic matter located in the prodelta, i.e. near the river mouth. The terrestrial signature of the OM deposited in this zone is progressively altered along the sediment transport pathway along the continental shelf as shown on Fig. 4. We pooled our data with the ones from Tesi et al. (2007) and Tesi et al. (2010a; 2010b) who had performed $\delta^{13}C_{\text{OC}}$, $\Delta^{14}C_{\text{OC}}$ and lignin
measurements in surface sediments further away in the Gulf of Lions continental shelf. The striking feature is the constancy of the particle signature on the entire shelf mud belt (Fig.4). Indeed, the $\Delta^{14}C_{OC}$, $\delta^{13}C_{OC}$ and OC contents presents less than 6% variation over a western 125 km transect across the shelf. Regarding the biogeochemical parameters from this study, 70% of the changes occur in the prodelta within a transition zone between the river mouth and the continental shelf. Most transformation, mixing, sorting and degradation processes altering/impacting the material delivered by the Rhône River appeared to occur within this narrow zone of 10 km radius area around the Rhône River mouth. On the contrary, shelf sediments display low organic carbon content, mixed $\delta^{13}C_{OC}$ (-24.5‰) and low $\Delta^{14}C_{OC}$ (around -400‰) with a constant signature over the entire shelf of the Gulf of Lions. These sediments are characteristic of inert particles which are redistributed and mixed on the continental shelf by wind induced currents (Ulses et al., 2008; Estournel et al., 2003; Roussiez et al. 2006).

The transition zone displays a continuous gradient of isotopic signature (Fig. 4) with increasing distance from the Rhône River mouth. The shallow Rhône prodelta is a significant zone of retention for riverine particles, e.g. Station A (Table 2) which is located at 2 km from the river mouth at a depth of 24 meters. In addition to high sedimentation rates, it was shown using $^{238}Pu$ that most particles delivered by the Rhône River were deposited and stored near the Rhône River mouth (Lansard et al., 2007). The isotopic composition of organic carbon in the sediment of station A reflects that of the river with a modern $\Delta^{14}C_{OC}$ (+ 60-140‰) and a $\delta^{13}C_{OC}$ of -27‰. Furthermore, the large lignin content of the sediment suggests that the organic material is mostly terrestrial. Although this station exhibits the highest mineralization rate of organic matter in the sediment (Cathalot et al., 2010), it is mostly an accumulation centre with a burial efficiency of 80% (Pastor, Cathalot et al., 2011).
Stations located further away from the river mouth (B, K, L, N, C) in the transition zone (3-10 km) showed a progressive change of the primary signature of the river particles. Δ\(^{14}\)C\(_{OC}\) decreases to values as low as -220‰ at station C and δ\(^{13}\)C\(_{OC}\) increases to -25‰, reflecting the apparent aging of organic carbon and its loss of terrestrial signature, respectively (Fig. 2, Table 2). In this region, several processes may modify the original signature of river particles: (1) selective degradation of relatively young terrestrial organic matter, (2) sorting of particles with different biogeochemical signatures (fossil versus labile carbon with different size/density characteristics (Tesi et al., 2007a), (3) mixing with the pool of old and refractory shelf particles. Mineralization rates are substantial in the sediment of the transition zone (Cathalot et al., 2010) and burial efficiency decreases from 60% (stations B, K, L) to 20% (station E) indicating that a substantial part of organic carbon is processed in these sediments (Pastor et al., 2011a).

In the next sections, we discuss the processes and their interplay which may lead to the observed isotopic and biomarkers gradient.

5.3. Hydraulic sorting within the prodelta area

Hydraulic transport mechanisms, which preferentially transport the finest material, alter the grain size distribution in surficial sediments (Marion et al., 2010). To assess the impact of grain size distribution on the export of OM in sediment of the Rhône River prodelta and the adjacent continental shelf, we plotted our radiocarbon signatures as a function of the silt/clay fraction content (Pastor et al., 2011b). Figure 7 clearly shows a dual behaviour of Δ\(^{14}\)C\(_{OC}\) signatures with respect to grain size distribution. In the prodelta, a clear gradient in the Δ\(^{14}\)C\(_{OC}\) values suggest a loss of a young coarse material in the transition zone (stations A, B, K) as the sediment is being exported towards the continental shelf along the main sediment
transport system. This corresponds most likely, to a “fresh” woody material associated with coarse-sized particles preferentially retained close to the river mouth (Tesi et al., 2007a). As a consequence of this initial hydraulic sorting, soil-derived OM bound to the particles and all small size particles are selectively transported further offshore (Tesi et al., 2007a).

Soil OM can display a wide range of $\Delta^{14}C_{OC}$ signatures ranging from modern to pre-aged values and has been proven to constitute a significant part of the sediment OM in many RiOMar systems (Hedges et al., 1999; Mannino and Harvey, 2000). Nevertheless, the sediment granulometry is homogeneous over the continental shelf (silt and clay < 63 µm fraction: 95.3 ± 1.0%, Fig. 7) and the wide range of $\Delta^{14}C_{OC}$ values (-102‰ to -400‰) suggesting a limited grain size sorting after the transition zone. The correlation between $\Delta^{14}C_{OC}$ and the particle size fraction < 63 µm ($r^2=0.730$, n=24, Fig. 7) disappears when considering only the continental shelf stations ($r^2=0.024$, n=16, Fig. 7). Previous studies described the very fine sediment of the continental shelf, demonstrating the presence of an uniform fine-grained mudbank all over the continental shelf (except for littoral sands)(Lansard et al., 2007; Roussiez et al., 2006). As evidenced for other deltaic systems, particle sorting is likely to be responsible for the gradient of radiocarbon values observed in the transition zone by retaining some coarse woody particles in the shallow prodelta (Toussaint et al., accepted). However, over the continental shelf, this process might be of less importance and fails to explain the distribution of $\Delta^{14}C_{OC}$ signatures over the continental shelf. Other mechanisms are likely acting along the main sediment transport system.

**5.4. Contribution of ancient OC to the continental shelf sediment**

The surface sediments of the continental shelf displayed highly depleted $\Delta^{14}C_{OC}$ values compared to the prodelta (Fig. 2, Table 2). Radiocarbon values in the continental shelf were about -310 ± 66‰. The residence time of the OM in the sediment cannot explain this low $\Delta^{14}C_{OC}$ values. Indeed, based on the published sedimentation rates (0.1-0.4 cm y⁻¹) and a 10
cm mixed layer (Miralles et al., 2005), the average $\Delta^{14}C_{OC}$ value of marine phytodetritus in the sediment mixed layer should be around 30‰; indeed, the $\Delta^{14}C_{OC}$ decay of 100 years from an initial fresh marine signature of 50‰ is <15‰ (Hansman et al., 2009; Wang et al., 1998). Even taking into account the potential reservoir age of 400 years for Mediterranean marine waters (Siani et al., 2001), the large difference between the estimated ages and our radiocarbon data (Table 2) showed that most of the carbon in the Rhône River continental shelf is much older than would be expected if it had been derived from contemporarily synthesized sources (e.g., phytoplankton, vascular plants).

The heavily depleted values observed on the continental shelf suggested the presence of aged OC, such as kerogens, graphite, petroleum residues or black carbon (Graz et al., 2010). Originating from bedrock-derived kerogen, fossil fuels combustion or oil contamination, fossil OC generally displays a $\Delta^{14}C_{OC}$ of around −1000 ‰ (>60 kyr: it contains nearly no $^{14}C$ (Drenzek et al., 2007; Goni et al., 2005). Indeed, high contributions of ancient carbon sources to river suspended sediments and surface shelf sediments have been observed in other RiOMar systems (Blair et al., 2003; Galy et al., 2008; Galy and Eglinton, 2011; Goni et al., 2006; Gordon and Goni, 2004; Masiello and Druffel, 1998; Masiello et al., 1998). Lateral export of this aged fraction can be promoted by both selective transport of aged material sorbed onto fine particles (i.e., winnowing) and selective degradation of fresh OM along the sediment dispersal system (Hedges et al., 1999; Mannino and Harvey, 2000). As a result, the fraction of terrestrially-derived aged OM becomes gradually more important with increasing distance from river mouth.

### 5.4.1. Oil residue and pyrolytic BC as ancient OC sources

As the Gulf of Lions is an intense transit area for tanker ships, we used the analysis of polycyclic aromatic hydrocarbons (PAHs) to estimate the actual contribution of fossil fuels, biomass/biofuels combustion as well as direct inputs of oil products in our sediment samples.
Levels of ΣPAH in the sediments of the Rhône River delta range from 450 to 600 µg kg\(^{-1}\) dw (Table 4), yielding a total PAH concentration of 10 mg/kg dw (see result section for calculation). These levels are characteristic of present-day, chronic, intermediary contamination by PAHs of marine sediments located close to the continental loads. Oil residues represent about 30% of total PAHs in the Rhône delta (Table 4) and the remaining 70% originates from fossil fuel and biomass combustion (pyrogenic origin).

Based on this distribution of PAHs sources, we can provide a rough estimate of ancient OC originating from petroleum and pyrogenic BC. The total oil residue-derived OC in the continental shelf sediment was estimated to be 15 mg kg\(^{-1}\) of OC i.e. 0.15% of OC whereas the pyrogenic fraction amounts to 140 mg kg\(^{-1}\), i.e. 1.4% of total OC. A total of 1.5% of OC is found which is consistent with results of Leaute (2008) in the Thau Lagoon, a mediterranean shallow lagoon.

Our PAHs measurements provide us with an estimate of the pyrogenic BC and petroleum fraction of ancient OC and indicate a major contribution of oil residues and soots from vehicle combustion. The low proportion of ancient OC originating from petroleum and pyrogenic BC does not support the observed \(^{14}\)C values on the shelf. Indeed, only 2% of ancient OC mixing up with recent organic material would lead to \(\Delta^{14}\)C\(_{OC}\) values of 78‰ in the sediment, when the observed radiocarbon signatures are around -400‰ (Fig 2, Table 2). Another aged source and other processes are needed to explain the old ages of the continental shelf sediments.

### 5.4.2. Black Carbon and proto-kerogen/BC fossil OC

Since the Rhône river catchment contains a lot of sedimentary rock, the depleted \(\Delta^{14}\)C\(_{OC}\) values, the slightly enriched \(\delta^{13}\)C\(_{OC}\) values and the low lignin content observed in the continental shelf sediments could reflect an important contribution of kerogen-BC mixture. Indeed, as stated above, fossil OC is almost completely depleted in \(^{14}\)C and is generally
assumed to have a $\Delta^{14}C_{OC}$ value of $\sim-1000\permil$ and a $\delta^{13}C_{OC}$ signature ranging between -30 and -12\permil (Drenzek et al., 2009; Goni et al., 2005). Such $\Delta^{14}C_{OC}$ signature is however a rough estimate since radiocarbon measurements on graphitic BC samples have shown a range of signatures from -800 to -1000\permil (Dickens et al., 2004; Drenzek et al., 2009; Drenzek et al., 2007). Likely, the rather depleted signature ($\Delta^{14}C_{OC} \sim -400\permil$) of continental shelf sediments indicate the presence of fossil material, probably inherited from the Rhône River material and preferentially exported along the dispersal transect.

As a matter of fact, our data indicate a contribution of BC to OC increasing from 12% at the river mouth to 50% on the continental shelf (Fig. 6). These values, although remarkable, are consistent with measurements carried out by Lim and Cachier (1996) in NW Mediterranean Sea. The authors, based on chemical oxidation and thermal treatments, estimated a BC/TOC ratio of 38%. The large difference between our pyrogenic BC estimates based on PAHs (1.4% of OC) and our BC measurements based on thermal oxidation (12-50% of OC) suggest a high contribution of graphite in BC. Indeed, the Thermal Oxidation method at 375°C applied here can isolate very highly condensed soot-BC and graphite but can also destroy charcoal-BC and kerogen (Elmquist et al., 2004). Therefore, the low PAH/BC ratios indicate that 90-98% of BC would be of graphitic origin. Graphitic C inputs originating from sedimentary rocks erosion occurring in the catchment of the Rhône River would thus deliver high BC fluxes and generate the high contribution of BC observed in the sediment from the prodelta and continental shelf.

In parallel, our data show a decrease of the proto-kerogen/BC fraction along the sediment dispersal system indicating a selective degradation of proto-kerogen like-OM as the terrestrial OM delivered by the Rhône River is exported towards the continental shelf. About 20% of proto-kerogen is lost during the export over the prodelta. Adsorption of otherwise labile organic compounds onto minerals can prevent their diagenetic degradation and promoting
their subsequent condensation into kerogen (Salmon et al., 2000). During the transport along
the transition zone and within the prodelta sediment, selective degradation mechanisms could
remove some kerogen-like material, leaving behind mineral matrix protected OM.

### 5.5. Degradation mechanisms along the sediment dispersal system

A plot of $\Delta^{14}C_{OC}$ and $\delta^{13}C_{OC}$ values against $1/OC$ provides us with a mixing model taking into
account changes in the bulk concentration of OC (Fig. 8). The $\Delta^{14}C_{OC}$ and $\delta^{13}C_{OC}$ ordinates at
0.5 (max. 2% OC in the shallow prodelta during our study) indicate the loss of a modern-like
OC source ($\Delta^{14}C_{OC} \sim 59\%$) with a very light $\delta^{13}C_{OC}$ terrestrial signature (~-27‰) as OC
decreases across the system. This loss certainly reflects the net decomposition of this
terrestrial material through degradation processes and the relative accumulation of old BC
offshore.

In this study, the lignin phenols contents of the sediments were used as another means
for investigating the fate and transfer mechanisms of the terrestrial OM delivered by the river
to the coastal ocean. First, a plot of $S/V$ vs. $C/V$ ratios (Fig. 3) indicates that angiosperm
woody and leaf materials are major sources of lignin in the shallow Rhône River prodelta
(station A). However, both $S/V$ and $C/V$ ratios gradually decrease with increasing distance
from the prodelta. Variations in these two ratios are likely caused by two processes: (1)
differential lignin degradation (Benner et al., 1991; Haddad et al., 1992; Hedges et al., 1988;
Opsahl and Benner, 1995); and (2) differential inputs from angiosperm and gymnosperm
woody and non-woody tissue (Hedges and Mann, 1979a).

We used lignin stable carbon isotopes to discriminate terrestrial OM between C3 and
C4 plant sources. Indeed, C3 plants yield lignin phenols with $\delta^{13}C$ values $\leq -27\%$ while C4
plants yield lignin phenols with $\delta^{13}C$ values ranging from -13 to -19‰ (Goni et al., 1997). In
the shallow prodelta sediments (station A), integrated lignin isotopic compositions ($\delta^{13}C_{S,V}$)
are below -30‰ (Table 3), clearly indicating a C3-plant origin. However, the $\delta^{13}C_{S,V}$ values of the syringyl and vanillyl lignins increase by ~ 5‰ from station A to station E (Table 3). The alteration of lignin $^{13}C$ with increasing distance from the river mouth can be caused by an increase in contribution from C4-derived OM or lignin degradation. The S/V and C/V ratios indicate that gymnosperm-derived lignin accounts for a dominating fraction in off-shore sediments (Fig. 3; see above). Since no gymnosperm plants utilize the C4 photosynthetic pathway (Ehleringer et al., 1997), an increase in contribution from C4-derived OM is unlikely important for the isotopic alteration of lignins in off-shore sediments. Therefore, both lignin phenols and lignin stable carbon isotopes indicate significant lignin degradation over the transition zone.

Lignin is generally degraded via propyl side chain oxidation, demethylation of the methoxyl groups, and aromatic ring cleavage (Benner et al., 1991; Ertel and Hedges, 1984). Lignin-derived acid to aldehyde ratio (Ad/Al)$_V$ or (Ad/Al)$_S$ has been used as an indicator of propyl side chain oxidation (Hedges et al., 1988; Opsahl and Benner, 1995). Demethylation results in selective loss of methoxyl groups (vanillyl and syringyl phenols) but does not affect non-methoxylated phenols (p-hydroxyl phenols). Thus, the methoxylated- to non-methoxylated phenol [P/(V+S)] ratio can also be used as a diagenetic indicator of lignin (Dittmar and Lara, 2001; Dittmar et al., 2001). However, p-hydroxyl phenols are derived from a variety of lignin and non-lignin materials, limiting the applications of the [P/(V+S)] ratio. The ratio of p-hydroxyacetophenone (PON) to total p-hydroxyl phenols (PON/P) can be used as an indicator to determine the source of this phenol group (Benner et al., 1990). When aromatic ring cleavage is a dominating pathway for lignin degradation, neither (Ad/Al) nor P/(V+S) ratio can be elevated (Dittmar and Lara, 2001). Our lignin data (Table 3) show that the (PON)/P ratios remain almost constant despite a remarkable decrease of total p-hydroxyl phenols from the prodelta to the shelf, indicating that the sources of this phenol group at
different sampling sites are the same and the PON has a reactivity similar to total p-hydroxyl phenols decomposition. Based on this, P/(V+S) ratios can be reliably used as an indicator for lignin degradation. In fact, we observed a doubling in P/(V+S) in offshore versus river mouth sediments while little changes are observed in (Ad/Al)v, suggesting that lignin becomes increasingly degraded with off-shore transport, mainly via a demethylation pathway. In addition, there is evidence that isotopic compositions of lignin compounds can be altered during degradation processes (Bahri et al., 2008). So, the degradation of lignin along the dispersal sediment system is likely responsible for the alteration in isotopic signature of lignin that we see in the transition zone.

Degradation of OM in sediments from the Rhône River estuary to continental shelf has been demonstrated using different proxies. For example, two independent indexes based on amino acid (Dauwe’s Index Dauwe et al., 1999) and pigments (ratio of intact chlorophyll-a to the sum of chlorophyll-a + phaeopigments) consistently indicate an increase in degradation state of OM along the transect (Pastor et al., 2011a; Bourgeois et al., 2011). The terrestrial material in Rhône River is largely composed of fresh and labile material (Cathalot et al., 2010; Pastor et al., 2011a), as indicated by the modern Δ14COC signatures observed at the river mouth, and its lability appears to drive degradation processes in the Rhône River prodelta. Indeed, the increase in degradation state of OM in the prodelta and the adjacent shelf is correlated with the decrease of both terrestrial biomarkers (fatty acids and chlorophyll-b) and benthic mineralization rates (Cathalot et al., 2010). Our radiocarbon data are significantly correlated with the Dauwe Index from Bourgeois et al (2011) (r²=0.89, p<0.005), suggesting that the distribution of Δ14COC signatures is directly related to the degradation processes.

Changes in OM composition during the offshore transport due to selective stabilization and degradation of organic compounds can be a predominant feature in the OM cycling of RiOMar systems (Goni et al., 2005; Zonneveld et al., 2010). Our data suggest that,
along its dispersion offshore, the OM is selectively degraded with fresh material and proto-
kerogen OM being removed through degradation processes, as evidenced by biomarkers and
oxygen demand of the sediment (Bourgeois et al., 2011; Cathalot et al., 2010). The OM on the
shelf corresponds to a degraded “aged” OM, which will then remain on the continental shelf
and be further exported or reworked. If the input of terrestrial organic matter in this system is
obvious, the proportion of marine OM is an open question.

5.6. Inputs of fresh marine Organic Matter

In addition to the selective degradation processes occurring along the main dispersal
system, many studies in deltaic environments have shown that isotopic and biogeochemical
characteristics of POM result from the dilution of the terrestrial material with freshly
produced marine phytoplankton (Fry and Sherr, 1984; Hedges et al., 1997; Tesi et al., 2007b).
To assess if such dilution processes could explain the radiocarbon signatures observed in the
sediments of the Gulf of Lions continental shelf, we applied a three end-members mixing
model to our Gulf of Lions sites based on isotopic composition ($\Delta^{14}C_{OC}$, $\delta^{13}C_{OC}$), and lignin
contents ($\ell_6$). This model has two contemporary terrestrial and marine sources, and a
kerogen-BC source (Fig. 5 and 9). Marine phytoplankton, exempt of lignin, was assumed to
display a $\Delta^{14}C_{OC}$ signature following the $\Delta^{14}C_{DIC}$ values (~ 100 - 120‰) of the Mediterranean
Sea surface waters (Yechieli et al., 2001) and $\delta^{13}C_{OC}$ signatures were taken from Harmelin-
Vivien et al. (2008). The parameters for the two contemporary and kerogen-BC terrestrial
end-members were taken from both our isotopic measurements and values from the literature.
Based on these end-members, we show that sediment of the continental shelf would need a
contribution of 30%, 40% and 30% of fresh terrestrial material from the Rhône River,
kerogen-BC and fresh marine OM respectively (Fig. 9).

The mixing model clearly indicates a gradient of increasing contributions of marine
OM and kerogen-BC mixture along the dispersal axis. Immediately after the transition zone,
the model-based contribution of kerogen-BC to OC increases from 10% in the prodelta to 30% all over the continental shelf (station C and E): this is in good agreement with our BC data (Fig. 6) confirming that the material delivered by the Rhône River consists of fossil OC (kerogen-BC mixture) mixed with a fresh terrestrial material quickly deposited within the prodelta. The fossil OC is exported to the continental shelf, reaching 50% of OC in the Gulf of Lions.

Similarly, the model-based marine fraction increases along the dispersal gradient from ~10% in the prodelta up to 30% over the continental shelf. This aspect is rather surprising since many proxies in the literature show no increase in labile marine OM over the continental shelf (Bourgeois et al., 2011; Pastor et al., 2011b). In addition, primary productivity within the Rhône River plume and over the continental shelf is rather low (Conan et al., 1998; Lefevre et al., 1997), in agreement with the gradient of mineralization activity along the dispersal transect which is governed by the fresh terrestrial inputs of the Rhône River in the prodelta (Cathalot et al., 2010) rather than inputs of fresh marine OM on the continental shelf. There is a clear discrepancy between our mixing model results and the biomarkers/mineralization features evidenced in previous studies. Likely, the presence of 30% of fresh marine OM in the continental shelf sediment as predicted by the mixing model is an overestimation. Reconciling these two approaches will require a better definition of the end-members of the model (i.e. OC sources) and the processes involved along the main dispersal transect.

5.7. Resuspension on the continental shelf

Although the accumulation of old BC-like carbon, dilution with fresh marine OM, and the mechanism of selective degradation of fresh terrestrial OM can explain the biomarker, isotopic and the age signature of OC in the continental shelf, some puzzling factors remain in
the understanding of the system. The decrease of OM quality/freshness is not obvious on all biochemical markers: the Enzymatically Hydrolysable / Total Hydrolysable Amino Acids ratios (EHAA/THAA), a proxy for degradation processes in the sediment, shows little decrease along the offshore transect (Pastor et al., 2011b). Other striking features are the homogeneity of the $\delta^{13}$C$_{POC}$ composition of the SPM over the entire prodelta (-23.7 ± 0.6‰), their depleted $\Delta^{14}$C$_{POC}$ signature (apart of station A), and their similarity with continental shelf sediments (see Tables 1 and 2, and Tesi et al., 2010).

These observations suggest that besides selective transport and accumulation of refractory BC-type OM, other mechanisms may be active in the transition zone. Resuspension, transport and redeposition of shelf sediments, consisting in a mixture of old marine OM and BC-kerogen material originating from the Rhône River, is one possible explanation which could contribute to the rapid apparent aging of river particles observed in the River prodelta by differential mixing with deposited shelf sediment. Intense resuspension events, associated with southeasterly storms, are frequent and repeated phenomena affect the inner-shelf sediment of the Gulf of Lions (Estournel et al., 2003; Ulses et al., 2008). Recent work performed on density-fractionated sediments (Toussaint et al., accepted) show that all density fractions from sediments located on the offshore gradient evolve in a similar way. This may be an indication of homogeneous mixing between shelf particles and sediments in the transition zone.

6. CONCLUSION

This study, based on radiocarbon, stable carbon isotopes, lignin phenols, Black Carbon and PAHs analyses, brings new insights on the origin of the organic particulate material on the Mediterranean continental shelf influenced by the Rhône River. In particular, $\Delta^{14}$C$_{OC}$ signatures indicate an important pool of aged OC in the continental shelf. Our data indicate an
important contribution of BC over the continental shelf. Selective degradation mechanisms along with coarse sediment trapping in the nearshore area promote the removal of fresh terrestrial organic matter but also kerogen-like OM delivered by the Rhône River, as it is exported off the prodelta. Clearly, degradation processes of OM plays a critical role in the aging of OM on the continental shelf off the Rhône River: entangled with OM deposition patterns, oxygen exposure time and benthic mineralization efficiencies, they are the results of an intricate interplay between the OM stock and fluxes in the system. Recent marine organic matter is hardly visible in biomarkers but a mixing model based on C isotopes and lignin indicate that it may constitute a significant proportion of OM in the sediment. An alternative model would be a resuspension/deposition/degradation loop for terrestrial and marine organic matter on the continental shelf which would mix with the sediment of the transition zone contributing to the large $\Delta^{14}C$ gradient over the area.
ACKNOWLEDGMENTS:

We thank the captains and crews of the R. V. Tethys II for their help during the two scientific cruises of this project. We would like to thank B. Bombled, E. Kaltnecker, C. Hatte, G. Gontier for their work and technical support during the cruises and laboratory analyses. We thank F. Eyrolle for providing us SPM samples collected in the Rhône River during the flood of June 2008.

We thank Robert C. Aller and Miguel Goñi for proofreading our article and improving the quality of this manuscript from its early stage to its more final version. This work was supported by the French National Research Agency, programme “Vulnérabilités: Milieux et Climat”, under the grant no. ANR-06-VULN-001 to the CHACCRA project, the French INSU-EC2CO program RiOMar.fr, the MISTRALS/Mermex programme and the CEA. This is a contribution ISMAR XXX. This is LSCE contribution XXX.
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Table 1. Summary of intermediate and bottom waters conditions in April 2007 cruise. Distance is reported respective to the Rhône River mouth.

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<th>Depth (m)</th>
<th>Temp (°C)</th>
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<th>[POC] (µgC l⁻¹)</th>
<th>[%POC]</th>
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<th>Radiocarbon ages (yr)</th>
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| Rhône     | Arles April 06 | 1.6 | -27.1 | 147.7 | + 2.8 | post-bomb          |
|           | Arles March 07  | 1.9 | -27.5 | 77.8  | + 2.8 | post-bomb          |
|           | Arles June 08** | 0.8* | -25.8* | -495.1* | + 1.7 | 5510 ± 30       |
|           | Arles September 08 | 1.6 | -27.2 | 40.6  | + 3.1 | post-bomb          |
|           | Arles November 08 | 2.7 | -26.8 | -89.7 | + 2.6 | 757 ± 25          |
|           | Arles February 09 | 1.6 | -27.8 | -37.0 | + 2.8 | 304 ± 24          |

* indicate the June 2008 atypical flood originating from the Durance basin.
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<th>δ13C (%o)</th>
<th>Δ14C (%o)</th>
<th>Age 14COC (yr BP)</th>
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<th>Δδ13C (‰) Syringinc + Vanillinc pool</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The error in AgeOC is ± 30 years for all samples.
* Units: mg/100mgOC. Sum of vanillyl + syringyl phenol yields (Λ₆) was calculated by excluding cinnamyl phenols to compare directly to previous data (Sheesley et al, 2009)

† Sum of vanillyl + syringyl + cinnamyl phenol yields (Λ₈) (Tesi et al, 2007)
Table 3: Composition of lignin parameters obtained in April 2007 from selected stations of the Rhône prodelta and adjacent continental shelf sediments

<table>
<thead>
<tr>
<th>Stations</th>
<th>Sediment depth (cm)</th>
<th>S*</th>
<th>V*</th>
<th>C*</th>
<th>P*</th>
<th>PON/P</th>
<th>S/V</th>
<th>C/V</th>
<th>(Ad/Al)_V</th>
<th>P/(S+V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Syringyl Phenols</td>
<td>Vanillin Phenols</td>
<td>Cinnamyl Phenols</td>
<td>p-hydroxyl Phenols</td>
<td>PON/p-hydroxyl ratio</td>
<td>Syringyl/Vanillin ratio</td>
<td>Cinnamyl/Vanillin ratio</td>
<td>Vanillin acid/aldehyde ratio</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1-2</td>
<td>1.40 ± 0.10</td>
<td>1.77 ± 0.03</td>
<td>0.20 ± 0.03</td>
<td>2.13 ± 0.05</td>
<td>0.042 ± 0.018</td>
<td>0.79 ± 0.07</td>
<td>0.11 ± 0.02</td>
<td>0.32 ± 0.04</td>
<td>0.67 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>3-4</td>
<td>1.41 ± 0.25</td>
<td>1.75 ± 0.01</td>
<td>0.23 ± 0.00</td>
<td>1.63 ± 0.18</td>
<td>0.049 ± 0.000</td>
<td>0.81 ± 0.14</td>
<td>0.13 ± 0.00</td>
<td>0.31 ± 0.05</td>
<td>0.52 ± 0.12</td>
</tr>
<tr>
<td>C</td>
<td>1-2</td>
<td>0.45 ± 0.09</td>
<td>1.31 ± 0.02</td>
<td>0.23 ± 0.05</td>
<td>1.87 ± 0.14</td>
<td>0.031 ± 0.018</td>
<td>0.35 ± 0.07</td>
<td>0.18 ± 0.03</td>
<td>0.43 ± 0.05</td>
<td>1.06 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>3-4</td>
<td>0.48 ± 0.07</td>
<td>1.01 ± 0.06</td>
<td>0.12 ± 0.06</td>
<td>1.52 ± 0.07</td>
<td>0.027 ± 0.003</td>
<td>0.47 ± 0.05</td>
<td>0.12 ± 0.06</td>
<td>0.28 ± 0.33</td>
<td>1.02 ± 0.03</td>
</tr>
<tr>
<td>E</td>
<td>1-2</td>
<td>0.09 ± 0.02</td>
<td>0.23 ± 0.03</td>
<td>0.02 ± 0.01</td>
<td>0.38 ± 0.02</td>
<td>0.037 ± 0.004</td>
<td>0.40 ± 0.04</td>
<td>0.07 ± 0.03</td>
<td>0.37 ± 0.12</td>
<td>1.17 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>3-4</td>
<td>0.08 ± 0.02</td>
<td>0.23 ± 0.02</td>
<td>0.02 ± 0.01</td>
<td>0.31 ± 0.02</td>
<td>0.048 ± 0.004</td>
<td>0.36 ± 0.08</td>
<td>0.02 ± 0.08</td>
<td>0.29 ± 0.10</td>
<td>1.00 ± 0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>δ^{13}C_{SV} (%)</th>
<th>δ^{13}C_{PV} (%)</th>
<th>δ^{13}C_{sd} (%)</th>
<th>δ^{13}C_{Sn} (%)</th>
<th>δ^{13}C_{SV} (%)</th>
<th>δ^{13}C_{iv} (%)</th>
<th>δ^{13}C_{vd} (%)</th>
<th>δ^{13}C_{pc} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syringinc+Vanillin pool</td>
<td>Syringinaldehyde</td>
<td>Syringic Acid</td>
<td>Acetosyringone</td>
<td>Vanillin</td>
<td>Acetovanillone</td>
<td>Vanillic Acid</td>
<td>p-Coumaric Acid</td>
</tr>
<tr>
<td>A 1-2</td>
<td>-31.3 ± 0.5</td>
<td>-28.7 ± 1.8</td>
<td>-39.9 ± 1.4</td>
<td>-31.3 ± 0.8</td>
<td>-29.9 ± 0.3</td>
<td>-29.1 ± 0.8</td>
<td>-38.7 ± 0.5</td>
</tr>
<tr>
<td>3-4</td>
<td>-30.3 ± 0.3</td>
<td>-30.4 ± 0.4</td>
<td>-34.4 ± 1.7</td>
<td>-30.1 ± 0.6</td>
<td>-28.5 ± 0.7</td>
<td>-28.2 ± 0.6</td>
<td>-35.6 ± 0.8</td>
</tr>
<tr>
<td>C 1-2</td>
<td>-28.1 ± 0.5</td>
<td>-24.1 ± 2.3</td>
<td>-32.5 ± 2.3</td>
<td>-32.8 ± 1.6</td>
<td>-26.2 ± 0.1</td>
<td>-29.0 ± 3.6</td>
<td>-32.2 ± 1.3</td>
</tr>
<tr>
<td>3-4</td>
<td>-29.7 ± 0.8</td>
<td>-27.5 ± 2.5</td>
<td>-29.2 ± 0.2</td>
<td>-33.2 ± 2.1</td>
<td>-28.7 ± 1.1</td>
<td>-28.3 ± 2.8</td>
<td>-36.8 ± 1.3</td>
</tr>
<tr>
<td>E 1-2</td>
<td>-27.0 ± 0.8</td>
<td>-21.9 ± 2.9</td>
<td>-29.1 ± 2.9</td>
<td>-24.5 ± 2.5</td>
<td>-27.9 ± 1.3</td>
<td>-32.1 ± 4.2</td>
<td>-27.0 ± 0.7</td>
</tr>
<tr>
<td>3-4</td>
<td>-23.0 ± 1.4</td>
<td>-13.9 ± 5.6</td>
<td>-30.1 ± 3.7</td>
<td>-18.0 ± 2.0</td>
<td>-28.7 ± 0.6</td>
<td>-39.6 ± 3.8</td>
<td>-39.6 ± 3.8</td>
</tr>
</tbody>
</table>

* units: mg/100mgOC
Sum of vanillyl + syringyl phenol yields ($\Lambda_6$) was calculated by excluding cinnamyl phenols to compare directly to previous data (Tesi et al, 2007).

Several compounds were used as internal standards for lignin oxidation, extraction, and analysis. Based off ethyl vanillin, the precision is $\pm 0.84\%$. It is greater for the other internal standards: 3.50% for cinnamic acid, and 1.77% for 3,4-dihydroxybenzoic acid. Ethyl vanillin and cinnamic acid both experience the full extraction method and derivitization, whereas 3,4-dihydroxybenzoic acid only experiences derivitization. Hence, 3,4-dihydroxybenzoic acid is most likely to be the most representative of instrumental variability.
Table 4. PAH concentrations (µg/kg d.w.) in the Rhône delta sediments.

<table>
<thead>
<tr>
<th>Station</th>
<th>Lat. N</th>
<th>Long. E</th>
<th>Depth (m)</th>
<th>Sampling date</th>
<th>Layer (cm)</th>
<th>% OC (dw)</th>
<th>PAH total (µg/kg d.w.)</th>
<th>ΣPAH₆ (µg/kg d.w.)</th>
<th>PAH (parent; µg/kg d.w.)</th>
<th>Petrogenic component (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>43°18.829N</td>
<td>04°51.145E</td>
<td>20</td>
<td>2005</td>
<td>1-2</td>
<td>1.81</td>
<td>2026.0</td>
<td>501.0</td>
<td>935.4</td>
<td>28.6</td>
</tr>
<tr>
<td>C</td>
<td>43°16.286N</td>
<td>04°46.474E</td>
<td>75</td>
<td>2005</td>
<td>1-2</td>
<td>1.02</td>
<td>2074.0</td>
<td>447.3</td>
<td>878.3</td>
<td>31.6</td>
</tr>
<tr>
<td>RHO 0*</td>
<td>43°13.903N</td>
<td>04°50.457E</td>
<td>98</td>
<td>2008</td>
<td>0-1</td>
<td>0.72</td>
<td>2278.7</td>
<td>554.0</td>
<td>1055.1</td>
<td>30.1</td>
</tr>
<tr>
<td>RHO 1*</td>
<td>43°13.903N</td>
<td>04°50.457E</td>
<td>98</td>
<td>2008</td>
<td>1-2</td>
<td>0.72</td>
<td>2360.4</td>
<td>598.2</td>
<td>1133.2</td>
<td>29.3</td>
</tr>
</tbody>
</table>

Figure 1.
Top panel. Map of the Rhône River prodelta indicating the locations of sampling stations, the main deposit entities and the main circulation direction. Circles indicate sampling stations for \( \delta^{13} \text{C} \) and \( \Delta^{14} \text{C} \) (\( \delta^{13} \text{C} \) measured during both cruises). Filled symbols indicate that stations were sampled for \( \Delta^{14} \text{C} \) at both cruises. Crosses indicate stations sampled only for \( \delta^{13} \text{C} \) and just once (April 2007 cruise). The arrow represents the main dispersal system direction.
Bottom panel. Rhône River discharge rates between 2006 and 2009. Sampling points for \( \delta^{13} \text{C}_{\text{POC}} \) (triangles) and \( \Delta^{14} \text{C}_{\text{POC}} \) (diamond) in riverine SPM (Arles monitoring station) are also indicated.
Figure 2. Spatial distribution of $\Delta^{14}C_{OC}$ in the Rhône River prodelta. Values close to 150 ‰ correspond to terrestrial enriched material whereas -400 ‰ indicates continental shelf old material.
Figure 3. Plot of cinnamyl:vanillyl (C/V) vs. syringyl:vanillyl (S/V) phenol ratios for Rhône River sediments. Typical ranges for angiosperm and gymnosperm woody and non-woody tissue are indicated (Hedges and Mann, 1979; Goñi and Hedges, 1992). Open symbols represent the 1-2 cm sediment layer, and the filled symbols represent the 3-4 cm sediment layer. Stations are denoted by letter.
Main dispersal system

this study
Tesi et al (2007; 2010a,b)
Figure 4. Biogeochemical parameters for surface sediment along the main dispersal system. The prodelta is highlighted as a transition zone for main biogeochemical characteristics. The continental shelf displays homogeneous values.
Figure 5. $\delta^{13}\text{OC} - \Delta^{14}\text{OC}$ mixing plot with the Rhône River end-members (bulk and black carbon (BC)) plotted.
Figure 6. Bulk organic carbon (OC), black carbon (BC) and proto-kerogen/BC mixture contents (top) and respective $\delta^{13}C_{OC}$ signatures (bottom) in the Rhône River Suspended Particulate Matter and in the prodelta sediment. The regression line in the bottom panel indicate the trend for the proto-kerogen/BC mixture in the sediment as a function of distance with the river mouth.
Figure 7. $\Delta^{14}C_{OC}$ - sand content correlation (%). The dashed line represents the exponential decay fit to the data. Stations A, B and K from the prodelta are indicated. Plain line figures the linear regression.
Figure 8. Mixing model of $\Delta^{14}C_{OC}$ (●) and $\delta^{13}C_{OC}$ (○) vs. 1/OC. Net loss of terrestrial modern material as OC decrease in the system is indicated by the linear regression lines (dashed – dot for $\Delta^{14}C_{OC}$, and short dashed for $\delta^{13}C_{OC}$). Both the linear regression fit and its 95% confidence interval are represented.
Fig. 9. Results of the mixing model considering 3 end-members: fresh terrestrial material from the Rhône River, a freshly produced marine phytoplankton (referred as marine) and a terrestrial mixture of kerogen-BC material (referred as kerogen-BC). Contributions are reported as fraction of OC.