
Isotopic Signature ($\delta^{13}\text{C}$, $\Delta^{14}\text{C}$) of DIC in Sediment Pore Waters: An Example from the Rhone River Delta

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Abstract :

A better understanding of the dynamics of different particulate organic matter (OM) pools in the coastal carbon budget is a key issue for quantifying the role of the coastal ocean in the global carbon cycle. To elucidate the benthic component of this carbon cycle at the land-sea interface, we investigated the carbon isotope signatures ($\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$) in the sediment pore waters dissolved inorganic carbon (DIC) in addition to the sediment OM to constrain the origin of the OM mineralized in sediments. The study site is located at the outlet of the Rhone River (Mediterranean Sea), which was chosen because this river is one of the most nuclearized rivers in Europe and nuclear $\Delta^{14}\text{C}$ can serve as a tracer to follow the fate of the OM discharged by the river to the coastal sea. The $\Delta^{14}\text{C}$ results found in the pore waters DIC show a general offset between buried and mineralized OM following a preferential mineralization model of young and fresh particles. For example, we found that the sediment OM has values with a mean $\Delta^{14}\text{C} = -33$ parts per thousand at sampling stations near the river mouth whereas enriched $\Delta^{14}\text{C}$ values around +523 parts per thousand and +667 parts per thousand respectively were found for the pore waters DIC. This indicates complete mineralization of a riverine fraction of OM enriched in $\Delta^{14}\text{C}$ in the river conduit during in-stream photosynthesis. In shelf sediments, the $\Delta^{14}\text{C}$ of pore waters DIC is slightly enriched (+57 parts per thousand) with sediment OM reaching -570 parts per thousand. A mixing model shows that particles mineralized near the river mouth are certainly of riverine phytoplanktonic origin whereas OM mineralized on the shelf is of marine origin. This work highlights the fact that pore waters provide additional information compared to sediments alone and it seems essential to work on both pools to study the carbon budget in river prodelta.

Keywords : pore waters, radiocarbon AMS dating, river prodelta, sediments, stable isotopes

INTRODUCTION

River deltas, despite their small size, are major compartments in the carbon cycle. These zones, which constitute only 0.7% of the global ocean surface, produce a quarter of the CO₂ absorbed by the whole ocean (Cai 2011). It is also estimated that 50% of the global oceanic carbon burial occurs in deltas (Bernier 1982). These areas of high sedimentation are key locations for the retention and mineralization of organic carbon and it is important to constrain its origin to better understand the role of different organic matter (OM) pools in the coastal carbon budget.

In river deltas and estuaries, sediments receive OM originating from land, ocean, and coastal wetlands as well as autochthonous, estuarine, and riverine production, which may have very different reactivity owing to their nature and residence time in the soils or aquatic system (Bauer et al. 2013). The use of stable and radiogenic carbon isotopes (¹³C and ¹⁴C) has proven useful in order to characterize the different carbon sources in the sediment. This approach has been widely adopted for river delta sediments (Hunt 1970; Fontugne and Jouanneau 1987; Goni et al. 1997; Goni et al. 1998, 2008; Lansard et al. 2009; Blair and Aller 2012; Cathalot et al. 2013; Toussaint et al. 2013) and also for their riverine sources (Raymond and Bauer 2001; Higuera et al. 2014; Coularis 2016).

Previous studies carried out on sediment OM showed that their origin is mainly terrestrial near the river mouth with a contribution of marine OM on continental shelves (Goni et al. 1997; Cathalot et al. 2013).

In this paper, we focus on the Rhône River delta and shelf sediments where it has been shown, using paired $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signatures (Cathalot et al. 2013), that the OM content of the sediments in the prodelta and neighboring shelf is old except for very near the Rhône river mouth and that the age increases with the distance from the river mouth. This observation suggests that the younger OM potentially originating from production in the river is promptly remineralized, conferring on the prodelta its major role of source of CO_2 in the carbon cycle of this part of the Mediterranean Sea. The Rhone River is one of the most nuclearized rivers in Europe. Fourteen nuclear power reactors grouped in four nuclear plants are located all along the Rhone River and legally discharge cooling water containing ^{14}C enriched dissolved inorganic carbon (DIC) (Eyrolle et al. 2015; Jean-Baptiste et al. 2018a). The isotopic signature of this DIC can be rapidly transferred to the autotrophic OM pool of the river by photosynthesis of plankton and algae (Fontugne et al. 2002; Coularis et al. 2016). In the Rhône River and its prodelta, ^{14}C can thus be a powerful tracer of the fresh OM produced in the river.

To verify Cathalot's hypothesis of rapid mineralization of riverine OM in sediments near the Rhone River mouth, it is essential to document the sediment pore waters DIC isotopic composition, using the nuclear ^{14}C released as a tracer. Previous papers (Aller and Blair 2006; Aller et al. 2008; Zetsche et al. 2011) have shown the importance of coupling the study of pore waters to the study of sediments because the isotopic information they provide can be significantly different. The DIC of sediments pore waters resulting from the oxidation of organic matter provides information on the fate of the most labile and freshest organic carbon. Conversely, sedimentary organic carbon informs about the most refractory component of organic matter.

The aim of this paper was to study the carbon isotope signatures ($\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$) in the sediment pore waters DIC in addition to the sediment itself to obtain new data and a better understanding of the origin of the OM fraction mineralized in the Rhône River prodelta sediment and its adjacent shelf.

We first present the study site with its characteristics and its background. Two periods will be considered and described with bibliographic ^{14}C data: the pre-nuclear or natural period and the last 50 years affected by nuclear anthropic activities. Different analyses (DIC concentration, $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$) conducted on sediment pore waters as well as on the sediment itself will be presented. Then, a mixing model calculating the original characteristics of the OM mineralized in the pore waters DIC will be introduced. Finally, the results will be discussed and compared with results from previous studies in order to better understand the fate of the different OM pools in the complex system of the Rhône River prodelta.

MATERIAL AND METHODS

Study Site

The Rhône River is a major source of freshwater, particles, and OM brought to the western Mediterranean Sea (De Madron et al. 2000; Sempere et al. 2000; Pont et al. 2002). The river's catchment basin covers an area of 97,800 km² with strong climatic and geological heterogeneity. The hydrological regime of the Rhône fluctuates between under 700 m³ s⁻¹ during the low flow period and over 3000 m³ s⁻¹ during the flood period. The majority of the terrigenous material is delivered by floods to the sea where it is rapidly deposited at the river mouth between 0 and 20 m water depth (Maillet et al. 2006) before redistribution to the prodelta by wave action. The sedimentation rates at the river mouth (20 m depth) vary between 30 and 40 cm yr⁻¹ (Charmasson et al. 1998), decreasing to 1 to 10 cm yr⁻¹ at 60 m water depth (Radakovitch et al. 1999 a and b) in

areas farther from the coast (prodelta) and reaching a rate of $<0.3 \text{ cm yr}^{-1}$ on the continental shelf (Miralles et al. 2005; Radakovitch et al. 1999a; Zuo et al. 1997).

It is also important to note that because of the microtidal context the freshwater plume from the Rhône River spreads on the surface of the sea and is only mixed with the seawater in the first meters of the water column (Many et al. 2017). At a depth of 20 m, the bottom water is strictly “pure” seawater with a salinity around 38‰. The Rhône plume is then driven westward by the Liguro-Provençal current along the Languedoc coast (Estournel et al. 1997).

In this study, we focused on three stations located along a north-south/west transect in the freshwater plume (Figure 1). Two of the stations are directly located at the mouth of the river at the top of the prodelta (stations A and Z, seabed at 20 m) while the third one, 12 km farther from the coast, is located on the continental shelf (station D, seabed at 75 m).

Background

The sources of riverine particles discharged to the delta are highly dependent on floods (Pont et al. 2002; Ollivier et al. 2010) carrying soils of various ages, vegetation debris and river phytoplanktonic production. During the warmer seasons, the in-stream photosynthesis based on riverine DIC delivers new sources of carbon with an isotopic signature that depends directly on the nature of the drainage basin for ^{13}C and ^{14}C and on anthropogenic ^{14}C input (Harmelin-Vivien et al. 2010; Coularis 2016). The ^{14}C activity of inorganic and organic carbon in the Rhône River and its delta have been affected for the last 50 years by releases from nuclear

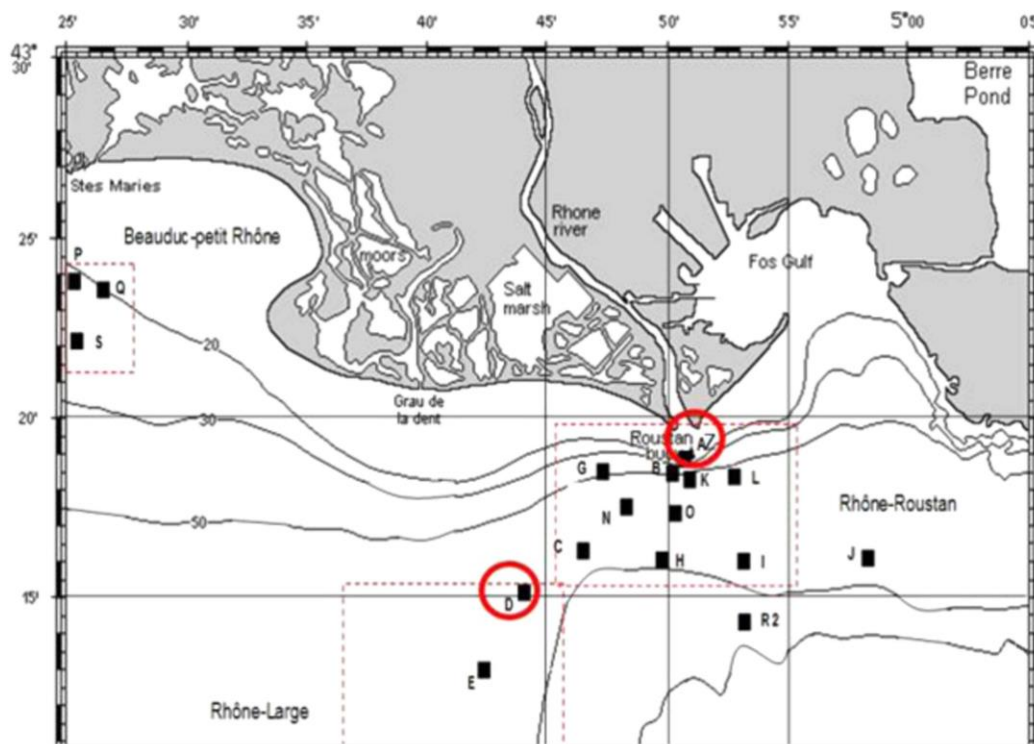


Figure 1 Map of the Rhône prodelta with the sampling stations A, D, and Z.

power plants and military reprocessing plants. These anthropogenic activities and particularly the nuclear inputs which bring enriched ^{14}C -DIC to the system lead to high ^{14}C activity of the OM synthesized in situ (Toussaint 2013; Eyrolle et al. 2015; Jean-Baptiste et al. 2018a). On the other hand, the old carbonates dissolved from the drainage basin generate a freshwater reservoir effect (FRE) for ^{14}C in DIC which could generate an apparent ^{14}C aging of freshly photosynthesized OM in the pre-nuclear period, as was observed in the Loire watershed upstream of nuclear power plants (Coularis et al. 2016). Nevertheless, the anthropogenic ^{14}C marked carbon offers the opportunity to trace the evolution of organic matter after its discharge to the coastal zone if the partitioning between natural (pre-nuclear) and nuclear ^{14}C is clear.

Pre-Nuclear Period

Before the anthropogenic nuclear activities of the last 50 years the ^{14}C signature of the OM in the Rhône River and its prodelta was linked to various natural ^{14}C sources such as soils and plant debris but also autotrophic phytoplankton and algae which depend on the isotopic signature of river DIC. As the course of the Rhône River in its final stretch flows through carbonate sedimentary formations, this induces a notable FRE (see for the Loire River, Coularis et al. 2016). For the Rhône River, the FRE measured on DIC was evaluated at $\Delta^{14}\text{C} = -114\%$, a value indicating the strong influence of the main tributary, the Durance river which is known to be depleted in $\Delta^{14}\text{C}$ as indicated by a value obtained in May 2014 ($\Delta^{14}\text{C} = -138\%$, Jean-Baptiste et al. 2018a). The FRE observed for the dissolved inorganic carbon can be transferred to the algal production present in the river. The work by Coularis et al. (2016) showed, for the Loire River basin, that the particulate organic carbon (POC) has the same activity as the total dissolved inorganic carbon. These results imply that the contribution of FRE to in-stream production can be high and contributes with the detritic geological carbon fraction and the contribution of soil to the ^{14}C activity of the total particulate organic carbon. The pre-nuclear signature of riverine plankton should thus show $\Delta^{14}\text{C} = -110\%$ in accordance with the FRE of the Rhône River.

During this period, the particulate organic carbon discharged during the flood and deposited in the Rhône pro-delta was a mixture of fresh POC ($\Delta^{14}\text{C} = -110\%$) and an older particulate carbon removed from the river catchment basin or resuspended from the bottom of the river. Previous studies of prodelta sediment cores show that OM ^{14}C activity during this period ranged between $\Delta^{14}\text{C} = -600\%$ and $\Delta^{14}\text{C} = -400\%$ depending on the distance from the mouth of the Rhône river (Cathalot et al. 2013; Toussaint et al. 2013; Jean-Baptiste et al. 2018b submitted). Far offshore, under typical marine influence, DIC from Mediterranean Seawater and phytoplankton had ^{14}C activities around $\Delta^{14}\text{C} = -50\%$ during the pre-nuclear period (Siani et al. 2000; Tisnérat-Laborde et al. 2013).

Modern Nuclear Period

The nuclear era started in 1955 with the first thermonuclear experiments in the Pacific Ocean and led to the doubling of ^{14}C activity in the atmosphere in 1963 ($\Delta^{14}\text{C}$ “indicative value” around 1000‰). The impact of these changes is not well known for photosynthetic matter in the Rhône river but according to the decrease of ^{14}C activity in the atmosphere, it also decreased by about 50% before 1970.

Later, the legal recurrent discharge of cooling water from the nuclear plants (Eyrolle et al. 2015) directly impacted the activity of the river DIC and consequently the fresh OM via algal

production. The ^{14}C activity of the OM in suspended particular material (SPM) of the river is very variable because it depends on the discharge by the nuclear industry and on the season.

Regulations prohibit discharges during floods and during periods of low water, limiting the impact of the release because of dilution of water and particles. However, at the end of spring and summer, the algal photosynthesis activity is strong and flows are relatively low which induces a stronger release impact than in winter.

For POC/SPM collected in Arles near the River outlet, the integrated monthly samples from 2010 to 2013 showed an amplitude of variation of $\Delta^{14}\text{C}$ values from -172‰ to $+908\text{‰}$ with an average value of $\Delta^{14}\text{C} = 285 \pm 320\text{‰}$ (Jean-Baptiste et al. 2018a). Between 2010 and 2013, measurements of $\Delta^{14}\text{C}$ activity of the POC collected in the Rhone prodelta sediments ranged from -120‰ to $+140\text{‰}$. (Cathalot et al. 2013; Toussaint 2013; Jean-Baptiste et al. 2018a). On the continental shelf, at depths greater than 75 m, the values decreased to between -200 and -400‰ . The DIC of coastal surface waters, beyond the influence of the Rhône, displayed an activity around $+30\text{‰}$ in 2010 and 2011 (Fontugne et al. 2012). This activity is close to the measurements conducted on biological materials (mussels, algae) in the Western Mediterranean region at the same time (Jean-Baptiste et al. 2018a). In this context of large changes in the ^{14}C activity of DIC and organic particles due to the nuclear activity in the watershed, it is important to understand the sources of OM in deltaic sediments and understand its mineralization through analysis of the isotopic composition of DIC in sediment pore waters (Aller and Blair 2004; Aller et al. 2008).

Sampling

The sampling campaign (Carbodelta II; Rabouille 2013) was carried out on the Rhône River delta and adjacent shelf on the CNRS/INSU R.V. Tethys II in April 2013, during a period of average freshwater discharge (April 2013: $2360 \text{ m}^3/\text{s}$). The three stations A, Z, and D were sampled during the Carbodelta II cruise. Sediment, bottom water and pore waters were collected at each station to analyze alkalinity, DIC, $\delta^{13}\text{C}$, and $\Delta^{14}\text{C}$.

Sediment

Sediment cores (internal diameter: 9.5 cm) were collected with a gravity corer (Uwitec), using PVC crystal clear tubes; their length varied between 20 and 40 cm, depending on the texture and hardness of the seabed. With current sedimentation rates of 20–30 cm/yr in the prodelta (station A and Z), the entire core corresponds to nearly one year of sediment deposition. Each core was sliced at the following depth intervals: 0.5 mm from 0 to 2 cm, 1 cm from 2 to 10 cm, 2 cm between 10 and 20 cm, and 5 cm from 20 cm to the end of the core.

Each slice was carefully stored in plastic bags, frozen at -20°C directly on board and kept frozen in the laboratory.

Pore Waters

Separate sediment cores were collected to extract pore waters. Predrilled tubes (every 2 cm) sealed with black tape were collected with the same corers. The extraction of the pore waters was done using 10 mm long $0.2 \mu\text{m}$ rhizons (Rhizosphere Research Products, see Seeberg-Elverfeldt et al. 2005) connected to rubber-free 10-mL syringes. During Carbodelta II, the samples to be analyzed for both ^{13}C and ^{14}C were placed in 10-mL Pyrex glass ampoules (previously combusted at 450°C for 5 hr) sealed immediately on board with a welding torch and

stored frozen at -20°C until analysis. A separate core was sampled similarly for DIC and alkalinity measurements.

Bottom Water

Bottom water samples were collected as close as possible to the bottom (around one meter) using a Niskin bottle. The water was poisoned with mercuric chloride (HgCl_2) and stored in 250-mL glass bottles (previously cleaned and combusted at 450°C for 5 hr). During the expedition, pore and bottom water samples analyzed for DIC/TIC (total inorganic carbon, see below) were placed in 15-mL falcon tubes, stored at 25°C and analyzed within the day.

Measurements

TIC/DIC Analysis

We discriminate between water TIC and DIC content. Inorganic carbon measured in bottom water samples will be referred to as TIC or total inorganic carbon because samples were not filtered before analysis. Inorganic carbon measured in pore waters will be referred to as DIC or dissolved inorganic carbon because during extraction the water passed through the $0.2\ \mu\text{m}$ ceramic filter inside the rhizons. The two notions are very similar when the particulate content of bottom water is low and the results are therefore comparable.

The analysis was carried out using an Apollo Scitech Dissolved Inorganic Carbon Analyzer with a LI-COR CO_2 detector (see Rassmann et al. 2016 for details). The uncertainty of DIC/TIC measurements is at most 0.5%.

^{13}C and ^{14}C Analysis

Preparation of all the samples and analysis of the ^{14}C was done at the LMC14 laboratory, Saclay and ^{13}C measurements were carried out by the Geotrac team of the LSCE laboratory.

a) Extraction of CO_2 from the pore waters:

The main difficulty of the sample preparation and analysis was the very limited volume of pore water available for processing. Extracting enough CO_2 to perform reliable ^{14}C measurements from 10 mL samples can prove challenging. On water column samples, such measures are normally done on much larger volumes (around 70 mL) to ensure enough C content. However, since pore waters DIC concentration is generally higher than in the water column (Aller and Blair 2004; Aller et al. 2008), the existing CO_2 extraction line used at the LMC14 described by Dumoulin et al. (2013) was well fitted to work on smaller pore waters volumes.

The main modification to the previous version of the line consisted in the sample introduction procedure for small volume samples. The glass ampoule containing the 10 mL pore water sample was defrosted and pre-cut on the upper part with a power saw. Then, the ampoule was broken and the sample rapidly (2 seconds) introduced inside the reactor to limit contact with air. Once broken, the ampoule was fitted with a gas tight stopper pierced by 2 microtubes, one used to deliver pure Argon gas (CO and $\text{CO}_2 < 10$ ppb) into the ampoule and the other to transfer the sample into the reactor. The sample delivery tube was sharpened and used to pierce an air-tight septum located on the inlet of the reactor vessel. Once the tubes were in place, the argon flux was started and the sample gently pushed from the ampoule directly into the reactor vessel.

Once the transfer was complete, 2 mL of 85% phosphoric acid (H₃PO₄) was added to the reactor via the septum and the acidification reaction started. After 45 min, all the DIC contained in the sample was transformed into CO₂ gas, which was then removed from the reactor by the helium flow and pushed through the line for 30 min to be dried in the two water traps at -78°C, condensed in the liquid nitrogen solenoid trap at -190°C, measured in the calibrated cold finger and finally split into two separate aliquots, one for the ¹⁴C measurement and the other for ¹³C measurement. The CO₂ aliquot for ¹⁴C measurement was then sent to the graphitization laboratory whereas the ¹³C aliquot was measured directly at the LSCE with an isotope ratio mass spectrometer (Dual Inlet VG Optima through a manifold).

The isotopic ratio ¹³C/¹²C is reported on the δ¹³C notation and is expressed relative to the PDB standard (fossil CaCO₃) in ‰:

$$\delta^{13}\text{C} = \frac{{}^{13}\text{C} = {}^{12}\text{C} \delta_{\text{sample}}}{{}^{13}\text{C} = {}^{12}\text{C} \delta_{\text{standard}}} - 1 \quad \omega \quad 1000$$

The precision of the isotopic measurements is ± 0.3‰.

b) Production of CO₂ for ¹⁴C analysis from the sediments:

After total decarbonation with HCl 0.5N to remove the carbonate fraction, sediments and filters were dried for one night in an oven at 65°C. The total organic carbon concentration (% TOC) of the sediment was obtained with an elemental analyzer (Thermo Fisher Scientific Flash 2000 series). The samples were precisely weighed according to their % TOC to get nearly 1 mg of CO₂ and then sealed in quartz tubes under vacuum (residual pressure < 10⁻⁵ mbar) with an excess of CuO and a 1 cm silver wire. The quartz tubes were then combusted at 850°C for 5 hr and cooled slowly. Finally, they were cracked inside a glass line under vacuum (< 10⁻⁵ mbar) and the CO₂ gas produced was cryogenically collected in tubes via liquid nitrogen. After collection, the tubes were sealed using a welding torch and sent to the graphitization laboratory (Dumoulin et al. 2017).

c) Graphitization and AMS measurements.

The CO₂ previously collected was reduced to graphite at the LMC14 laboratory using hydrogen and iron powder at 600°C (Vogel et al. 1984; Cottreau et al. 2007; Dumoulin et al. 2017). The iron and graphite powder was pressed into the 1 mm hole of an aluminum cathode and loaded into the ion source of the ARTEMIS facility for the AMS measurement (Moreau et al. 2013).

The ¹⁴C activities were calculated with respect to the international standard of Oxalic Acid II. Data were corrected for the isotopic fractionation measured in the AMS and ¹⁴C activities were normalized for a -25‰ δ¹³C. Conventional radiocarbon calculations were done using the Mook and van der Plicht method (1999). Errors take into account the statistics, variability of results and background correction. The Δ¹⁴C uncertainty values are ± 3‰ at a confidence interval of 1 σ. The ¹⁴C contents are expressed in Δ¹⁴C which is defined as the deviation in parts per mil from the modern standard. All Δ¹⁴C values were then recalculated to 1950, and corrected for the delay between sampling and measurement year (Mook and van der Plicht 1999).

$$\Delta^{14}\text{C} = \frac{pMC}{100} e^{\lambda \delta_{\text{date measure}} - \text{date sampling}} - 1 \quad \omega \quad 1000$$

with

decay constant of ¹⁴C λ = ln2/ T with T = 5730 yr BP.

and

$$pMC_{\delta} \text{ percent modern carbon } p = 100 \frac{A_{na}}{A_{std}}$$

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 “typical” uncertainty of the results is $\pm 3\%$.

d) Mixing model for calculating the isotopic signature of mineralized organic matter:

At each depth in the sediment, pore waters DIC is a mix of bottom water DIC and DIC originating from the mineralized OM, carbonate dissolution being ruled out in these sediments (Rassmann et al. 2016).

To ascertain the origin of the OM mineralized in the sediment, we have to calculate the original isotopic signature of the organic matter mineralized in the sediment using a mixing model. This information is crucial in order to better understand the relative contribution of terrigenous versus marine organic carbon in the mineralization process and compare it to known sources in the river basin, or marine production.

The pore waters mixing model used is similar to that of Bauer et al. (1995). The first step consists in calculating the fraction of bottom water in the mix (x) by calculating the ratio between bottom water DIC concentration [DIC_{BW}] and measured pore waters DIC concentration [DIC_{pore}] in $\mu\text{mol/L}$.

$$x = \frac{[\text{DIC}_{\text{BW}}]}{[\text{DIC}_{\text{pore}}]}$$

In association $(1-x)$ is the fraction of DIC produced by the mineralization of organic matter present in the sediments.

The second step consists in using these fractions (x) and $(1-x)$ to calculate the real isotopic signature ($\delta^{13}\text{C}_{\text{OM}}$, $\Delta^{14}\text{C}_{\text{OM}}$) of the mineralized OM, knowing the isotopic signature of the pore waters ($\delta^{13}\text{C}_{\text{pore}}$, $\Delta^{14}\text{C}_{\text{pore}}$) and the bottom water ($\delta^{13}\text{C}_{\text{BW}}$, $\Delta^{14}\text{C}_{\text{BW}}$).

$$\delta^{13}\text{C}_{\text{pore}} = x \omega \delta^{13}\text{C}_{\text{BW}} + \delta(1-x) \omega \delta^{13}\text{C}_{\text{OM}}$$

$$\delta^{13}\text{C}_{\text{OM}} = \frac{\delta^{13}\text{C}_{\text{pore}} - x \omega \delta^{13}\text{C}_{\text{BW}}}{\delta(1-x) \omega}$$

A similar set of equations leads to the ^{14}C signature of mineralized organic matter:

$$\Delta^{14}\text{C}_{\text{OM}} = \frac{\delta \Delta^{14}\text{C}_{\text{pore}} - x \omega \Delta^{14}\text{C}_{\text{BW}}}{\delta(1-x) \omega}$$

where $\Delta^{14}\text{C}_{\text{BW}}$ is the $\Delta^{14}\text{C}$ signature of DIC in bottom waters (in ‰), $\Delta^{14}\text{C}_{\text{pore}}$ is the $\Delta^{14}\text{C}$ signature of DIC in the pore waters at depth in sediments, and $\Delta^{14}\text{C}_{\text{OM}}$ is the $\Delta^{14}\text{C}$ signature of the mineralized organic matter.

RESULTS

Sediment Pore Waters DIC Concentrations

As shown in Table 1 and Figure 2, bottom seawater [DIC] was quite constant at the three stations (around $2530 \mu\text{mol/L}$) with a salinity around 38‰, indicating that bottom waters are

Table 1 Dissolved inorganic carbon (DIC) concentrations measured in bottom seawater (BW) and sediment pore waters. ND means no data.

	St. A (prodelta)	St. Z (prodelta)	St. D (Cont. Shelf)
Depth (cm)	DIC [$\mu\text{mol/L}$]	DIC [$\mu\text{mol/L}$]	DIC [$\mu\text{mol/L}$]
BW	2533	ND	2530
1	5907	4739	2857
3	11664	6556	2854
5	13874	ND	3264
7	ND	11614	3112
9	14964	ND	3303
11	16717	16693	ND
13	18273	ND	3766
15	ND	22750	ND
17	21304	ND	4024
21	23839	ND	ND
23	ND	29778	ND

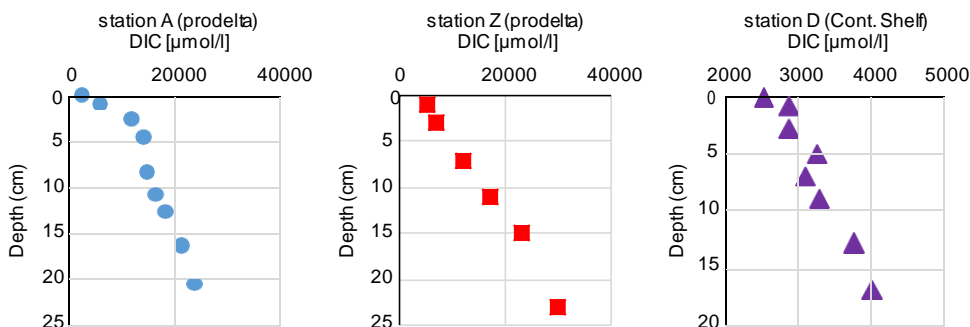


Figure 2 Evolution of the DIC concentrations ($\mu\text{mol/L}$) as a function of the sediment core depth (cm) at stations A, D and Z.

from the same origin and under the influence of Mediterranean seawater. [DIC] in sediment pore waters increased with depth at all stations. For station Z, the DIC concentration ([DIC]) varied between 2530 $\mu\text{mole/L}$ for bottom seawater to about 29,800 $\mu\text{mole/L}$ in sediment pore waters at 23 cm depth. At station A, a larger increase in [DIC] was observed in the first 5 cm than at station Z, followed by a slower increase in [DIC]. At station D, in the first centimetre, [DIC] was 2857 $\mu\text{mol/L}$, 1.5 to 2 times lower than the DIC concentration in the prodelta. We also observed a tenfold smaller increase (100 $\mu\text{mol/L}$ per cm) for the marine station D compared to the prodelta stations A and Z (nearly 1000 $\mu\text{mol/L}$ per cm).

$\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ of Pore Waters DIC, Bottom Seawater and Sediment Organic Carbon

All the results are presented in Table 2 station by station for the two different pools: sediments and pore waters.

$\delta^{13}\text{C}$ values of DIC of bottom water is -1.17‰ at Station A. $\delta^{13}\text{C}$ values of the sediment pore waters ranged between -19.8 to -24.7‰ at the prodelta stations (A and Z). At marine Station D,

Table 2 $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ data of pore waters DIC, bottom seawater water, and sediments. Values are given in per mil notation (‰). The values with * refer to a range of literature values for these stations from Cathalot et al. (2013) and Toussaint (2013).

Station	Sample N°	Nature	$\delta^{13}\text{C}$ (‰)	±	Err (‰)	$\Delta^{14}\text{C}$ (‰)	±	Err (‰)
St. A bottom water	SacA41281	Seawater	-1,17	±	0.12	39	±	3
St. A 7-8 cm	SacA39826	Sediments	-27.2 to -26.8*			46	±	3
St. A 20-25 cm	SacA39827	Sediments	-27.2 to -26.8*			-64	±	3
St. A 8 cm	SacA38736	Pore waters	-19.81	±	0.05	697	±	4
St. A 20 cm	SacA38739	Pore waters	-22.37	±	0.07	499	±	3
St. A 24 cm	SacA38740	Pore waters	-23.59	±	0.12	452	±	3
St. Z 7-8 cm	SacA39828	Sediments	-26.3 to -26.0*			-125	±	3
St. Z 20-25 cm	SacA39829	Sediments	-26.3 to -26.0*			12	±	4
St. Z 8 cm	SacA38738	Pore waters	-24.16	±	0.15	456	±	3
St. Z 24 cm	SacA38745	Pore waters	-24.71	±	0.07	613	±	4
St. Z 28 cm	SacA38746	Pore waters	-22.85	±	0.04	623	±	4
St. D 7-8 cm	SacA48074	Sediments	-24.8 to -24.5*			-335	±	3
St. D 20-25 cm	SacA48076	Sediments	-24.8 to -24.5*			-569	±	2
St. D 7 cm	SacA38737	Pore waters	-8.82	±	0.44	57	±	4
St. D 11 cm	SacA38742	Pore waters	-8.70	±	0.13	57	±	3
St. D 19 cm	SacA38744	Pore waters	NA	±	NA	25	±	3

$\delta^{13}\text{C}$ values are around -8.8‰ and were notably higher than the prodelta ones. However, $\delta^{13}\text{C}$ of DIC pore waters at the three stations presented a similar decrease with core depth indicating the addition of ^{13}C -mineralized OM DIC.

At stations A and Z, pore waters DIC- $\delta^{13}\text{C}$ values reached, at depth, values around -23‰ to -25‰, which is slightly higher than that of sediment organic carbon which has varied between -25.5‰ to -27.5‰ (Lansard et al. 2009; Jean-Baptiste et al. 2018b submitted) during the last 50 years.

At station D pore waters DIC showed higher $\delta^{13}\text{C}$ values than prodelta stations (around -9‰) indicating that in the continental shelf station, a lower proportion of ^{13}C -mineralized OM DIC is added to the pore waters DIC. Note that the station D profile is shorter because the carbon content of the last two samples was too low to provide reliable measurements (Figure 3).

The results of the $\Delta^{14}\text{C}$ analysis of both sediment organic carbon and the corresponding pore waters DIC as well as bottom seawaters are reported in Figure 4. The $\Delta^{14}\text{C}$ signature of the bottom seawater was analyzed for station A ($\Delta^{14}\text{C} = +39‰$) and we assume that this value is the same for all three stations which is confirmed by Pozzato et al. (2018), since, as shown above, the concentration of DIC is the same and the salinity of bottom waters is consistently around 38‰ at the three stations, suggesting that no mixing with fresh river water occurred.

$\Delta^{14}\text{C}$ of prodelta pore waters DIC (stations A and Z) presented similar values varying between +452 to +697‰ while sediment organic carbon varied between 46 to -125‰. At station D on the continental shelf, the $\Delta^{14}\text{C}$ values of pore waters DIC were not very different from bottom seawater water, at between 25 and 57‰. Figure 4 shows clearly that organic carbon in sediment is systematically ^{14}C depleted compared to the pore waters DIC of these sediments. At Station D, the $\Delta^{14}\text{C}$ values of sediment were low, between $-335 \pm 3‰$ and $-569 \pm 2‰$, in good agreement with a previous study (Cathalot et al. 2013).

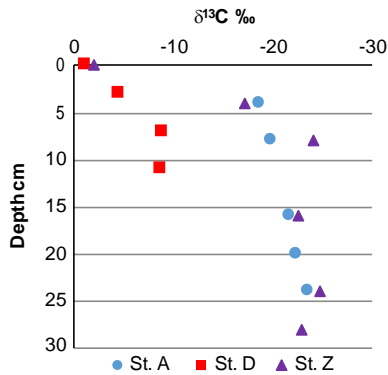


Figure 3 Results of ^{13}C analysis, expressed in $\delta^{13}\text{C}$ (‰), at the three stations A, Z (prodelta) and D (shelf) for sediment pore waters DIC.

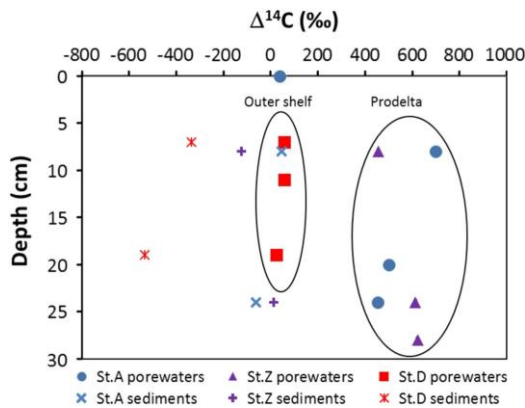


Figure 4 Results of ^{14}C analysis, expressed in $\Delta^{14}\text{C}$ (‰), at the three stations A, Z, and D and for two different kinds of samples: sediment pore waters DIC (symbols) and sediment organic carbon (crosses). Colors refer to stations. (Please see online version for color figures.)

Original Isotopic Signature of Organic Matter Mineralized in Sediment Pore Waters

Using the mixing model, the isotopic signature of the organic matter mineralized in the sediment was calculated. The results are given in Table 3. In order to provide a more robust estimate, we used the asymptotic values of [DIC], $\delta^{13}\text{C}$, $\Delta^{14}\text{C}$ to calculate this signature. We chose the deepest result for [DIC] and the mean between the two deepest values for $\delta^{13}\text{C}_{\text{pore}}$ and $\Delta^{14}\text{C}_{\text{pore}}$. For bottom water composition we used the values measured at station A: $\delta^{13}\text{C}_{\text{bw}} = -1\text{‰}$ and $\Delta^{14}\text{C}_{\text{bw}} = +38.5\text{‰}$.

Table 3 shows that with the assumptions made here, the original isotopic signature of the OM remineralized at each station of the prodelta (A and Z) has a $\delta^{13}\text{C}$ signature ranging between -25.3‰ and -25.7‰ and a $\Delta^{14}\text{C}$ signature between $+475\text{‰}$ and $+618\text{‰}$, whereas values of -20.1‰ and $+41\text{‰}$ respectively are obtained further on the shelf at station D.

Table 3 Parameters and results of the DIC mixing model with the fraction of bottom water (x) and pore waters (1-x) DIC in the mix, the signature of pore waters (pore) and bottom waters (BW) adopted from the results ($\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$) and the calculated signature of mineralized OM in $\delta^{13}\text{C}$ OM and $\Delta^{14}\text{C}$ OM.

Station	[DIC BW] ($\mu\text{mol/L}$)	[DIC pore] ($\mu\text{mol/L}$)	x	(1-x)	$\delta^{13}\text{C}$ pore (‰)	$\delta^{13}\text{C}$ BW (‰)	$\delta^{13}\text{C}$ OM (‰)	$\Delta^{14}\text{C}$ pore (‰)	$\Delta^{14}\text{C}$ BW (‰)	$\Delta^{14}\text{C}$ OM (‰)
A	2323	23839	0.10	0.90	-23.0	-1	-25.3	475	39	523
Z	2330	29778	0.08	0.92	-23.8	-1	-25.7	617	39	667
D	2388	4023	0.59	0.41	-8.8	-1	-20.1	41	39	45

It is worth mentioning that the recalculated isotopic parameters for the mineralized OM are quite uncertain especially for station D where the DIC increase is limited. The mixing model would perform much better with a denser set of data at depth, since for this station, a slight change of 200 $\mu\text{mol/L}$ in the asymptotic DIC concentration changes the recalculated $\delta^{13}\text{C}$ by almost 1%. Nevertheless, the aim of this work was to constrain the origin of OM mineralized in delta sediment using simultaneous ^{13}C and ^{14}C measurements of pore waters DIC and limited uncertainty does not alter the conclusions drawn from this study.

DISCUSSION

At stations A and Z located close to the river mouth, DIC concentrations in pore waters show a large increase downcore and reach around 30 mM at 23 cm depth, a factor of 10 larger than bottom seawater water. Lansard et al. (2009), Cathalot et al. (2010), and Pastor et al. (2011) showed that the Rhône River delta sediments form a significant deposition zone where large quantities of OM brought by the Rhône River are mineralized and accumulation of particles is high (between 30 and 40 cm yr^{-1}). This organic-rich environment promotes the presence of a community of benthic fauna, bacteria and archaea that actively transforms the incoming Org-C into DIC via oxic and anoxic remineralization processes (Pastor et al. 2011; Rassmann et al. 2016). On the continental shelf, however, the deposition of organic matter is much lower ($<0.3 \text{ cm yr}^{-1}$) and its mineralization displays a lower intensity (Lansard et al. 2009; Pastor et al. 2011). In the prodelta area, the SPM Org-C content is around 10% whereas on the shelf near station D it is around 4% (Cathalot et al. 2013; Toussaint et al. 2013). This is also noticeable from the Org-C content of surface sediments which decreases from 2% in prodelta sediments to 1% in continental shelf sediments (Cathalot et al. 2013; Toussaint et al. 2013).

In order to elucidate the sources of sediment OM and remineralized OM, all $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ results are plotted in the same graphic. We also report the isotopic signatures of different sources of organic carbon in the square boxes. These fractions can possibly be mineralized in the sediments (Olsson and Osabede 1974) (Figure 5).

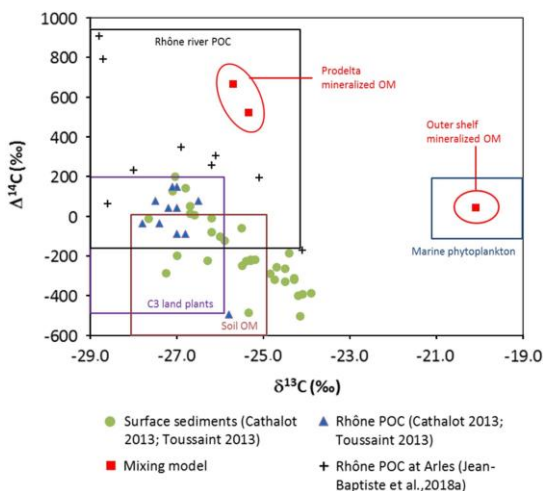


Figure 5 All $\Delta^{14}\text{C}$ versus $\delta^{13}\text{C}$ data measured on the Rhône river POC, in the Rhône delta surface sediments from previous studies (Cathalot 2013; Toussaint 2013; Jean-Baptiste et al. 2018a) and values calculated with the mixing model.

Terrestrial organic matter has a stable isotopic carbon composition estimated around $26 \pm 1\%$ (Cathalot et al. 2013; Higuera et al. 2014) and values between -19% and -21% for marine material (Harmelin-Vivien et al. 2010). The $\delta^{13}\text{C}$ values around -25.5% calculated for the mineralized OM in the prodelta sediments (station A and Z) indicate strong mineralization of terrigenous sources whereas the calculated $\delta^{13}\text{C}$ value around -20% at station D on the outer shelf indicates a marine source. These results are in accordance with Toussaint et al. (2013) and the idea that most of the terrestrial OM is rapidly deposited and mineralized in the prodelta (Pozzato et al. 2018) whereas further on the shelf less terrigenous substrate is deposited and it is mainly marine OM that is mineralized. In this zone, mineralization has a lower impact on the $\delta^{13}\text{C}$ of pore waters DIC than in the prodelta with an isotopic composition strongly influenced by the seawater bicarbonate ($\delta^{13}\text{C} = -1\%$). These results contrast with the stability observed in particulate organic carbon isotopic compositions which range between -25 and -27.5% on the entire continental shelf (Jean-Baptiste et al. 2018a; Cathalot et al. 2013).

Radiocarbon distribution in pore waters and sediments is also different in the prodelta and the outer shelf. At Station D, degraded OM with a calculated ^{14}C signature around $+45\%$ presents a value very close to that of surface or bottom marine waters while sediments are heavily depleted in ^{14}C (mean $\Delta^{14}\text{C} = -335$ to -569%) in agreement with previous measurements (Cathalot et al. 2013). Conversely, at stations A and Z, the signature of mineralized OM recalculated using the mixing model shows enriched $\Delta^{14}\text{C}$ values around $+523\%$ (A) and $+667\%$ (Z), comparable to the high range of values observed in the Rhône River SPM in Arles (Jean-Baptiste et al. 2018a) and the few previous measurements available.

Sediments do not display such extremely enriched values as pore waters with a mean of $\Delta^{14}\text{C} = -33\%$ at stations A and Z. This ^{14}C distribution can be explained by the preferential and rapid mineralization by organisms of fresh SPM rich in ^{14}C in the prodelta sediments. In the sediment, the fraction that remains is composed mostly of old ^{14}C -depleted organic matter corresponding to residues from previous mineralization and carbon from erosion or stored for a long time in the river conduit.

These observations are in agreement with the findings of Aller et al. (2008) in the Fly River delta who showed that younger, labile, more reactive fractions of organic matter are preferentially degraded in sediments whereas a major semi-refractory fraction is mostly buried in the sediment. These two combined processes can create an “apparent aging” of the sediment and may distort interpretation of the data. Such a discrepancy ultimately justifies the importance and the necessity of working on both sediment and pore waters simultaneously in order to understand the origin and dynamics of OM in deltaic/estuarine sediments.

CONCLUSION

The results obtained by the paired $^{13}\text{C}/^{14}\text{C}$ DIC isotopes associated with a mixing model are compatible with the reported view of a prodelta system dominated by riverine inputs near the river mouth and progressively losing the river influence offshore on the shelf. However, this paper provides interesting insights into the origin of mineralized organic matter. In shelf sediments, mineralization is largely dominated by marine organic matter, as calculated by the mixing model. In prodelta sediments where mineralization of continental organic matter dominates, the enriched ^{14}C signature of sediment pore waters DIC indicates that in-stream production, freshly produced and possibly marked by anthropogenic nuclear activities, is preferentially mineralized in the pore waters and does not remain in the sediment. A shift exists between $\Delta^{14}\text{C}$ values of deposited OM and mineralized OM. Two different classes of

particulate OM with contrasted properties are discharged by the Rhône River to the prodelta sediments. One is a labile and fresh OM originating from river algae production via photosynthesis with a nuclear ^{14}C signature which is mostly and quickly mineralized in surface sediments. The other is a semi-refractory OM originating from soil erosion or long-stored material transported by floods, which is mostly buried. If the young and labile component is preferentially mineralized and the old and refractory material is buried, this explains the large difference in $\Delta^{14}\text{C}$ activities between the two different pools which creates an apparent aging of the sediment. Pore waters prove to be an extremely useful tool for understanding the fate of organic carbon in marine sediments and provide additional information to sediments alone. It therefore seems promising to couple the two approaches to better understand the carbon budget in estuarine sediments.

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REFERENCES

- Aller RC, Blair NE. 2004. Early diagenetic remineralization of sedimentary organic C in the Gulf of Papua deltaic complex (Papua New Guinea): Net loss of terrestrial C and diagenetic fractionation of C isotopes. *Geochimica et Cosmochimica Acta* 68:1815–25.
- Aller RC, Blair NE. 2006. Carbon remineralization in the Amazon–Guianas tropical mobile mudbelt: A sedimentary incinerator. *Continental Shelf Research* 26:2241–59.
- Aller RC, Blair NE, Brunskill GJ. 2008. Early diagenetic cycling, incineration, and burial of sedimentary organic carbon in the central Gulf of Papua (Papua New Guinea). *Journal of Geophysical Research-Earth Surface* 113.
- Bauer JE, Reimers CE, Druffel ERM, Willimas PM. 1995. Isotopic constraints on carbon exchange between deep ocean sediments and sea water. *Nature* 373:686–9.
- Bauer JE, Cai WJ, Raymond PA, Bianchi ST, Hopkinson CS, Regnier PAG. 2013. The changing carbon cycle of the coastal ocean. *Nature* 504:61–70.
- Berner RA. 1982. A rate model for organic decomposition during bacterial sulfate reduction in marine sediments [Biogéochimie de la matière organique à l'interface eau-sédiment marin]. *Colloques Internationaux du CNRS*. Paris. p 35–44.
- Blair NE, Aller RC. 2012. The fate of terrestrial organic carbon in the marine environment. *Ann. Rev. Earth Sci.* 4:17.11–23.
- Cai WJ. 2011. Estuarine and coastal ocean carbon paradox: CO_2 sinks or sites of terrestrial carbon incineration? *Ann Rev Mar Sci* 3:123–45.
- Cathalot C, Rabouille C, Pastor L, Deflandre B, Viollier E, Buscaill R, Gremare A, Treignier C, Pruski A. 2010. Temporal variability of carbon recycling in coastal sediments influenced by rivers: assessing the impact of flood inputs in the Rhone River prodelta. *Biogeosciences* 7:1187–205.
- Cathalot C, Rabouille C, Tisnerat-Laborde N, Tousseint F, Kerherve P, Buscaill R, Loftis K, Sun MY, Tronczynski J, Azoury S, Lansard B, Treignier C, Pastor L, Tesi T. 2013. The fate of river organic carbon in coastal areas: A study in the Rhone River delta using multiple isotopic ($\delta^{13}\text{C}$, $\delta^{14}\text{C}$) and organic tracers. *Geochimica et Cosmochimica Acta* 118:33–55.
- Charmasson S, Bouisset P, Radakovitch O, Pruchon AS, Arnaud M. 1998. Longcore profiles of Cs-137, Cs-134, Co-60 and Pb-210 in sediment near the Rhone River (Northwestern Mediterranean Sea). *Estuaries* 21:367–78.
- Cottureau E, Arnold M, Moreau C, Baque D, Bavay D, Caffy I, Comby C, Dumoulin JP, Hain S, Perron M, Salomon J, Setti V. 2007. Artemis, the new C-14 AMS at LMC14 in Saclay, France. *Radiocarbon* 49:291–9.
- Coularis C. 2016. Dynamique et transfert du carbone dans le bassin versant de la Loire : Traçage par les isotopes du carbone [PhD dissertation]. Univ. Paris-Saclay. 252 p.

- Coularis C, Tisnérat-Laborde N, Pastor L, Siclet F, Fontugne M. 2016. Temporal and spatial variations of freshwater reservoir ages in the Loire River watershed. *Radiocarbon* 58:549–63.
- De Madron XD, Abassi A, Heussner S, Monaco A, Aloisi JC, Radakovitch O, Giresse P, Buscail R, Kerherve P. 2000. Particulate matter and organic carbon budgets for the Gulf of Lions (NW Mediterranean). *Oceanologica Acta* 23:717–30.
- Dumoulin JP, Caffy I, Comby-Zerbino C, Delquéc-Kolic E, Hain S, Massault M, Moreau C, Quiles A, Setti V, Souprayen C, Tannau J-F, Thellier B, Vincent J. 2013. Development of a line for dissolved inorganic carbon extraction at LMC14 Artemis Laboratory in Saclay, France. *Radiocarbon* 55:1043–49.
- Dumoulin JP, Comby-Zerbino C, Delquéc-Količ E, Moreau C, Caffy I, Hain S, Perron M, Thellier B, Setti V, Berthier B, Beck L. 2017. Status report on sample preparation protocols developed at the LMC14 Laboratory, Saclay, France: from sample collection to ^{14}C AMS measurement. *Radiocarbon* 59:713–26.
- Estournel C, Kondrachoff V, Marsaleix P, Vehil R. 1997. The plume of the Rhone: Numerical simulation and remote sensing. *Continental Shelf Research* 17:899–924.
- Eyrolle F, Antonelli C, Renaud P, Tournieux D. 2015. Origins and trend of radionuclides within the lower Rhône River over the last decades. *Radioprotection* 50:27–34.
- Fontugne M, Jouanneau JM. 1987. Modulation of the particulate organic carbon flux to the ocean by a macrotidal estuary: organic carbon isotopes evidence from the Gironde system. *Estuarine Coastal and Shelf Sc* 24:377–87. doi.org/10.1016/0272-7714(87)90057-6.
- Fontugne M, Sadouni N, Salot A, Siclet F, Bouloubassi I. 2002. La distribution des activités en ^{14}C des eaux, du bouchon vaseux et des sédiments dans l'estuaire de la Loire. *Radioprotection - Colloques* 37:1–8.
- Fontugne M, Jean-Baptiste P, Fourré E, Bentaleb I, Dezileau L, Charmasson S, Antonelli C, Marang L, Siclet F. 2012. Carbon 14 inputs from the Rhône River to the Western Mediterranean Sea during fall 2010 and spring 2011. 21st International Radiocarbon Conference, Abst. S16-P-212. Paris 2012.
- Goni MA, Ruttenger KC, Eglinton TI. 1997. Sources and contribution of terrigenous organic carbon to surface sediments in the Gulf of Mexico. *Nature* 389:275–8.
- Goni MA, Ruttenger KC, Eglinton TI. 1998. A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico. *Geochimica et Cosmochimica Acta* 62:3055–75.
- Goni MA, Monacci N, Gisewhite R, Crockett J, Nittrouer C, Ogston A, Alin SR, Aalto R. 2008. Terrigenous organic matter in sediments from the Fly River delta-clinoform system (Papua New Guinea). *J. Geophys. Res.* 113, F01S10, doi:10.1029/2006JF000653.
- Harmelin-Vivien M, Dierking J, Banaru D, Fontaine MF, Arlhac D. 2010. Seasonal variation in stable C and N isotope ratios of the Rhone River inputs to the Mediterranean Sea (2004–2005). *Bio-geochemistry* 100:139–50.
- Higuera M, Kerherve P, Sanchez-Vidal A, Calafat A, Ludwig W, Verdoit-Jarraya M, Heussner S, Canals M. 2014. Biogeochemical characterization of the riverine particulate organic matter transferred to the NW Mediterranean Sea. *Bio-geosciences* 11:157–72.
- Hunt JM. 1970. The significance of carbon isotopes variations in marine sediments. In: Hobson GB, Speers GC, editors. *Advances in Organic Chemistry*. p 27–35.
- Jean-Baptiste P, Fontugne M, Fourré E, Marang L, Antonelli C, Charmasson S, Siclet F. 2018a. Tritium and radiocarbon levels in the Rhône river delta and along the French Mediterranean coastline. *Journal of Environmental Radioactivity* 187:53–64.
- Jean-Baptiste P, Fontugne M, Fourré E, Marang L, Charmasson S, Siclet F. 2018b. Tritium and carbon-14 temporal variations in the organic matter of sediments off the Rhône River mouth (NW Mediterranean). *Journal of Environmental Radioactivity* (submitted).
- Lansard B, Rabouille C, Denis L, Grenz C. 2009. Benthic remineralization at the land-ocean interface: A case study of the Rhone River (NW Mediterranean Sea). *Estuarine Coastal and Shelf Science* 81:544–4.
- Maillet GM, Vella C, Berne S, Friend PL, Amos CL, Fleury TJ, Normand A. 2006. Morphological changes and sedimentary processes induced by the December 2003 flood event at the present mouth of the Grand Rhone River (southern France). *Mar. Geol.* 234:159–77.
- Many G, Bourrin F, Durrieu de Madron X, Ody A, Doxaran D. In press. Glider and satellite monitoring of the variability of the suspended particle distribution and size in the Rhône ROFI. *Progress in Oceanography* 163:123–35. http://dx.doi.org/10.1016/j.pocean.2017.05.006
- Miralles J, Radakovitch O, Aloisi JC. 2005. Pb-210 sedimentation rates from the Northwestern Mediterranean margin. *Mar. Geol.* 216:155–67.
- Mook WG, van der Plicht J. 1999. Reporting C-14 activities and concentrations. *Radiocarbon* 41:227–39.
- Moreau C, Caffy I, Comby C, Delquéc-Količ E, Dumoulin J-P, Hain S, Quiles A, Setti V, Souprayen C, Thellier B, et al. 2013. Research and development of the Artemis ^{14}C AMS facility: status report. *Radiocarbon* 55(2–3).
- Ollivier P, Hamelin B, Radakovitch O. 2010. Seasonal variations of physical and chemical erosion: A three-year survey of the Rhone River (France). *Geochimica et Cosmochimica Acta* 74:907–27.

- Olsson, Osadebe. 1974. Carbon isotope variations and fractionation corrections in ^{14}C dating. doi: 10.1111/j.1502-3885.1974.tb00672.x.
- Pastor L, Deflandre B, Viollier E, Cathalot C, Metzger E, Rabouille C, Escoubeyrou K, Lloret E, Pruski AM, Vétion G, Desmalades M, Buscail R, Gremare A. 2011. Influence of the organic matter composition on benthic oxygen demand in the Rhone River prodelta (NW Mediterranean Sea). *Continental Shelf Research* 31:1008–9.
- Pont D, Day JW, Hensel P, Franquet E, Torre F, Rioual P, Ibanez C, Coulet E. 2002. Response scenarios for the deltaic plain of the Rhone in the face of an acceleration in the rate of sea-level rise with special attention to Salicornia-type environments. *Estuaries* 25:337–58.
- Pozzato L, Rassmann J, Lansard B, Dumoulin J-P, van Brugel P, Rabouille C. 2018. 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. *Progress in Oceanography* 163 (2018):112–22.
- Rabouille C. 2013. CARBODELTA cruise, RV Thélys II, <http://dx.doi.org/10.17600/13450060>.
- Radakovitch O, Charmasson S, Arnaud M, Bouisset P. 1999a. Pb-210 and caesium accumulation in the Rhone delta sediments. *Estuarine Coastal and Shelf Science* 48:77–92.
- Radakovitch O, Cherry RD, Heussner S. 1999b. Pb-210 and Po-210: tracers of particle transfer on the Rhone continental margin (NW Mediterranean). *Deep-Sea Res. I* 46:1539–63.
- Rassmann J, Lansard B, Pozzato L, Rabouille C. 2016. Carbonate Chemistry in sediment pore waters of the Rhône River delta driven by early diagenesis (NW Mediterranean). *Biogeosciences* 13:5379–94.
- Raymond PA, Bauer JE. 2001. Use of ^{14}C and ^{13}C natural abundances for evaluating riverine, estuarine, and coastal DOC and POC sources and cycling: a review and synthesis. *Org. Geochem.* 32:469–85.
- Seeberg-Elverfeldt J, Schlüter M, Feseker T, Kölling M. 2005. Rhizon sampling of pore waters near the sediment-water interface of aquatic systems. *Limnol. Oceanogr.-Methods* 3: 361–71.
- Sempere R, Charriere B, Van Wambeke F, Cauwet G. 2000. Carbon inputs of the Rhone River to the Mediterranean Sea: Biogeochemical implications. *Global Biogeochemical Cycles* 14:669–81.
- Siani G, Paterne M, Arnold M, Bard E, Métiévier B, Tisnérat N, Bassinot F. 2000. Radiocarbon reservoir ages in the mediterranean Sea and Black sea. *Radiocarbon* 42:271–80.
- Tisnérat-Laborde N, Montagna P, Frank N, Siani G, Silenzi S, Paterne M. (2013) A high-resolution coral-based $\Delta^{14}\text{C}$ record of surface water processes in the western Mediterranean Sea. *Radiocarbon* 55(2–3):1917–30.
- Toussaint F. 2013. Variabilité temporelle des processus biogéochimiques influençant le carbone organique terrigène dans les sédiments du prodelta du Rhone, LSCE. Université de Versailles Saint-Quentin-en-Yveline. p 215.
- Toussaint F, Tisnérat-Laborde N, Cathalot C, Buscail R, Kerherve P, Rabouille C. 2013. Depositional processes of organic matter in the Rhone river delta (Gulf of Lions, France) traced by density fractionation coupled with d^{14}C and d^{13}C . *Radiocarbon* 55:920–31.
- Vogel JS, Southon JR, Nelson DE, Brown TA. 1984. Performance of catalytically condensed carbon for use in accelerator mass spectrometry. *Nuclear Instruments and Methods in Physics Research B* 5(2):289–93
- Zetsche E, Thornton B, Midwood AJ, Witte U. 2011. Utilisation of different carbon sources in a shallow estuary identified through stable isotope techniques. *Continental Shelf Research* 31: 832–40.
- Zuo Z, Eisma D, Gieles R, Beks J. 1997. Accumulation rates and sediment deposition in the northwestern Mediterranean. *Deep-Sea Res. II* 44:597–609.