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Origin of remineralized organic matter in sediments from the Rhone River prodelta (NW Mediterranean) traced by $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ signatures of pore water DIC



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ABSTRACT

Rivers are important links between continents and oceans by transporting terrestrial particulate organic matter (POM) to continental shelf regions through estuaries or deltas and the Mediterranean basin is a good example of this strong linkage. In the vicinity of river mouths, an important fraction of the terrestrial POM settles on the seafloor, sometimes mixed with marine POM, where both can be recycled or buried. In the Rhone River prodelta, previous studies have investigated the origin of the POM in the sediments. They pointed at the large fraction of terrestrial POM in the sediments and the transition to older POM fractions in offshore direction. These studies suggested that terrestrial POM could be an important food source for benthic heterotrophic organisms in this area. In this study, the $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signatures of dissolved inorganic carbon (DIC) and DIC: NH_4^+ ratio in sediment pore water have been measured along a nearshore-offshore transect. The data were compared with available datasets concerning isotopic signature and C:N of the POM in bottom waters and suspended particles from the Rhone River and sediments from its delta, in order to determine which fraction of the POM is actually mineralized. Our results show that a fraction of terrestrial POM corresponding to riverine plankton is preferentially mineralized. Indeed, ^{13}C -depleted riverine POM ($\delta^{13}\text{C} = -25$ to -27‰) which is enriched with ^{14}C ($\Delta^{14}\text{C} = +400$ to $+500\text{‰}$) and shows a C:N < 8 gets mostly mineralized. This isotopic signature differs from that of sediment POM which highlights the selective mineralization already observed in other river deltas. In the Mediterranean context with large human influence in river watersheds such as dam building, our results highlight the importance of riverine primary production versus eroded organic matter in coastal carbon budgets.

Keywords:

Rhone River
River delta
Sediment organic matter
Isotopic signature
Radiocarbon

1. Introduction

River deltas are among the most biogeochemically active areas on Earth (Bianchi et al., 2014; Bianchi and Allison, 2009; Cai, 2011). They receive large amounts of particulate organic matter (POM) from the continent (McKee et al., 2004) and nutrient inputs stimulate high primary production rates in coastal waters (Dagg et al., 2004). These coastal areas also contribute to the global ocean carbon burial by a large amount (>80%; Burdige, 2007) and are, at the same time, considered as net sources of CO_2 to the atmosphere due to their heterotrophic nature (Chen and Borges, 2009). This occurs

in a context of temporal variability linked to hydrological variations of river discharge, interaction with seasonal variability of the ocean and extreme events characterized by floods and storms (Cathalot et al., 2010), typical of the Mediterranean basin.

Deltaic regions are also characterized by very different pools of POM, in both origin and reactivity (Bauer et al., 2013). POM with diverse origins, terrestrial, riverine and marine, and with differential remineralization/burial potentials, influence biogeochemical cycles and therefore the ability of coastal ocean to sequester atmospheric CO_2 (Bianchi et al., 2014). Therefore, a finer view of the reactivity of terrestrial POM is crucial. As an example, the organic matter (OM) from salt marshes or floodplains influences the rate of POM mineralization in coastal regions (Bauer et al., 2013; Cai, 2011), whereas soil OM favors preservation (Tesi et al., 2013);

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recent vegetation provides fresh and reactive organic matter whereas older carbon originating from rock and soil erosion on land (Cathalot et al., 2013; Galy et al., 2008, 2015) is less prone to degradation. In order to close the boundless carbon cycle in river deltas (Battin et al., 2009), a sound knowledge of organic carbon reactivity and burial capacity is required.

POM of different origins generally exhibit different isotopic signatures and elemental C:N ratio (Bianchi and Allison, 2009; Goñi et al., 1998; Lansard et al., 2009; Tesi et al., 2007). In temperate climates, where C3 plants dominate, terrestrial POM has a low $\delta^{13}\text{C}$ signature, ranging between -28‰ and -26‰ , compared to marine POM, with a $\delta^{13}\text{C}$ between -22‰ and -17‰ (Burdige, 2006; Goñi et al., 1998). $\Delta^{14}\text{C}$ signature of OM delivered by rivers displays a high range of variation from -980 to $+100\text{‰}$ which is influenced by the signal of the drainage basin, the soil residence time, vegetation cover and nuclear activities along the river (Cathalot et al., 2013 and references therein; Raymond and Bauer, 2001a, 2001b). In contrast, the range of $\Delta^{14}\text{C}$ signature in marine OM is much more restricted with values between -45 and $+110\text{‰}$ (Wang et al., 1998). The C:N ratio of POM is a third trait often used to differentiate between OM pools. Generally, the organic matter of marine origin has a lower C:N ratio (5–10) than terrestrial OM (14–500) (Burdige, 2006).

The isotopic composition of dissolved inorganic carbon (DIC) in sediment pore water partly results from POM mineralization. It thus provides indications about the type of OM that undergoes mineralization and about actual diagenetic processes (Aller et al., 2008; Aller and Blair, 2004). The mineralization of OM does not fractionate carbon isotopes (Bickert, 2006) and DIC can thus integrate the isotopic signal of OM mineralization (Zetsche et al., 2011), provided that other mechanisms such as precipitation/dissolution of carbonate or methane production/oxidation are negligible. The dual isotope ($^{13}\text{C}/^{14}\text{C}$) technique applied in pore water DIC and coupled to mixing models can be used to assess simultaneously the origin and reactivity of mineralized organic matter in marine sediments (Aller et al., 2008).

The Rhone River is the largest contributor of water and terrestrial POM to the NW Mediterranean (Pont et al., 2002) and discharges in the Gulf of Lions (Sempéré et al., 2000; UNEP/MAP/MED-POL, 2003). Its drainage basin hosts 14 nuclear power reactors grouped in 4 nuclear plants and a former reprocessing plant which legally discharge effluents containing ^{14}C in the Rhone River (Eyrolle et al., 2015). This enriched ^{14}C (mostly in the form of DIC) can be transferred to vegetation and river phytoplankton (Fontugne et al., 2002; Coularis, 2016) and can be used as a tracer of in stream production. It was also reported using a suite of biomarkers that the contribution of freshwater algae in the River and surficial sediments of the delta was substantial in the spring (Cathalot et al., 2010; Harmelin-Vivien et al., 2010; Bourgeois et al., 2011; Galeron et al., 2015). Previous studies indicated that terrestrial POM accounts for more than 85% in the sediments from the Rhone River prodelta (Cathalot et al., 2013; Lansard et al., 2009), but showed a small influence of this nuclear radiocarbon in the solid phase. Based on correlations between organic matter mineralization and terrestrial carbon fraction, these studies suggested that terrestrial OM contributes in a significant way to the mineralization processes in the prodelta sediments, close to the river mouth (Cathalot et al., 2010; Lansard et al., 2009; Pastor et al., 2011). As a result, the origin of the mineralized POM in deltaic sediments at the Rhone River mouth remains unclear.

The objective of this paper is to constrain the origin of the POM fraction mineralized in the Rhone prodelta sediment using isotopic and elemental ratio. Therefore, we measured the $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ isotopic signature of DIC and the C:N ratio in sediment pore waters along a transect from the river mouth towards the continental

shelf. By using a mixing model and comparing its endmembers with the isotopic signatures and C:N ratio of POM in the river suspended matter, we estimate which OM fraction transported by the Rhone River is actually mineralized in prodelta sediments. We then discuss the origin of POM in other large Mediterranean Rivers (Po, Ebro) and compare the human activity impact on POM discharge. Identifying the dominant OM sources for mineralization gives a better understanding of reactivities and importance of different OM pools in coastal carbon budgets, which are among the main objectives of Mermex through its WP3 (“River-Sea connection including extreme events”).

2. Material and methods

2.1. Sampling site

The Rhone River prodelta is a microtidal environment (Got and Aloisi, 1990) with a river plume mostly oriented southwestwards (Estournel et al., 1997). Its drainage basin is dominated by ancient soils and carbonates that lead to a naturally low $\Delta^{14}\text{C}$ signature of DIC and suspended particles. The natural $\Delta^{14}\text{C}$ signature of riverine primary production, which should be low, is actually increased by the presence of nuclear power plants that release ^{14}C -rich effluents mostly under the DIC form into the Rhone River (Eyrolle et al., 2015), which can rapidly be incorporated into POC by photosynthesis in the river as shown in the Loire River (Coularis, 2016).

Therefore, the organic matter in the suspended particles in the Rhone River has a variable $\Delta^{14}\text{C}$ ranging from -90 to $+150\text{‰}$ (Cathalot et al., 2013; Toussaint, 2013). It also displays a mean $\delta^{13}\text{C}$ isotopic signature of $-27.1 \pm 0.6\text{‰}$ (Cathalot et al., 2013; Higuera et al., 2014; Kerhervé et al., 2001; Toussaint, 2013).

From the river outlet to the continental shelf break, the Rhone River prodelta can be divided into three main areas that differ in water depth and sedimentation rate: The proximal, the prodelta and the distal domains (Got and Aloisi, 1990). The proximal domain is characterized by high sedimentation rates ranging from 30 to 40 cm yr^{-1} (Charmasson et al., 1998). With increasing distance from the river mouth, the sedimentation rates decrease rapidly to 1–10 cm yr^{-1} and then to 1 cm yr^{-1} in the prodelta domain (Radakovitch et al., 1999a, 1999b) and to values below 1 cm yr^{-1} in the distal domain (Miralles et al., 2005). In this paper, we group the proximal and the prodelta domain under the name prodelta as they show common characteristics regarding the origin of POM mineralization.

About 80% of the riverine material is deposited at least temporarily close to the river mouth (Cathalot et al., 2010; Lansard et al., 2009; Roussiez et al., 2005). Bourgeois et al. (2011) showed that 97% of POM in prodelta sediments contains fatty acids that are typical of land-derived OM and Tesi et al. (2007) showed that POM has a terrestrial $\delta^{13}\text{C}$ signature mostly from C3 type material (see also Cathalot et al., 2013). As demonstrated by Antonelli et al. (2008) and Cathalot et al. (2010) flood events account for the majority of the particle deposition at the seafloor in the prodelta area and can influence the organic matter recycling in the sediments. Consequently, the sediment respiration rates are highest close to the river mouth and decrease in offshore direction.

The DICASE cruise took place from 2nd to 11th June 2014, onboard the RV Téthys II, after 2 months of low water discharge from the Rhone River. During this expedition, contrasted sediment sites along the river plume were investigated and are reported in Fig. 1 and in Table 1. The stations A and Z are situated just in front of the river mouth, station AK is situated further away in the prodelta domain and station C is located close to the continental shelf break.

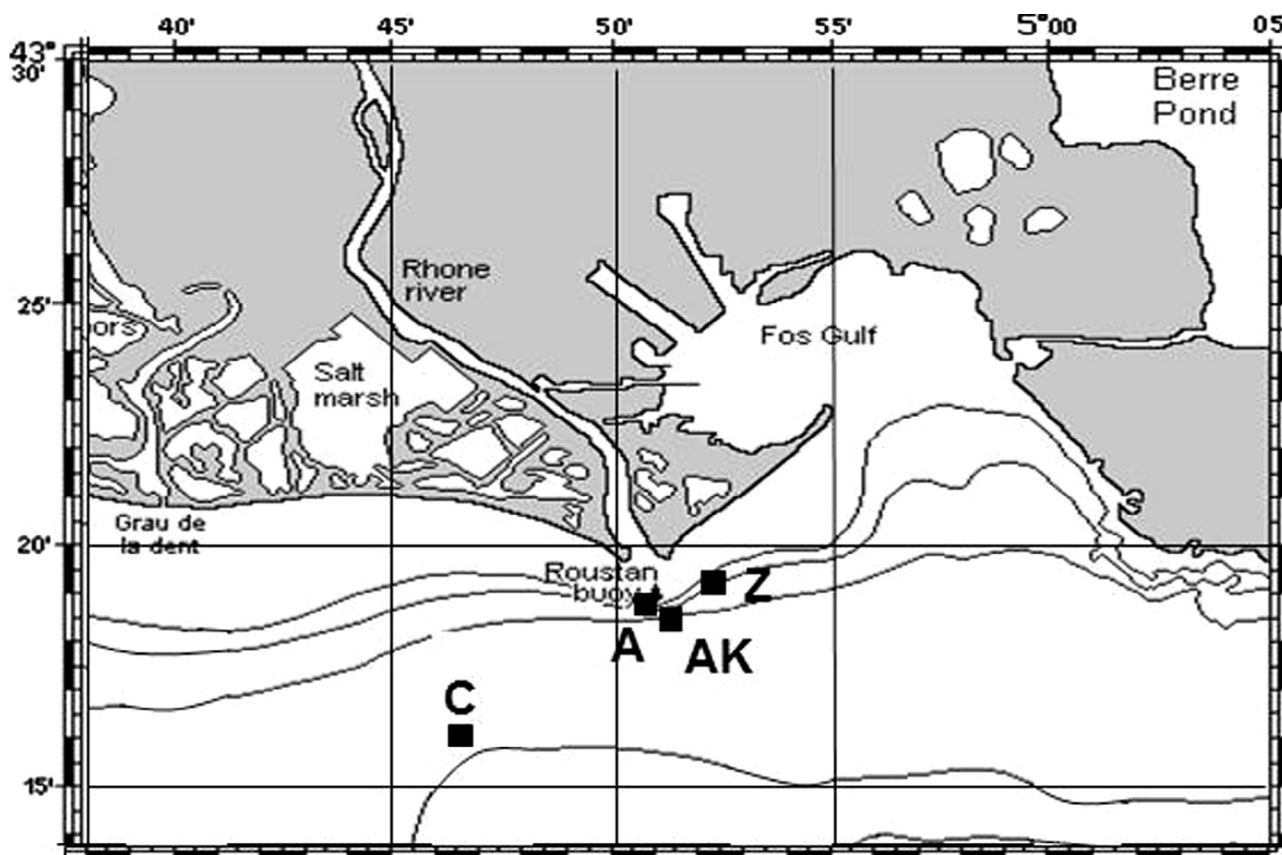


Fig. 1. Map of the Rhone River prodelta and adjacent shelf with the investigated stations. The main characteristics of the sampling sites are given in Table 1.

Table 1
Sampling sites and main characteristics of the bottom water. The $\delta^{13}\text{C}$ -DIC and $\Delta^{14}\text{C}$ -DIC values correspond to the signature of bottom water DIC. The $\delta^{13}\text{C}$ signature was measured on overlying water during the DICASE cruise, the $\Delta^{14}\text{C}$ bottom water values at station Z and AK during the AMORAD-II cruise in December 2014.

Station	Lat. (°N)	Long. (°E)	Depth [m]	Temp. [°C]	Salinity	DIC [$\mu\text{mol l}^{-1}$]	$\delta^{13}\text{C}$ -DIC [‰]	$\Delta^{14}\text{C}$ -DIC [‰]
A	43.312	4.851	18	16.8	38.2	2323 ± 4		
Z	43.317	4.865	18	16.6	38	2330 ± 1	−1.9	41
AK	43.307	4.856	48	15.8	38.1	2335 ± 4		36
C	43.271	4.773	75	14.4	38.2	2354 ± 2	−2.2	

2.2. Sediment coring and pore water extraction

Sediment cores were taken with a gravity corer (60 and 90 cm length and 9 cm inner diameter). Sediment pore water samples were extracted using 5 cm long rhizons every 2 cm (Seeberg-Elverfeldt et al., 2005). Samples were put into 15 ml Pyrex glass ampoules for the $\Delta^{14}\text{C}$ analysis and into 4 ml glass vials with a rubber septum for the $\delta^{13}\text{C}$ analysis. The vials for $\Delta^{14}\text{C}$ samples have been previously burned at 450 °C for 5 h and were sealed after sampling with a welding torch. After sealing, the samples were frozen (−20 °C) onboard following Aller et al. (2008). The $\delta^{13}\text{C}$ samples were poisoned with a saturated solution of HgCl_2 . Pore waters for DIC analysis were sampled into 14 ml Falcon tubes and were analyzed onboard within 6 h after sampling. Ammonium samples were stored in 2 ml Teflon tubes and frozen at −20 °C until analysis.

2.3. Bottom water samples

Seawater and bottom water were sampled with a 12 L Niskin bottle. DIC samples were stored in 50 ml Falcon tubes and analyzed onboard within 6 h. Samples for isotope analysis were stored in

previously burned 250 ml Pyrex bottles and poisoned with HgCl_2 . Since the spatial distribution of the stations is limited and the bottom water shows constant salinity (>38‰) indicating little mixing with other water masses, only two samples of bottom water were analyzed for $\delta^{13}\text{C}$ on water overlying the cores (station Z and C). The samples for the determination of bottom water $\Delta^{14}\text{C}$ -DIC were collected during the AMORAD-II (December 2014) on two stations (Z and AK) at similar salinity (>38‰).

2.4. Analysis and data treatment

At each station, pore waters from one core were used for DIC and NH_4^+ measurements and pore waters from a second core were used to measure the isotopic DIC signatures. Concentrations of DIC in both bottom waters and in sediment pore waters were measured with a DIC analyzer (<aS-C3, Apollo SciTech®) on 1 ml sample volumes at 25 °C (Rasmann et al., 2016). The DIC analyzer was calibrated twice a day using certified reference material (CRM-batch no. 122, provided by A. Dickson, Scripps Institution of Oceanography, UC San Diego). The precision of this method was ±0.5% of the final DIC value. Concentrations of NH_4^+ were analyzed after appropriate dilution by a colorimetric method following

Koroleff's work and reported in Grasshof et al. (1983). The uncertainty of the method is about 5%.

The $\delta^{13}\text{C}$ signatures of DIC ($\delta^{13}\text{C}\text{-DIC}$) have been measured at the Royal Netherlands Institute for Sea Research (NIOZ). A head-space was created in the sample vials, CO_2 was extracted via acidification with 99% H_3PO_4 and the ratios of the carbon isotopes were measured by isotope ratio mass spectroscopy (IR-MS) right after extraction (Pozzato et al., 2013). The isotopic ratio $^{13}\text{C}/^{12}\text{C}$ is reported on the $\delta^{13}\text{C}$ notation and is expressed relative to the V-PDB standard in ‰:

$$\delta^{13}\text{C} = \left[\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} - 1 \right] * 1000 \quad (1)$$

Precision of the isotopic measurements are $\pm 0.3\%$. By stripping the CO_2 out of the samples, the NIOZ provides a DIC concentration with a precision of $\pm 5\%$ together with the isotopic signatures. These DIC values have been used in the equations to determine the signature of the source of OM as they were measured on the same samples as the $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ isotopes.

The $\Delta^{14}\text{C}$ analyses were carried out at the LMC-14 (Saclay, France). The CO_2 from the DIC of the porewaters sampled was extracted by adding 2 ml of 85% phosphoric acid (H_3PO_4) in a full glass extraction line (Dumoulin et al., 2013), transformed into graphite and then measured on the ARTEMIS national facility with the Accelerator Mass Spectroscopy (AMS) method. The $\Delta^{14}\text{C}$ concentrations were corrected for the sampling time (in ‰):

$$\Delta^{14}\text{C} = \left[\frac{\text{PMC}}{100} e^{\lambda(\text{date measure} - \text{date sampling})} - 1 \right] * 1000 \quad (2)$$

with λ = disintegration constant of ^{14}C ($3.8 \cdot 10^{-12} \text{ s}^{-1}$) and

$$\text{PMC} = 100 * \frac{A_{\text{na}}}{A_{\text{std}}} \quad (3)$$

where A_{na} is the normalized ^{14}C activity of the sample and A_{std} the activity of the standard 'oxalic acid II' in 1950. The uncertainty of the final $\Delta^{14}\text{C}$ value is $\pm 3\%$. In parallel, ^{14}C free charcoal blanks have been used to validate the method (Dumoulin et al., 2013).

2.5. Isotopic signature of the metabolic DIC fraction

The DIC in sediment pore water is a mixture of bottom water DIC and metabolic DIC produced by diagenetic processes. To determine the signature of the DIC resulting from internal sediment processes, it is necessary to take this mixing into account. Aller and Blair (2004) and Aller et al. (2008) generalized the mixing model by Bauer et al. (1995) and provided a mathematical model to determine the isotopic signature of the diagenetically-added DIC pool. Assuming a mixture of different sample components of distinct DIC concentrations (C_i), having an isotopic signature (P_i), the following relation holds (if concentrations are normalized to total pore water volume or total sediment weight):

$$P_{\Sigma} C_{\Sigma} = \sum_{i=1}^n P_i C_i \quad (4)$$

with $P_{\Sigma} C_{\Sigma}$ being the product of the observed pore water DIC concentration (C_{Σ}) by the property (P_{Σ} either $\Delta^{14}\text{C}$ or $\delta^{13}\text{C}$). C_{Σ} is the sum of the concentrations of all components:

$$C_{\Sigma} = \sum_{i=1}^n C_i \quad (5)$$

If a concentration ΔC_{Σ} (DIC of another signature P_{Δ}) is added to the mix (C_{Σ}), the mixture becomes:

$$P_{\Sigma} C_{\Sigma} = \sum_{j=1}^n P_j(i) * C_j(i) + P_{\Delta} \Delta C_{\Sigma} \quad (6)$$

where P_{Δ} is the signature of the DIC added that leads to a progressive variation of the total DIC concentration of ΔC_{Σ} and $P_j(i)$ and $C_j(i)$ the initial concentration and properties of the mix. After rearrangement, this gives

$$(dP_{\Sigma} C_{\Sigma}) / dC_{\Sigma} = P_{\Delta} + (dP_{\Delta} / dC_{\Sigma}) * \Delta C_{\Sigma} \quad (7)$$

Eq. (7) represents the regression of a $P_{\Sigma} C_{\Sigma}$ versus C_{Σ} plot, in which the slope P_{Δ} gives the isotopic signature of the organic matter that was mineralized to produce the metabolic DIC. In the present study, we use this relation to determine the isotopic signature of the OM remineralized into pore water DIC, and therefore to constrain its origin.

3. Results

Table 1 displays the position and main bottom water characteristics of the stations investigated during the DICASE cruise. The 4 stations are located in front of the river mouth at a depth ranging from 18 to 75 m. Bottom water salinity is fairly constant between 38 and 38.2 and temperature varies from 15.8 to 16.8 °C. Bottom water DIC concentrations range between 2323 and 2354 $\mu\text{mol l}^{-1}$. The two samples of bottom water analyzed for $\delta^{13}\text{C}\text{-DIC}$ show the typical marine value of -2.2 to -1.9% . Two samples were analyzed for $\Delta^{14}\text{C}$ signature showing very similar values of +41 and +36‰.

3.1. The chemistry of pore waters

At stations A and Z, the DIC concentrations increase with sediment depth and reach up to about 40 mmol l^{-1} in the first 20 cm of the sediment and 50 mmol l^{-1} at 30 cm depth (Fig. 2a). At station AK, the DIC concentration increases a bit slower and reaches 20 mmol l^{-1} at the bottom of the profile. The weakest DIC gradient is observed at station C and leads to a maximum DIC concentrations of 7 mmol l^{-1} at the bottom of the profile.

The same distribution is observed for NH_4^+ concentrations (Fig. 2b). The production of ammonium is strongest at stations A and Z where NH_4^+ concentration reaches 3.5 mmol l^{-1} at 30 cm depth. In offshore direction, the NH_4^+ gradients in the porewaters decrease. At station AK and C, a NH_4^+ concentration of only 0.5 mmol l^{-1} is reached at 20 cm depth.

The ratio of produced DIC to produced NH_4^+ ($\Delta\text{DIC}:\Delta\text{NH}_4^+$) varies in the pore waters of the Rhone River prodelta (Fig. 3), where Δ represents the concentration difference between pore water at a given depth z and bottom water. As DIC and NH_4^+ diffuse with different rates in pore waters (D_s), this ratio has been corrected for molecular diffusion according to Berner (1980) and using his diffusion coefficients:

$$\frac{\Delta\text{DIC}}{\Delta\text{NH}_4^+} = \frac{\text{DIC}_{(z)} - \text{DIC}_{(\text{BW})}}{\text{NH}_4^+_{(z)} - \text{NH}_4^+_{(\text{BW})}} * \frac{D_s(\text{DIC})}{D_s(\text{NH}_4^+)} \quad (8)$$

With $D_{\text{NH}_4^+} = 19.8 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $D_{\text{HCO}_3^-} = D_{\text{DIC}} = 11.8 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 25 °C following Li and Gregory (1974).

This $\frac{\Delta\text{DIC}}{\Delta\text{NH}_4^+}$ is the signature of the C:N ratio of the mineralized OM. As a general pattern, the $\Delta\text{DIC}:\Delta\text{NH}_4^+$ ratio decreases seawards from the river mouth. At most stations, except station C, the $\frac{\Delta\text{DIC}}{\Delta\text{NH}_4^+}$ ratio increases with depth with some variability. At station A and Z, the ratio increases in the first 30 cm of the sediment from 6.5 to 8.5. At station AK, the $\Delta\text{DIC}:\Delta\text{NH}_4^+$ ratios are lower: they first decrease from 5.2 to 4.5 and increase to 6.9. At station C this ratio scatters around 5.0.

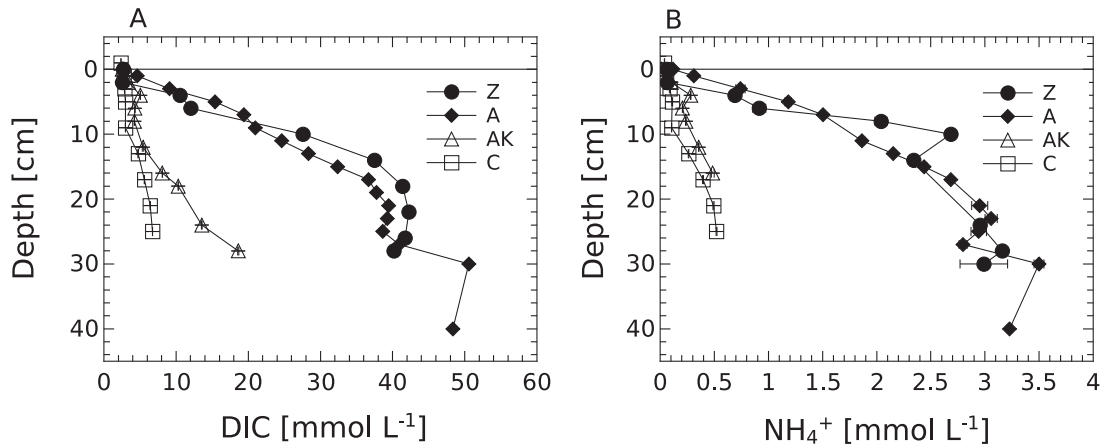


Fig. 2. Vertical concentration profiles of (a) dissolved inorganic carbon (DIC) and (b) ammonium (NH_4^+) in sediment pore water measured at stations A and Z, located close to the river mouth, station AK in the prodelta and station C on the continental shelf.

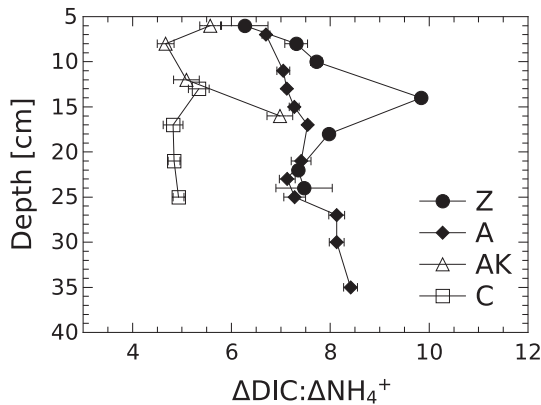


Fig. 3. $\Delta\text{DIC}:\Delta\text{NH}_4^+$ pore water ratio (i.e. corrected by diffusion) at the investigated stations.

The DIC profiles measured at the same stations by LSCE and NIOZ are very similar, but not identical (Fig. 4), especially at station C. At this station, the difference between the two profiles is important at depth. In the core measured onboard, the DIC concentration increases to 7 mmol l^{-1} , whereas it shows a maximum in the NIOZ core of 3.1 mmol l^{-1} at 18 cm depth and decreases below to reach the bottom water concentration.

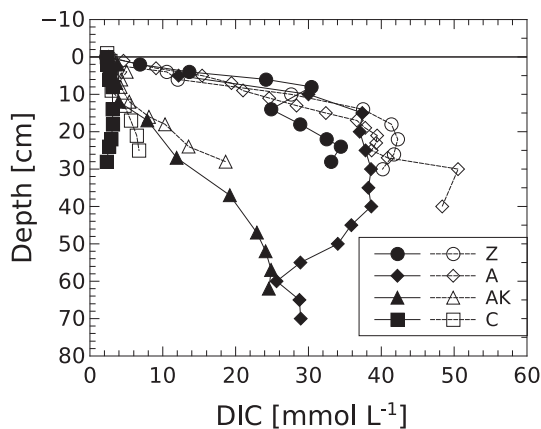


Fig. 4. Comparison of pore water DIC concentrations measured by LSCE and NIOZ. The pore water samples were collected at the same stations, but on different sediment cores.

At all the investigated stations, the $\delta^{13}\text{C}$ -DIC decreases with depth into the sediment (Fig. 5). At stations A and Z, $\delta^{13}\text{C}$ -DIC values of -25‰ are reached in the first 10 cm of the sediment and remain constant until a slight increase below 60 cm. At station AK, the $\delta^{13}\text{C}$ -DIC decreases in a relatively constant manner to very low values of -33‰ at 65 cm depth. At station C, pore water DIC is less depleted in $\delta^{13}\text{C}$ than at the other stations. Between 5 and 25 cm, the values scatter around -7‰ and increase below to reach the bottom water signal at 28 cm depth (in agreement with DIC concentrations from the same core, Fig. 4).

Similarly, sediment pore waters are enriched with ^{14}C isotopes and the profiles measured at station A, Z and AK seem to be very similar. Pore waters have $\Delta^{14}\text{C}$ -DIC values between $+400$ and $+450\text{‰}$ at 30 cm depth (Fig. 5) much larger than bottom waters which show $\Delta^{14}\text{C}$ -DIC values around $+40\text{‰}$ (Table 1). At station C, only two data points are available at 7 and 26 cm depth with much lower $\Delta^{14}\text{C}$ -DIC values of $+97$ and $+35\text{‰}$, respectively.

3.2. Isotopic signature of the mineralized OM

Following Aller et al. (2008), the isotopic signatures of the POM fractions that have been mineralized were identified by the slopes of the $\delta^{13}\text{C}^*/\text{DIC}$ versus DIC curve (Fig. 6) and $\Delta^{14}\text{C}^*/\text{DIC}$ versus DIC curve (Fig. 7). The regression slope provides the signature of the source of metabolic DIC. At stations A, Z and AK, the $\delta^{13}\text{C}$ signature of the mineralized OM varies between -27.4‰ and -25.4‰ and $\Delta^{14}\text{C}$ between $+409$ and $+498\text{‰}$. At station AK, a secondary slope is visible on the $\delta^{13}\text{C}$ plot (Fig. 6) with a value of -81‰ . At station C, the average $\delta^{13}\text{C}$ value of the mineralized OM equals -22.1‰ (see Table 2). There are not enough data points and the scatter is too large to determine the $\Delta^{14}\text{C}$ value of the mineralized OM at this station.

4. Discussion

4.1. Metabolic pathways of OM mineralization

The $\Delta\text{DIC}:\Delta\text{NH}_4^+$ ratio in pore water reflects the C:N ratio of the mineralized POM pool. The strong DIC and NH_4^+ gradients observed in the pore waters (Fig. 2a and b) result from high mineralization rates. The two sets of profiles have the same shape which shows a close coupling between DIC and NH_4^+ production during anoxic mineralization. The $\Delta\text{DIC}:\Delta\text{NH}_4^+$ ratio shows two different trends: an increase with depth in the sediments and a decrease in offshore direction (Fig. 3). The increase of $\Delta\text{DIC}:\Delta\text{NH}_4^+$ with depth can be

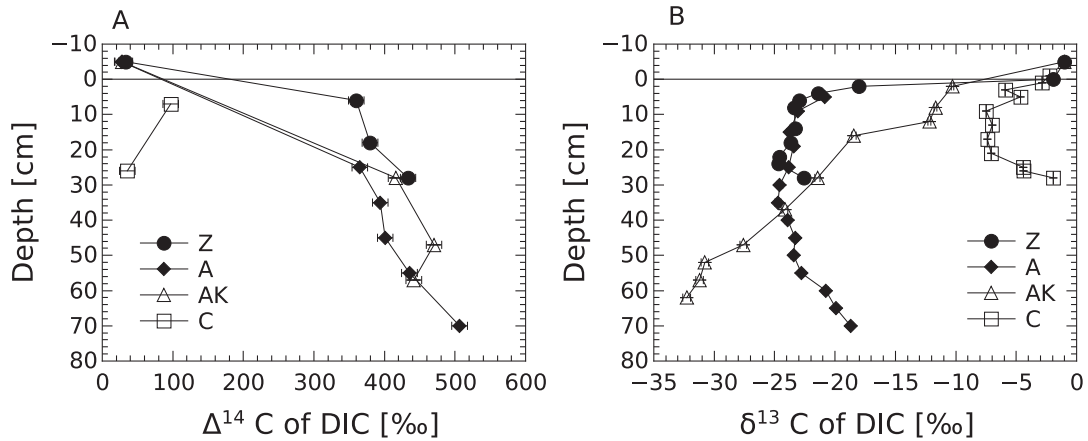


Fig. 5. Vertical distribution of $\delta^{13}\text{C}$ (a) and $\Delta^{14}\text{C}$ (b) of pore water DIC.

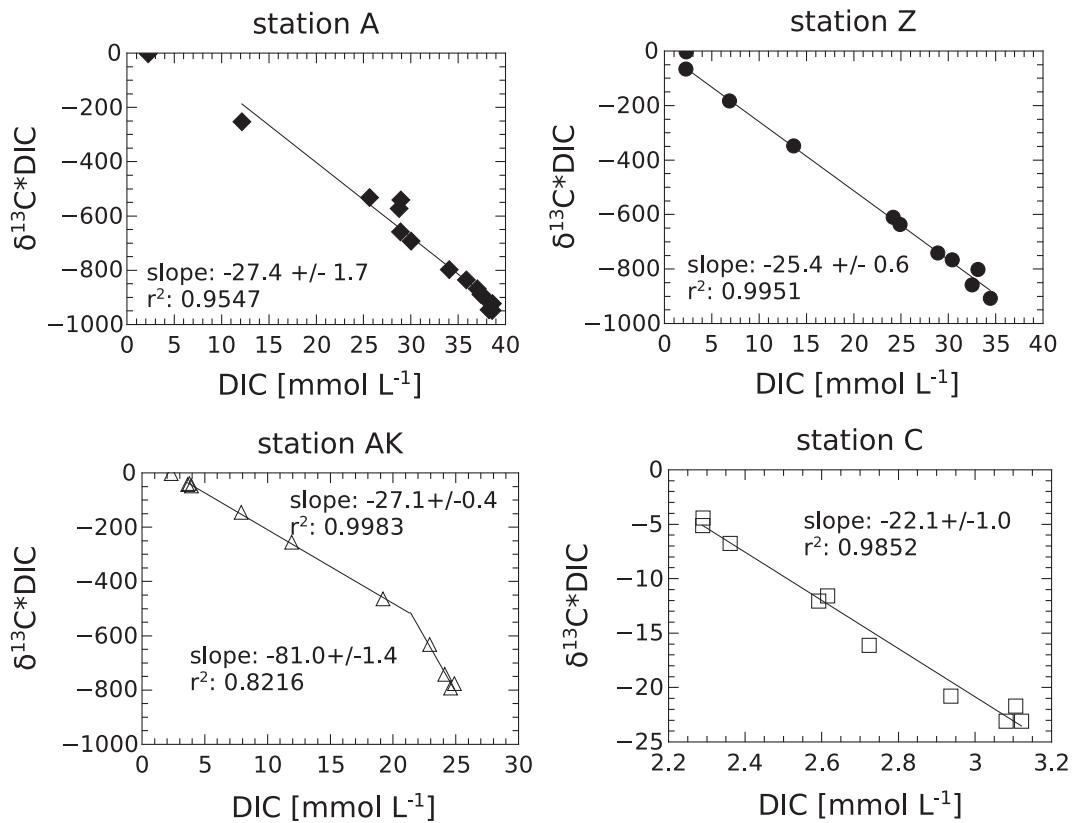


Fig. 6. $\delta^{13}\text{C}$ pore water mixing plots. Following Aller et al.'s model (2008), the slope indicates the signature of the OM which was remineralized to produce the measured DIC.

related either to (i) an increase of DIC production without production of NH_4^+ by carbonate dissolution or methane oxidation (Burdige, 2006), or to (ii) preferential mineralization of N-rich organic matter in upper sediment layers by the benthic community and changes in the OM composition with sediment depth, also due to macro and meiofauna bioturbation and bioirrigation.

Carbonate dissolution can be excluded for the anoxic part of the sediments, as carbonate precipitation occurs in this zone, consuming DIC. Rassmann et al. (2016) showed that at stations A and Z up to 10 mmol l^{-1} of Ca^{2+} is consumed in the first 20 cm of the sediments by carbonate reprecipitation which could reduce pore water DIC by up to 10 mmol l^{-1} . Compared to the measured DIC concentrations of up to 40 mmol l^{-1} , this could indicate that the ΔNH_4^+ pore water ratio underestimates the C:N ratio of the miner-

alized OM by up to 20%. This would raise the C:N ratio at station A and Z from 7.5 to 9.

Oxidation of methane, either aerobic or anaerobic, could potentially occur at depth in these sediments, since methane has been detected at shallow sediment depth (Garcia-Garcia et al., 2006; Rassmann et al., in prep.). As methane is generally depleted in ^{13}C carbon isotopes, with typical signatures of $\delta^{13}\text{C}\text{-CH}_4 \leq -50\text{‰}$ (Alperin et al., 1992; Boehme et al., 1996; Whiticar, 1999), its oxidation should produce depleted $\delta^{13}\text{C}\text{-DIC}$ in pore water. On the contrary, pore water DIC at stations A and Z is enriched with ^{13}C below 40 cm (Fig. 5a) which probably indicates metabolic methane formation, as it produces ^{13}C -enriched DIC together with ^{13}C -depleted CH_4 . The ^{13}C depletion of DIC is observed only at station AK, at the bottom of the pore water profile with a source value

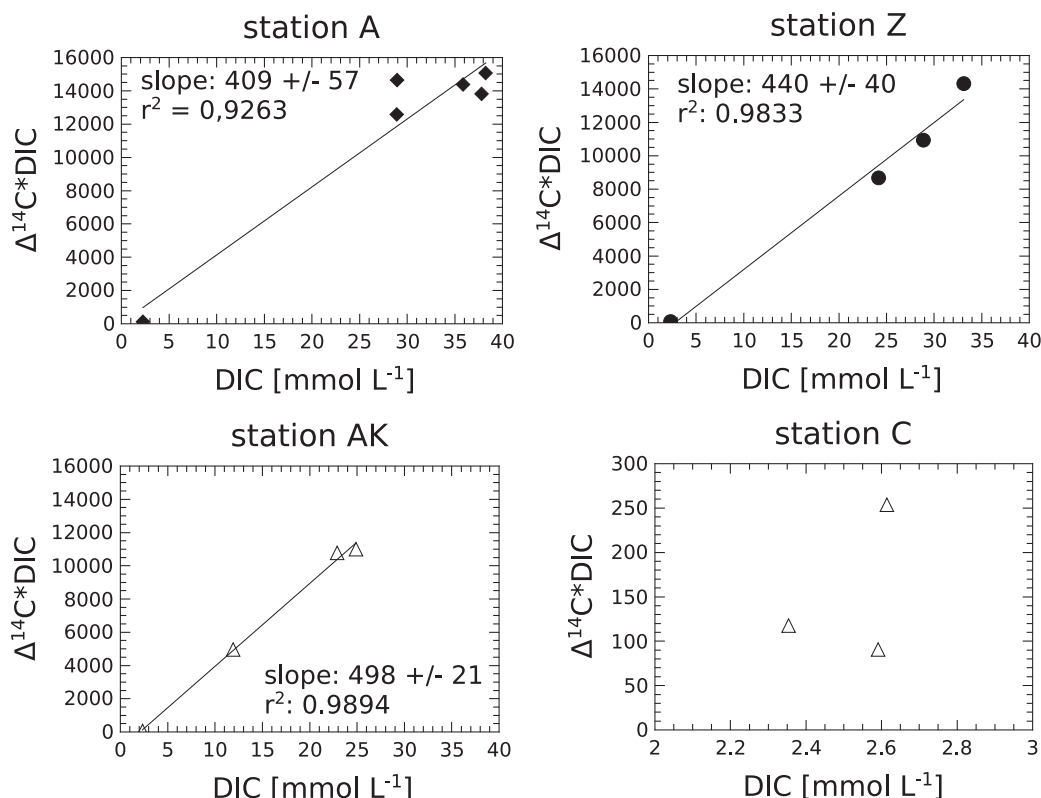


Fig. 7. $\Delta^{14}\text{C}$ pore water mixing plots. Following Aller et al.'s model (2008), the slope indicates the signature of the OM which was remineralized to produce the measured DIC. At station C (different scale) not enough data points are available to perform a linear regression.

Table 2
Average C:N and isotopic signature of remineralized organic matter (ref. Figs. 3, 6 and 7).

Station	C:N	$\delta^{13}\text{C}$ [‰]	$\Delta^{14}\text{C}$ [‰]
A	7.5 ± 0.5	-27.4 ± 1.7	$+409 \pm 57$
Z	7.7 ± 1.1	-25.4 ± 0.6	$+440 \pm 40$
AK	5.6 ± 1.0	-27.1 ± 0.4	$+498 \pm 21$
C	5.0 ± 0.2	-22.1 ± 1.0	/

as low as -81% , pointing towards potential methane oxidation at this station. ^{13}C -poor methane diffusing from below is probably oxidized at depth, creating relatively light $\delta^{13}\text{C}$ -DIC. As a conclusion, except at station AK, the production of DIC by processes which do not generate NH_4^+ is very unlikely.

The most likely explanation for the downward increase in $\Delta\text{DIC}:\Delta\text{NH}_4^+$ is therefore the preferential degradation of N-rich OM, in which fauna and microorganisms prefer to digest N-bearing compounds of OM (Fenschel et al., 2012). This differential mineralization modifies the OM composition and increases the C:N ratio of POM with sediment depth. Such modification due to the metabolic preferences of the benthic community is then reflected by the increasing $\Delta\text{DIC}:\Delta\text{NH}_4^+$ pore water ratios (Burdige, 2006).

Another striking feature of the Rhone prodelta and shelf is the offshore decrease of average porewater $\Delta\text{DIC}:\Delta\text{NH}_4^+$ ratio, from 7.5–7.7 to 5.0–5.6 (Table 2). This decrease offshore could be attributable to the increased mineralization of N-rich marine POM on the shelf compared to the N-depleted land-derived POM near the river mouth. Indeed, as pointed out by (Cloern et al., 2002), marine and freshwater phytoplankton display low C:N of 6–7 whereas larger C:N values generally occur for vascular plant debris with values above 14 (Goñi et al., 2003) and soil OM with values between 8 and 14 (Tesi et al., 2007). Very low values down to 4 are generally

associated to large microbial biomass (Hedges and Oades, 1997). Our average ratio for stations AK and C vary between 5.6 and 5.0 respectively (Table 2) which indicates mineralization of a mix of phytoplankton and bacteria. Indeed, Bourgeois et al. (2011) using biomarkers showed that the sediment organic matter on the shelf contains an assemblage of bacteria and degraded phytoplankton. In the proximal zone, the $\Delta\text{DIC}:\Delta\text{NH}_4^+$ ratio is larger with an average of 7.6. For these stations located near the River mouth, it indicates that mineralization does not imply vascular plant debris (with C:N > 14) and is in the lowest range of soil OM. Indeed, to explain the low values found, it must include mineralization of freshwater or marine plankton.

Carbon stable isotopic composition is a useful tool to define the source of organic matter mineralized in prodelta and shelf sediments. Using $\delta^{13}\text{C}$ analysis on the solid phase, previous studies (Tesi et al., 2007; Lansard et al., 2009; Cathalot et al., 2013) demonstrated that the proportion of terrestrial POM in surface sediments around the proximal domain (stations A and Z) is superior to 80%. In this domain, early diagenesis occurs under very high sedimentation rates (Charmasson et al., 1998) and the $\delta^{13}\text{C}$ signature of surface sediment is very similar to that of the SPM particulate matter exported by the Rhone River (Cathalot et al., 2013). The pore water DIC, mostly originating from OM mineralization shows also depleted $\delta^{13}\text{C}$ signatures similar to those of the SPM and the POM (Fig. 8), confirming the prevalent terrestrial origin of the mineralized OM. When C:N and $\delta^{13}\text{C}$ are combined (Fig. 8), the mineralized OM in prodelta sediments (AK) is within the riverine algae domain whereas it falls at the limit between the domain of riverine algae and soil-OM at proximal stations (A and Z).

Moving seaward (station C), the $\delta^{13}\text{C}$ signature of the pore water DIC increases to -22% , which points towards a prevalence of marine POM mineralization in the sediment at this station. This is compatible with the findings of Cathalot et al. (2013) who

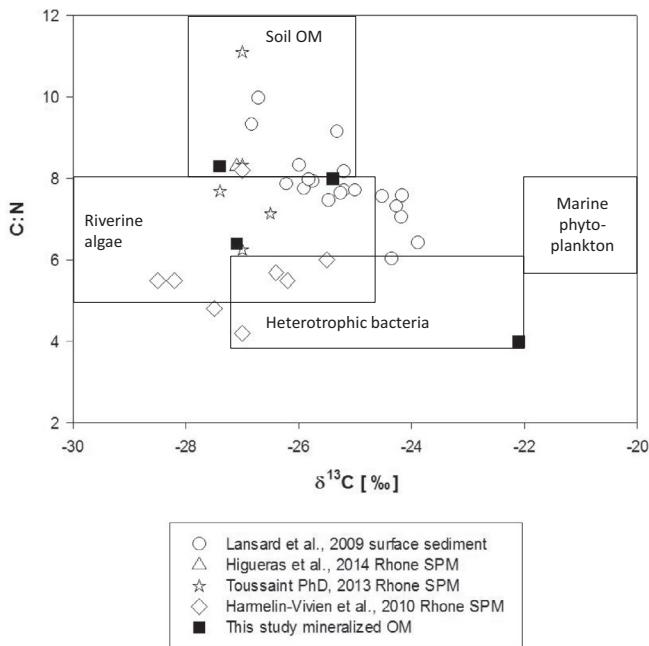


Fig. 8. Comparison of $\delta^{13}\text{C}$ signature and C:N ratio of surface sediments and suspended particles in the Rhone River measured during previous studies and the signature of the mineralized OM calculated in this study.

conducted an extensive analysis of the Rhone delta and shelf sediments measuring POM ^{13}C and ^{14}C signature. They reported a dominant aged OM fraction in shelf sediments including station C, with high contents of black carbon (up to 50%) and no indications of fresh marine POM despite the river plume production. The $\delta^{13}\text{C}$ -DIC of -22‰ could thus indicate that most of the marine material with a $\delta^{13}\text{C}$ of -19 to -21‰ (Harmelin-Vivien et al., 2010) is actually mineralized leaving refractory fractions (soil and black carbon) in the sediments.

4.2. The importance of riverine primary production in the local carbon cycling

The dual carbon isotope method based on $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ signatures of porewater DIC allows to better identify the fraction of POM that undergoes mineralization (Aller et al., 2008; Aller and Blair, 2004, 2006) among the various types of POM, from soils, riverine primary production and marine plankton. The correct use of isotopic signature ($\delta^{13}\text{C}$) and radiocarbon ($\Delta^{14}\text{C}$) to analyze sediment and pore water samples can however be impaired by potential contamination during sampling, handling and measurement. Despite the high $\Delta^{14}\text{C}$ values measured by this study in the pore waters at station A, Z and AK, we can rule out such contamination because the measurements blanks prepared with the samples were very low (close to their certified values, Dumoulin et al., in prep.) and low $\Delta^{14}\text{C}$ values were measured at station C and in the bottom waters. Therefore, such a contamination can be firmly excluded.

A limited set of data exist for the $\Delta^{14}\text{C}$ signature of the Rhone River POM. Cathalot et al. (2013) reported a range between -90 and $+150\text{‰}$ for river flows above $2000\text{ m}^3/\text{s}$, but in extreme cases with low water discharge, enrichments up to $+596\text{‰}$ have been measured (Toussaint, 2013). Eyrolle et al. (2015) reported maximal activities of $+300\text{‰}$ in the Rhone River POM. The comparison of the $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signatures of pore waters, surface sediment and SPM in the Rhone River and in the delta together with literature data shows that the organic matter mineralized in prodelta sediments lies outside the known pools (Fig. 9). Indeed, as quoted above, its

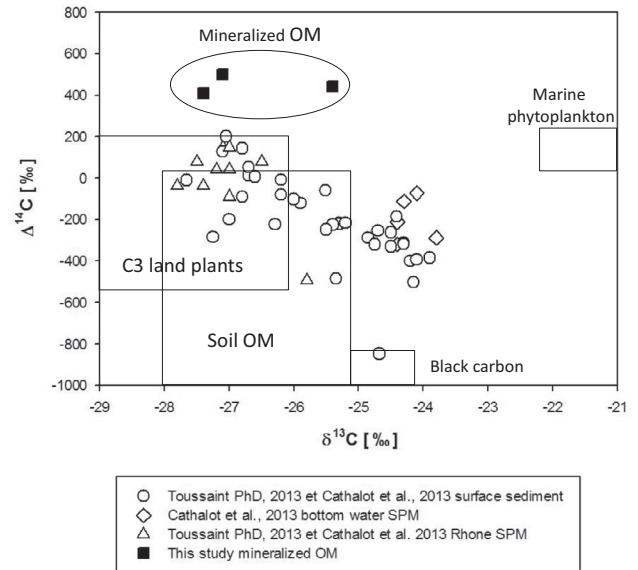


Fig. 9. Comparison of $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signature of surface sediments and suspended particles in the Rhone River measured during previous studies and characteristics of mineralized OM determined with the slopes of Figs. 6 and 7.

$\delta^{13}\text{C}$ signature is very similar to that of the Rhone River particles, demonstrating the high percentage of material discharged by the river in the sediments of this zone. But the $\Delta^{14}\text{C}$ signature of mineralized OM is much higher than the bulk sediment (Fig. 9) or Rhone average SPM. The only plausible source for the high $\Delta^{14}\text{C}$ is in-stream primary production containing radiocarbon from nuclear power plants which is deposited/mineralized in prodelta sediments. Such high $\Delta^{14}\text{C}$ values have been previously found in watersheds with nuclear power plants: Fontugne et al. (2002) reported $\Delta^{14}\text{C}$ values up to $+500\text{‰}$ in the organic fraction of SPM and sediments from the Loire River. These high values may be related to ^{14}C -enriched POM produced in the river as proposed by Coularis (2016) who reported in-stream primary production with $\Delta^{14}\text{C}$ of $+750\text{‰}$ in the POM for the Loire River.

The release of radiogenic material into the river basin is legally allowed at discrete time intervals (149 GBq in 2010; Eyrolle et al., 2015) but data about the periods of such releases are not available and quantifying their impacts is therefore very difficult. In the absence of similar studies in the Rhone River, we can only suppose that the same phenomenon occurs as a consequence of nuclear activities, and that the $\Delta^{14}\text{C}$ signature of the riverine POM deposited in proximal sediments can be high at certain periods.

Our porewater isotopic DIC data thus indicate that material enriched in terrestrial radiocarbon very likely produced in the river is mineralized in delta sediments.

Furthermore, the $\Delta\text{DIC}:\Delta\text{NH}_4^+$ and the $\delta^{13}\text{C}$ -DIC are in agreement with a riverine plankton source (Fig. 8). The role of riverine phytoplankton in the input of degradable organic matter to the prodelta has been already proposed according to the analyses of chlorophyll pigments and biomarkers (Bourgeois et al., 2011; Cathalot et al., 2010; Galeron et al. (2015). Harmelin-Vivien et al. (2010) analyzed seasonal variations of Chl *a* and *b*, C:N ratios and $\delta^{13}\text{C}$ of the suspended particles in the Rhone River and highlighted the potential importance of riverine primary production in the labile carbon export to the delta region in spring and summer.

These findings confirm that the rapid mineralization of relatively fresh riverine OM may play an important role in the early diagenesis of the Rhone River prodelta sediments. With a POC mass budget, Lansard et al. (2009) estimated that only a small portion of

the deposited POC (18%) is rapidly mineralized in prodelta sediments, leaving an important refractory fraction in the sediments which could constitute most of the POM input flux to the delta. As proposed by [Aller and Blair \(2004\)](#), [Aller et al., 2008](#), young and reactive OM fractions, generally characterized by high $\Delta^{14}\text{C}$ values are preferentially mineralized in delta sediments producing a difference in ^{14}C signature between porewater DIC and sediment OM. This was exemplified in the Fly River delta, where high $\Delta^{14}\text{C}$ values are found in porewater DIC whereas lower $\Delta^{14}\text{C}$ values of sediments are found associated to refractory material such as black carbon, or soil OM.

As a consequence, the role of OM delivery by river floods in benthic mineralization, which constitutes part of the CO_2 source in estuaries, should be reconsidered ([Cathalot et al., 2010](#)). During floods, less fresh and labile riverine phytoplankton grow and is delivered to the delta, whereas the large fraction of the flood material deposited is already semi-refractory and is likely buried. In contrast, periods with low water level could result in higher proportions of labile and ^{14}C enriched riverine OM and lead to intensified carbon mineralization in prodelta sediments. [Cathalot et al. \(2010\)](#) and [Pastor et al. \(2011\)](#) following the evolution of oxygen uptake in the sediments as a function of OM deposits suggested a higher OM lability near the river outlet. As suggested by [Harmelin-Vivien et al. \(2010\)](#), riverine phytoplankton is therefore likely to be a significant OM source in the prodelta sediments metabolism, preferentially during low discharge periods and especially in spring and summer when phytoplankton blooms occur. They could play a major role in the early diagenesis of these sediments.

As proposed by some authors in the aquatic environments, the co-existence of organic substrates with different lability may induce a potential “priming effect” ([Bianchi, 2011](#) and reference therein). It consists in the use of labile OM by the micro-, meio- and macro-organisms to co-metabolize more refractory substrates: such a “priming effect” would be possible in the Rhône delta sediments where labile riverine algal material and more refractory flood-originated organic matter are present in similar sediment layers. From our data, we cannot rule out that some priming occurs, but it should be very limited as the ^{14}C signature of the mineralized OM (+400 to +500‰) is very close to the potential source of impacted phytoplankton (around +500‰). If a large proportion of flood-originated organic matter with a ^{14}C signature of -90‰ (typical autumn flood, see [Cathalot et al., 2013](#)) was mineralized, the $\Delta^{14}\text{C}$ signal in the porewater would be considerably lower, namely +200‰ for a 50/50 mix of the two sources. These are very preliminary thoughts that clearly deserve more work.

4.3. The Rhone River in the Mediterranean Sea context and the anthropogenic alterations

In the preceding sections, we highlighted the different fate of the organic matter fractions exported by the river to the delta and continental shelf. In the context of large Mediterranean rivers and deltas, which undergo substantial alterations by human activities, the mix between the different phases of terrestrial organic matter in the POM discharge has also been altered. It is thus interesting to assess how these changes may determine the fate of POM for these large Mediterranean rivers, i.e. the Rhone and Ebro Rivers which are the two largest rivers in the Western Mediterranean Basin and the Po River which is the largest in the Eastern Basin. The Rhone River (average annual discharge $1700 \text{ m}^3 \text{ s}^{-1}$) displays a similar discharge as the Po River ($1500 \text{ m}^3 \text{ s}^{-1}$ in the Adriatic), the Ebro River being smaller with a freshwater discharge of $290 \text{ m}^3 \text{ s}^{-1}$ ([UNEP/MAP/MED POL, 2003](#)).

These three rivers are typical Mediterranean streams with large fluctuations of the freshwater discharge due to extreme precipita-

tion in fall and winter, which create large floods ([MERMEX group, 2011](#)); they are also subject to large anthropic pressure on water resources ([UNEP/MAP/MED-POL, 2003](#)). Furthermore, their river mouths are located in large floodplains with extensive salt marshes which are prone to nutrient and organic carbon trapping ([Calvo-Cuberoa et al., 2014](#)). However, the river-floodplain connections of these three estuaries have been altered by human activity to convert marshes to cultivated land after channeling the river ([Cabezas et al., 2009](#)). At the same time, numerous dams have been built for regulating water discharge and irrigating upstream fields during summer droughts. These dams act as sediment traps which decrease the sediment discharge to the river outlet including eroded soil POM, as has been shown in the Ebro ([Guillen and Palanques, 1992](#); [Rovira et al., 2015](#)) and the Rhone watersheds ([Provansal et al., 2014](#)).

In this context, the type of organic matter delivered to their deltas has certainly evolved under human pressure. As the dams retain eroded particles containing soil OM and favor aquatic primary production in reservoir lakes by increasing water residence time, they may decrease the ratio of soil to *in-situ* produced particulate organic matter delivered to the deltas. In the Ebro River where particle flux was reduced over the 20th century by a factor of 100 ([Guillen and Palanques, 1992](#)), algal OM in the particulate fraction of the salt-wedge estuary now represents an important fraction of POM ([Gómez-Gutiérrez et al., 2011](#)).

In this study, we propose that the recycling/burial budget of POM in Mediterranean deltaic sediments is largely related to the inputs of riverine POM versus soil POM. In the Rhone River prodelta, we showed that most of the mineralized POM originates from riverine phytoplankton. In contrast, the isotopic signature of the soil-eroded organic matter does not appear in the mineralized fractions, indicating that it is semi-refractory and mostly buried by large sedimentation rates prevailing in delta sediments. Indeed, in most sediments surrounding river deltas, terrestrial POM is largely preserved, as it is the case in the Po and Rhone Rivers ([Cathalot et al., 2013](#); [Tesi et al., 2013, 2008](#)). In these two deltas, the dual isotopic signature of POM ($\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$) indicates soil organic matter with a substantial residence time in continental sub-systems as a major constituent of buried organic matter ([Tesi et al., 2013](#)).

In the Mediterranean area, the combined effects of diminishing floodplains, river channeling and increased damming upstream have certainly modified the quality of POM discharge. It is difficult to quantify the long-term effects of these changes which will also include climate change. But, if the fate of soil and aquatic POM is as different in other Mediterranean deltas as shown for the Rhone River in this study, these changes will certainly affect (or have already affected) the fate of POM in deltas and the partitioning between recycling and burial which is important for the CO_2 budget of these areas.

5. Conclusions

This study shows that riverine organic matter enriched with ^{14}C is the fraction that is predominantly mineralized, whereas the ‘older’ fractions remain in the sediment. The low $\delta^{13}\text{C}$ signature of pore water DIC with the high $\Delta^{14}\text{C}$ ratios indicates together, that riverine phytoplankton is the fraction that is preferentially mineralized in the sediments close to the river mouth. Offshore, a mix of fresh marine OM and bacteria becomes rapidly the dominant fraction that undergoes mineralization. This trend is supported by the C:N ratio of the investigated pore waters. As a consequence, the influence of flood events on coastal carbon mineralization could be less important than previously thought for organic matter mineralization and lead to burial of the majority of the imported

particles. The POM transported in such events is not reactive enough and gets buried by high sedimentation rates while riverine phytoplanktonic components continue to be the dominant mineralized fraction. In the Mediterranean context, with large human alteration of river watershed, river conduits and floodplains, this may lead to a change in the mineralization/burial balance in large river deltas.

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