Biogeoquímica dels fluxos de partícules en canyons submarins de la Mediterrània nord-occidental: Els efectes de les cascades d'aigües denses de plataforma

Biogeochemistry of particle fluxes in submarine canyons of the Northwestern Mediterranean Sea:
The effects of dense shelf water cascading

Catalina Pasqual Mas

BIOGEOQUÍMICA DELS FLUXOS DE PARTÍCULES EN CANYONS SUBMARINS DE LA MEDITERRÀNIA NORD-OCCIDENTAL: ELS EFECTES DE LES CASCADES D'AIGÜES DENSES DE PLATAFORMA

BIOGEOCHEMISTRY OF PARTICLE FLUXES IN SUBMARINE CANYONS OF THE NORTHWESTERN MEDITERRANEAN SEA: THE EFFECTS OF DENSE SHELF WATER CASCADING

Memòria de Tesi Doctoral presentada per

Catalina Pasqual Mas

per a optar al grau de Doctora per la Universitat de Barcelona.

Programa de Doctorat de "Ciències del Mar", adscrit al Departament d'Estratigrafia, Paleontologia i Geociències Marines de la Universitat de Barcelona (bienni 2006-2008).

Barcelona, març de 2011.

La Doctoranda,   El Director,   La Directora,

Catalina Pasqual Mas   **Antoni M. Calafat Frau**   **Anna Sànchez Vidal**

Capítol 3

Across margin export of organic matter traced by stable isotopes during and off cascading events, Northwestern Mediterranean Sea

A. Sanchez-Vidal,[a,b*] C. Pasqual,[b] P. Kerhervé,[a] S. Heussner,[a] A. Calafat,[b] A. Palanques,[c] X. Durrieu de Madron,[a] M. Canals,[b] and P. Puig[c]

[a] CEntre de Formation et de Recherche sur l'Environnement Marin. *Centre National de la Recherche Scientifique -* Univ. Perpignan. Perpignan, France

[b] Grup de Recerca Consolidat en Geociències Marines. Facultat de Geologia. Univ. Barcelona. Barcelona, Spain

[c] Institut de Ciències del Mar, CSIC. Barcelona, Spain

Abstract

We present a one-year (2005-06) record of organic carbon (OC) and total nitrogen (TN) contents and their isotopic ratios ($\delta^{13}C_{OC}$ and $\delta^{15}N$) in sinking particles from the western Gulf of Lions. Maximum OC and TN fluxes recorded in January 2006 and March-April 2006 were associated with negative near-bottom temperature anomalies. This reveals large inputs of resuspended organic matter from the shelf basinwards to depths >1500 m by dense shelf water cascading. The first pulse of organic matter had low $\delta^{13}C_{OC}$ (-25.5‰) and N:C (0.08) and high $\delta^{15}N$ (6.6‰) values, indicative of the arrival of organic matter of terrestrial origin. In contrast, the second pulse had high $\delta^{13}C_{OC}$ (-21.9‰) and N:C (0.15) and extremely low $\delta^{15}N$ (0.0‰) values, indicative of the transfer of organic matter with higher marine contribution. Though down-slope export of organic matter from the adjacent shelf predominated, particles escaping from surface waters remained an important source of organic matter during low-energy and low-flux periods and especially during summer conditions, with significant contribution of N_2 fixation to organic matter export. Overall, our results suggest the export of organic matter form different sources to the deep Mediterranean basin, which in turn might alter within a couple of months the quality of the sedimentary organic matter deposited on the sea floor and thus the dynamics of the deep ecosystems.

Resum

Es presenta el contingut de carbó orgànic (OC) i nitrogen total (TN), així com la seva composició isotòpica ($\delta^{13}C_{OC}$ i $\delta^{15}N$), enregistrats durant un any (2005-2006) a les partícules que sedimentaven a la zona oest del Golf de Lleó. Els fluxes màxims de OC i TN enregistats al gener 2006 i març-abril de 2006 foren associats a anomalies negatives de la temperatura del fons. Això revela grans aportacions de matèria orgànica resuspesa de la plataforma cap a conca, fins a profunditats de 1500 m, per la cascada d'aigua densa de la plataforma. El primer pols de la matèria orgànica va tenir valors baixos de $\delta^{13}C_{OC}$ (-25,5 ‰) i N:C (0,08) i alts de $\delta^{15}N$ (6,6 ‰), la qual cosa indica l'arribada de la matèria orgànica d'origen terrestre. Per contra, el segon pols tingué valors elevats de $\delta^{13}C_{OC}$ (-21,9 ‰) i N:C (0,15) i valors molts baixos de $\delta^{15}N$ (0,0 ‰), la qual cosa indica la transferència de matèria orgànica amb una major contribució marina. Encara que les exportacions de matèria orgànica mar endins des de plataforma adjacent predominaren, les partícules procedents de aigües superficials foren una font important de matèria orgànica durant els períodes de baixa energia i, especialment, durant l'estiu, amb una important contribució de la fixació de N_2 a l'exportació de la matèria orgànica. En general, els nostres resultats suggereixen una exportació de matèria orgànica de diferents fonts cap a la conca profunda del Mediterrani, que al seu torn poden alterar amb un parell de mesos la qualitat de la matèria orgànica sedimentària dipositada al fons de la mar i, per tant, la dinàmica dels ecosistemes profunds.

Introduction

Continental margins, as the interface between land and the open ocean, are the most important areas within the ocean in terms of terrigenous input and biological production, which make these zones an area of high deposition of particulate matter including organic carbon and nitrogen. Besides accumulation, physical processes occurring at the shelf edge are capable of transferring matter to the deep sea. Identifying sources of particulate matter in continental margins and the cross-slope exchange mechanisms involved is therefore essential to understand carbon and nitrogen cycling in the overall marine environment. Studies of sources and biogeochemical cycles of particulate carbon and nitrogen have been based on the use of their isotopes as measured in settling particles. Indeed, the isotopic ratios of organic carbon ($\delta^{13}C_{OC}$) and nitrogen ($\delta^{15}N$) in particulate matter vary when processes leading to its production, transformation and decomposition undergo isotopic fractionation between heavy (^{13}C, ^{15}N) and light (^{12}C, ^{14}N) isotopes.

$\delta^{13}C_{OC}$ has been widely used in oceanography jointly with N:C ratios as a first provenance proxy to distinguish between marine or terrestrial organic matter in continental margin environments. Marine organic matter from temperate phytoplankton has a $\delta^{13}C$ value from -19‰ to -22‰, while terrestrial organic matter has typically a $\delta^{13}C_{OC}$ value between -25‰ to -28‰ if C3 plants are the dominant constituents, and -12‰ to -15‰ if C4 plants are prevailing (Hedges et al. 1997). In addition, vascular plant derived organic matter is typically depleted in nitrogen (N:C<0.06), whereas phytoplankton and bacterioplankton organic matter sources are characterized by higher nitrogen content (N:C>0.12) (Goñi and Hedges 1995).

$\delta^{15}N$ reflects the isotopic composition of the N-containing nutrients acquired by the organisms. While terrestrial plants and marine nitrogen fixers rely on the atmospheric N_2 source ($\delta^{15}N$~0‰), marine primary producers assimilate dissolved nitrogen ($\delta^{15}N$~4.8‰, Sigman et al. 2000). However, transformation processes of the N-source cause isotopic fractionation such that the $\delta^{15}N$ of organic matter essentially records these processes. Thus, mineralization in soils and denitrification in suboxic water columns enriches nitrate in the heavier isotope (Amundson et al. 2003; Ganeshram et al. 2000), and isotopic fractionation during planktonic nitrate uptake produces organic matter isotopically lighter than the nitrate pool (Altabet 1996).

Therefore, $\delta^{13}C_{OC}$ and $\delta^{15}N$ are together potentially useful tools to characterize nitrogen and carbon transport and transformation processes in continental margin environments. Here we investigate temporal variations of OC and TN content and their isotopic ratios in sinking particles collected over a complete seasonal cycle by an array of nine instrumented lines with sediment traps moored in the western Gulf of Lions (NW Mediterranean Sea). Various studies carried out in the Gulf of Lions have described the major mechanisms controlling cross-slope exchanges of OC (Canals et al. 2006; Heussner et al. 2006), although the biogeochemical features of the transferred organic material were not thoroughly discussed. Recently, Fabrés et al. (2008) described the role of the submarine canyons in the transfer of OC by means of organic tracers, limiting their 5-month investigation (winter 2003-04) to the canyon heads. In

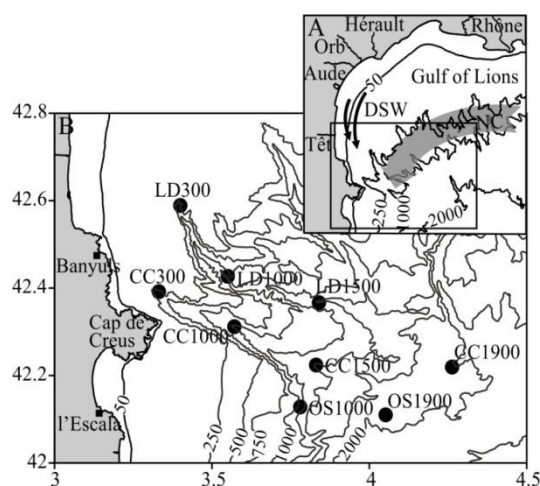Fig. 3.1. (A) General bathymetric map of the Gulf of Lions with main river systems referred to in the main text. Grey arrow shows direction of the along-slope Northern Current (NC), and black arrows of Dense Shelf Water circulation on the shelf (DSW). (B) Location of the mooring lines within Lacaze-Duthiers Canyon (LD), Cap de Creus Canyon (CC) and the southern open slope (OS) (number in station labels correspond to the water depth).

addition, Sanchez-Vidal et al. (2008) described the 'immediate' effect of the winter 2005-06 major dense shelf water cascading event on the quality and distribution of OC using $\delta^{13}C_{OC}$ on a short 2-month study (December 2005 to January 2006). In this entire 1-year study we provide most of the ingredients to better understand physical and biological processes regulating organic matter fluxes and transfer from the Gulf of Lions canyon heads to the deep Mediterranean basin by means of $\delta^{13}C_{OC}$ and $\delta^{15}N$. This investigation is framed within the research project HERMES (Hotspot Ecosystem Research on the Margins of European Seas) and other related research projects at both European and national levels, whose main aim is to gain new insights into the biodiversity, structure, function and dynamics of ecosystems along Europe's deep-ocean margin. In fact major questions about the functioning of these ecosystems concern their dependence on element cycles and energy fluxes, therefore the quantitative and qualitative assessment of settling organic matter will enhance our ability to characterize the environmental variables regulating diversity and faunal distributions.

Methods

STUDY AREA - The Gulf of Lions is a 200 km long and 80-90 km across progradational continental margin located in the NW Mediterranean Sea with a crescent-shaped shelf and an upper slope densely cut by a network of submarine canyons (Fig. 3.1A). Several sources feed shelf waters with particulate matter including river discharge, biological production and particle resuspension. Most of the riverine material reaching the Gulf of Lions comes from the Rhône river, in the north-eastern part of the area, which delivers more than 80% of the total river discharge into the Gulf of Lions (Aloïsi et al. 1977). In addition, smaller torrential rivers along the western coast (i.e., Hérault, Orb, Aude, and Têt rivers) can significantly contribute to riverine inputs via the occurrence of short and violent flash-flood events (Serrat et al. 2001). Biological production is characterised by a spring diatom bloom that lasts generally until May and is initiated by the increase of insolation and thermal stratification (Bosc

et al. 2004). Secondary blooms appear in summer and autumn and are linked to marine upwelled or river nutrient inputs (Lefèvre et al. 1997). Finally, resuspension of superficial sediment and freshly deposited material that has not become incorporated into the sediment provide an additional input of material, which can contribute to up to 70% of the total particulate matter settling on the upper slope (Heussner et al. 2006).

Sedimentary particles in the Gulf of Lions are transported and exchanged at the shelf break and through the heads of submarine canyons by the general surface circulation, storm-induced downwelling and dense shelf water cascading. Sea surface circulation in the Gulf of Lions is dominated by the Northern Current (NC), which flows along the slope as a part of the cyclonic circulation of the western Mediterranean Sea (Fig. 3.1A; Millot 1990). The Northern Current is associated to a permanent shelf-slope density front separating less saline shelf waters with continental influence from saltier and denser open-sea waters, which constrains shelf-slope exchanges and advects suspended matter (Lapouyade and Durrieu de Madron 2001). Storm-induced downwelling occurs when strong and humid E and SE winds cause heavy rainfall and flash floods. These episodes are associated with large waves on the shelf and intense sediment resuspension (Guillén et al. 2006). River plumes and resuspended sediments are advected along the shelf to the southwestern end of the Gulf, where a massive convergence of shelf water causes intense downwelling along with down-canyon sediment transport (Palanques et al. 2006). The occurrence of Dense Shelf Water Cascading (DSWC) also relates to meteorological forcing. Winter heat losses and evaporation caused by cold, dry, and persistent N and NW winds induce cooling and mixing of shelf waters, which eventually get dense enough to sink, overflow the shelf edge and cascade downslope (Béthoux et al. 2002). The preferential cyclonic circulation and the narrowing of the southern end of the shelf cause flow convergence and acceleration (Fig. 3.1A), which provides a mechanism for shelf sediment erosion due to high effective shear stress (Bourrin et al. 2008). The dense water plume, which overflows the shelf edge and cascades at high

velocities (up to 80 cm s^{-1}) down the upper course of the westernmost submarine canyons, has the ability to entrain and transport coarse sediments and abrade the seafloor (Canals et al. 2006).

3.1.1 Experiment design and analytical methods

Nine mooring lines were deployed from October 2005 to October 2006 along the axes of the Lacaze-Duthiers and Cap de Creus submarine canyons at 300, 1000, and 1500 m depth, at their confluence at 1900 m depth, and on the adjacent southern open slope at 1000

and 1900 m depth (Fig. 3.1B). Moorings at 300 m were located in the canyon head, those at 1000 m in the upper canyon course, those at 1500 m in the middle canyon and that at 1900 m in the lower canyon course, as described by Lastras et al. (2008). Each mooring was equipped with one sequential sampling (12 cups) PPS3 Technicap sediment trap (0.125 m^2 opening) at 30 m above the bottom. Samples were collected over 12 months and consisted of two successive deployment periods: 17 or 24 October 2005 to 14 April 2006, and 01 May 2006 to 23 October 2006, with sampling intervals set at 15 days. Unfortunately, no samples were recovered from October 2005 to
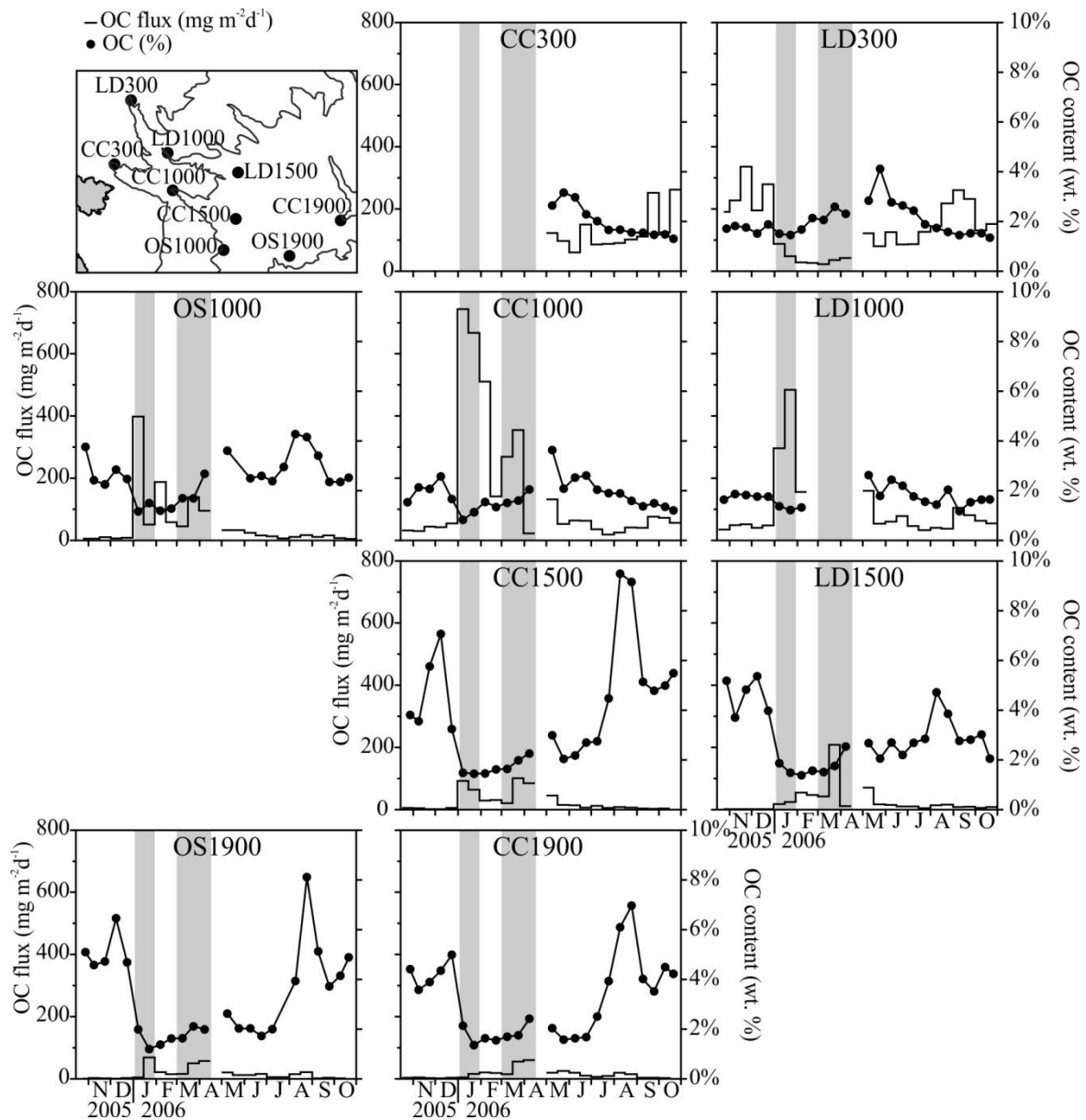

Fig. 3.2. Temporal evolution of OC flux (mg m^{-2} d^{-1}, columns) and OC content (wt. %, black dots) at the mooring stations. Grey bands show main pulses of dense shelf water.

April 2006 at CC300 and from February to April 2006 at LD1000 because of failure of the sediment trap rotating motor. Each mooring had one Aanderaa RCM9/11 current meter 5 m above bottom, recording with a sampling interval of 20 min. Temperature data was calibrated using contemporary CTD measurements.

Sediment trap sample processing is described in detail in Heussner et al. (1990). Large swimming organisms were removed by wet sieving through a 1 mm nylon mesh, while organisms <1 mm were hand-picked under a microscope with fine-tweezers. Samples were repeatedly split into aliquots using a high precision peristaltic pump robot to obtain 20-50 mg sub-samples. Sample dry weights, from which total mass fluxes were calculated, were determined on four subsamples filtered onto 0.45 mm Millipore cellulose acetate filters and dried at 40ºC for 24 h. Sub-samples for organic carbon and total nitrogen analysis were filtered onto Millipore Fiberglass Filters (APFF) and dried at 40ºC. Samples for organic carbon analysis were first decarbonated using repeated additions of 25% HCl with 60ºC drying steps in between until no effervescence was observed. OC and TN were measured on a Thermo NA 2100 elemental analyzer at the Scientific-Technical Services of the
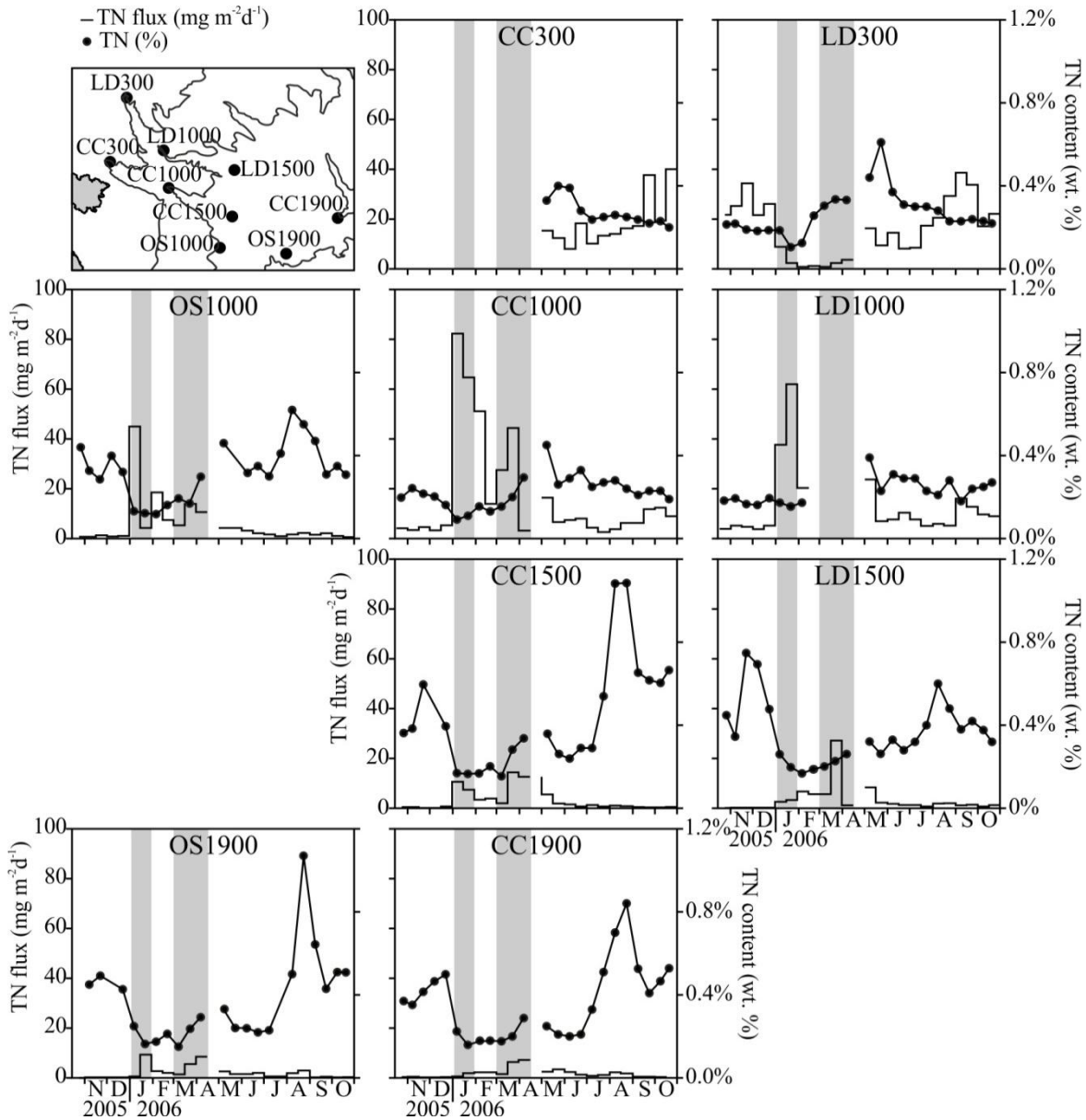

Fig. 3.3. Temporal evolution of TN flux (mg m^{-2}d^{-1}, columns) and TN content (wt. %, black dots) at the mooring stations. Grey bands show main pulses of dense shelf water.

University of Barcelona. Uncertainties were lower than 0.1% as determined from replicates of the certified estuarine sediment MESS-1. Fluxes of OC and TN have been obtained by multiplying OC and TN contents by total mass flux.

Sub-samples (20 to 50 mg) for OC and TN isotopic analyses were freeze-dried and ground to a fine powder. Samples for OC isotopic analyses were first decarbonatated using repeated additions of 2N HCl. Stable isotopic compositions of OC ($\delta^{13}C_{OC}$) and TN ($\delta^{15}N$) were measured with an Eurovector elemental analyzer coupled to a GVI-Isoprime mass spectrometer at the Centre de Formation et de Recherche sur l'Environnement Marin (CNRS-University of Perpignan). Uncertainties were lower than 0.2‰ as determined from routine replicate measurements of the IAEA reference samples CH-3 for $\delta^{13}C$ and N-1 for $\delta^{15}N$. Isotopic data are expressed in the conventional $\delta^{13}C_{OC}$ and $\delta^{15}N$ notations relative to Pee Dee Belemnite and atmospheric N_2, respectively.

Results

Particulate OC and TN fluxes and contents are shown in Figs. 2, 3. High OC and TN fluxes were recorded in January 2006 at all stations (with the exception of the LD300 station), with fluxes up to 745 mg OC m^{-2} d^{-1} and 82 mg TN m^{-2} d^{-1} at station CC1000. There was an overall seaward decrease of the maximum OC and TN fluxes recorded, but even at the deeper stations OC and TN fluxes were 3 to 65 times higher than those measured during the preceding month. Fluxes decreased after this remarkable event, and peaked again in March-April 2006 with values up to 355 mg OC m^{-2} d^{-1} and 44 mg TN m^{-2} d^{-1} (station CC1000). Maxima OC and TN fluxes decreased, once more seawards and downcanyon. OC and TN fluxes remained low during the following months (May to August 2006), with small fluctuations in September-October 2006 at the head of both canyons.

OC and TN contents were relatively low during both events and especially during the first maxima, with OC contents below 2.1 wt. % and 2.9 wt. %, and TN contents below 0.2 wt. % and 0.3 wt. % in January and March-April 2006, respectively (Figs. 2, 3). In contrast, noticeable increases of OC (up to 9.5 wt. %) and TN (up to 1.1wt. %) contents were recorded during OC and TN flux minima in December 2005 and August-September 2006 at the more offshore stations (1500-1900 m of water depth).

Isotopic compositions of settling OC ($\delta^{13}C_{OC}$) and TN ($\delta^{15}N$) are shown jointly with N:C ratios in Figs. 4, 5. The good correlation of OC and TN contents of sediment trap samples (r^2=0.92 and almost zero TN content interception at zero OC content, data not shown) suggests that most of the TN is organic, so atomic N:C (i.e., TN:OC) is used. During the study period $\delta^{13}C_{OC}$ ranged from -21.4‰ to -25.5‰, and $\delta^{15}N$ ranged from 6.6‰ to 0.0‰. $\delta^{13}C_{OC}$ values show a common decrease at all stations in early January 2006, which was exceptionally pronounced at the CC1000 station (-25.5‰). These low isotopic ratios were followed by a progressive $\delta^{13}C_{OC}$ and N:C ratio increase in late March until May 2006 at the whole study area. $\delta^{15}N$ values show the inverse pattern than that of $\delta^{13}C_{OC}$, with high values recorded in early January 2006 (up to 6.6‰) followed by a noticeable decrease in late March 2006 (-0.1‰). In addition, a secondary depletion of $\delta^{15}N$ (minimum of 1.0‰) was recorded at the more offshore stations in August 2006.

Discussion

3.1.2 Physical factors controlling organic carbon and total nitrogen fluxes

High OC and TN fluxes similar to those found during the reported period have been already documented in NW Mediterranean Sea submarine canyons and related to cross-slope exchange mechanisms such as downwelling induced by E-SE storms and DSWC (Heussner et al. 2006; Fabrés et al. 2008). Indeed, strong negative near-bottom temperature anomalies (Fig. 3.6) recorded by moored current meters revealed that a major DSWC event occurred in winter 2005-06, the latest up to date recorded, which followed those occurred in winters 1998-99 and 2004-05 (Figs. 7A). Northerly winds were particularly intense in winter 2005-06, with daily means above 15 cm s^{-1} for several consecutive days in

January and March 2006 (Fig. 3.7B), causing strong heat loss and cooling of surface waters, that ultimately sunk and cascaded down the slope (Fig. 3.6). Intensified DSWC occurred for 4-months at the upper canyon sections, with temperature and current speed anomalies peaking at the onset of the cascading period (early January 2006, with velocities >70 cm s^{-1} at the CC1000 station as shown Sanchez-Vidal et al., 2008) and in late March 2006 (Palanques unpubl.). Temperature anomalies caused by DSWC decreased in duration and intensity with depth, but could be tracked along the Cap de Creus and Lacaze-Duthiers

submarine canyons and on the southern slope down to 1900 m (Fig. 3.6). Temperature drops recorded down to 1500 m in the canyons and on the slope indicate that the dense water reached the equilibrium level (neutral density contrast) at depths between 1500 m and 1900 m. Moreover it reveals the preferential along isobath path along the southern open slope once dense water is no more constrained by the canyons' walls (Figs. 3.1, 3.6).

Both cascading pulses of dense shelf water coincided with maxima OC and TN fluxes recorded by the sediment traps (Figs. 3.2, 3.3), which is a direct
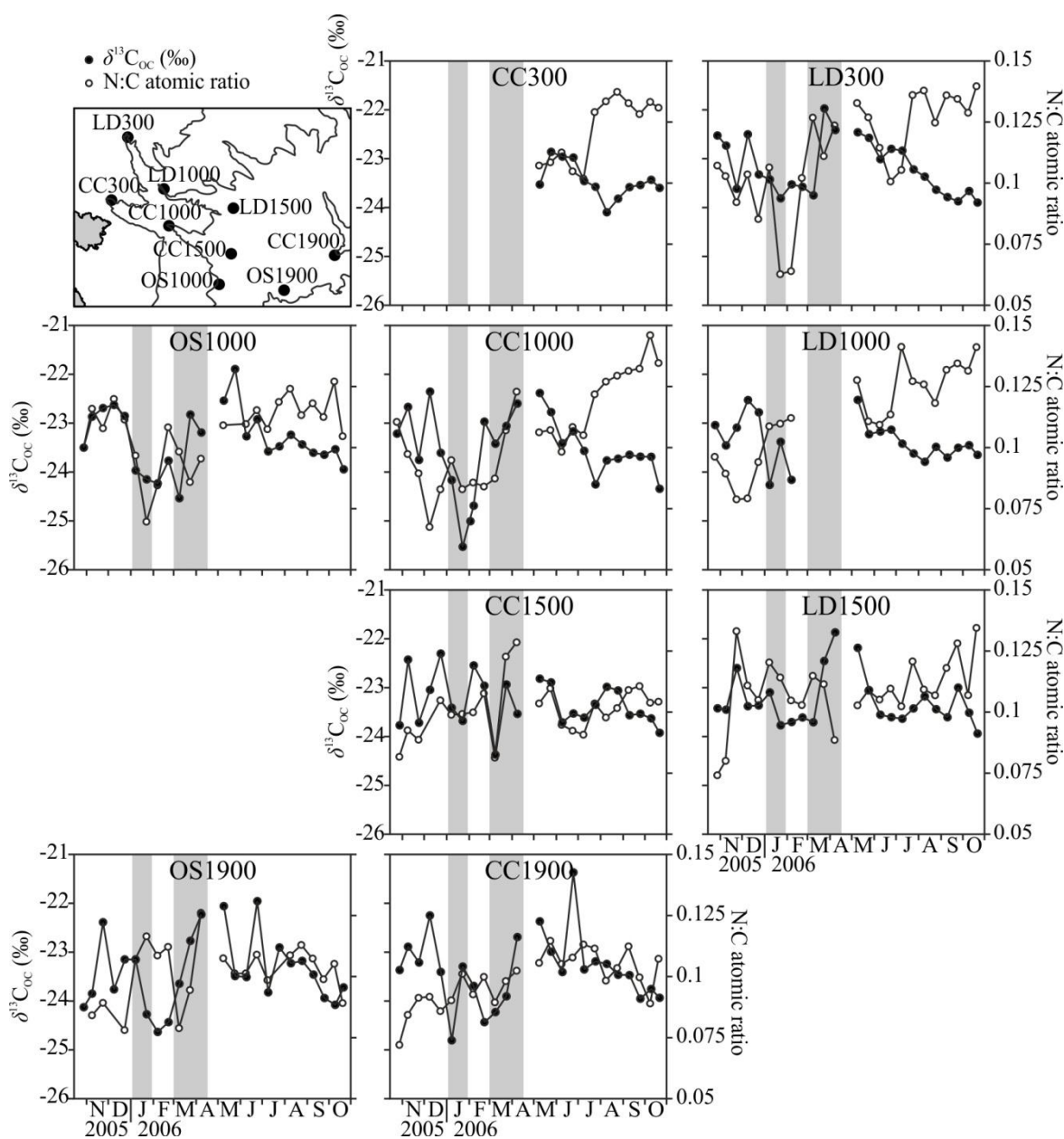

Fig. 3.4. Temporal evolution of $\delta^{13}C_{OC}$ (‰, black dots) and N:C atomic ratio (white dots) of settling particles at the mooring stations. Grey bands show main pulses of dense shelf water.

evidence of the capacity of the strong cascading currents to carry and transport massive amounts of material, including OC and TN, several kilometers offshore in few days. The decreasing transport capacity of the dense shelf water plume along its down canyon and slope propagation caused progressive deposition of particles and a downstream geochemical gradient (Sanchez-Vidal et al. 2008), as shown by the decreasing OC and TN fluxes with distance to the shelf edge during both cascading pulses (Figs. 3.2, 3.3). The noticeably higher current speeds (Sanchez-Vidal et al. 2008) and OC and TN flux (Figs. 3.2, 3.3) recorded at the Cap de Creus canyon in comparison with those at

the Lacaze-Duthiers canyon during both pulses reinforces the idea of a coastal topographic constraint of the Cap de Creus promontory (Fig. 3.1A), which may favour most of the shelf sediment transport to occur preferentially through the Cap de Creus canyon (Canals et al. 2006; Palanques et al. 2006), with spill over towards the southern slope. In addition, the lack of OC and TN fluxes increase in the Lacaze-Duthiers canyon head station may be caused by low particle deposition due to very strong currents at the canyon head, hence favouring sediment deposition at higher depths (Figs. 3.2, 3.3), as suggested by Bonnin et al. (2008) from winter 2003-04 observations.
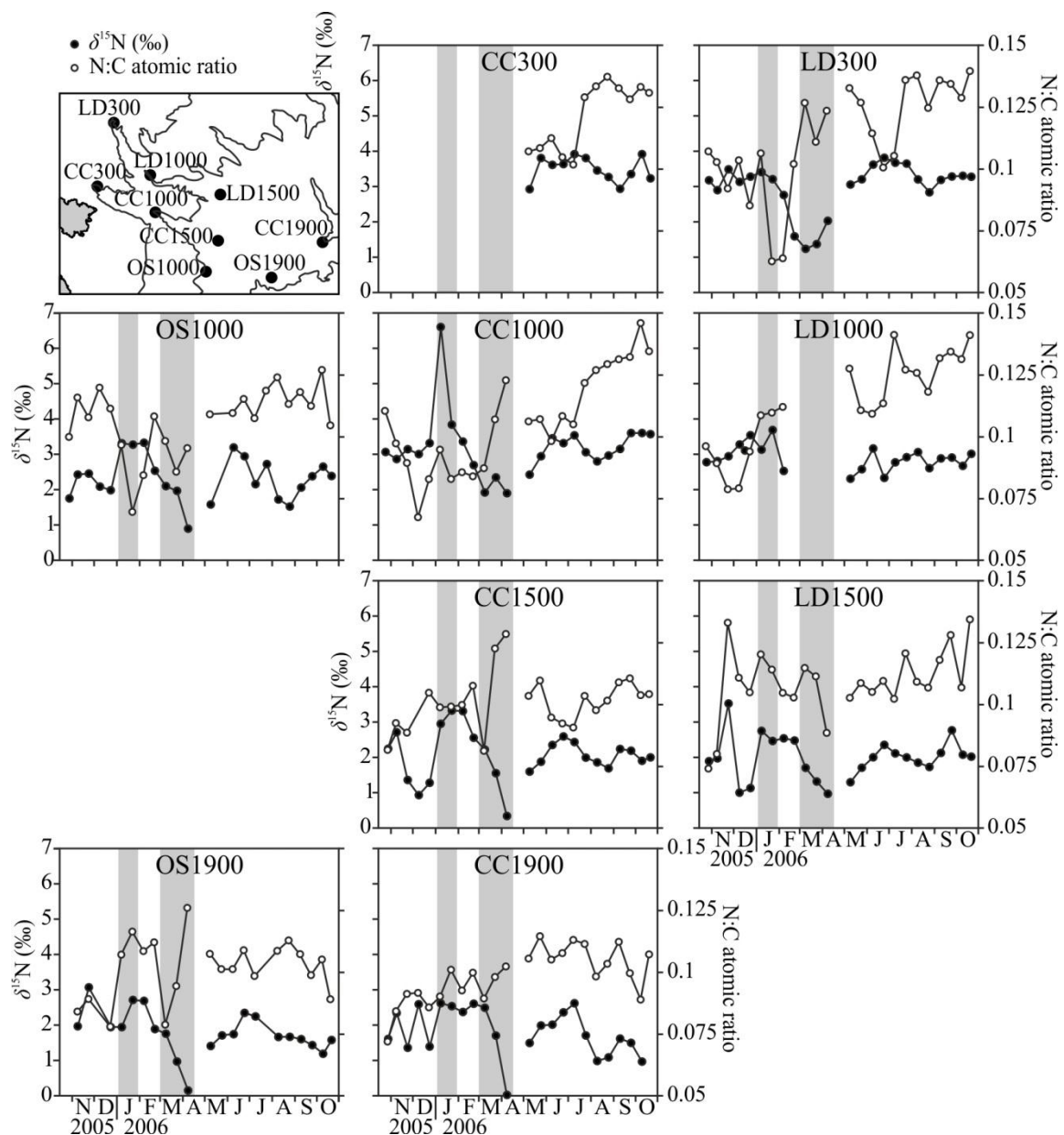
Fig. 3.5. Temporal evolution of $\delta^{15}N$ (‰, black dots) and N:C atomic ratio (white dots) of settling particles at the mooring stations. Grey bands show main pulses of dense shelf water.

Despite OC and TN fluxes that remained low during the following months, small fluctuations were recorded in September-October 2006 at the head of the canyons. These inputs of OC and TN particles restricted to the canyon heads were likely related to sporadic events of shelf and/or canyon head sediment resuspension (Heussner et al. 2006), which caused an entrance of material with low OC and TN content (Figs. 3.2, 3.3). On the contrary, minimum OC and TN flux intensity associated to marked increases of OC and TN contents at the more offshore stations in late summer 2006 would reflect the predominant contribution of biogenic particles originating from surface waters (Figs. 3.2, 3.3). This compositional evolution linked to the flux intensity has been already reported in the studied area and reflects the dual origin of particles, i.e., sediment resuspension and primary

flux signal from surface waters (Heussner et al. 2006).

3.1.3 Sources of organic matter as revealed by stable isotopes of carbon and nitrogen

The provenance of organic matter in continental margin environments can be assigned to different sources, which include marine algae, soil derived organic matter and woody-debris (see review in Altabet et al. 1996 and Hedges et al. 1997). Each source has distinct biogeochemical characteristics. Marine algae exhibit a wide isotopic range as recently observed for the Gulf of Lions, with typical $\delta^{13}C_{OC}$ values from -18.6‰ to -21‰ (mean value of -20.1‰) and $\delta^{15}N$ values from 3.7‰ to 5.8‰ (mean value of 4.4‰) (Harmelin-Vivien et al. 2008). Soil derived organic matter and plant debris carried by rivers discharging into the
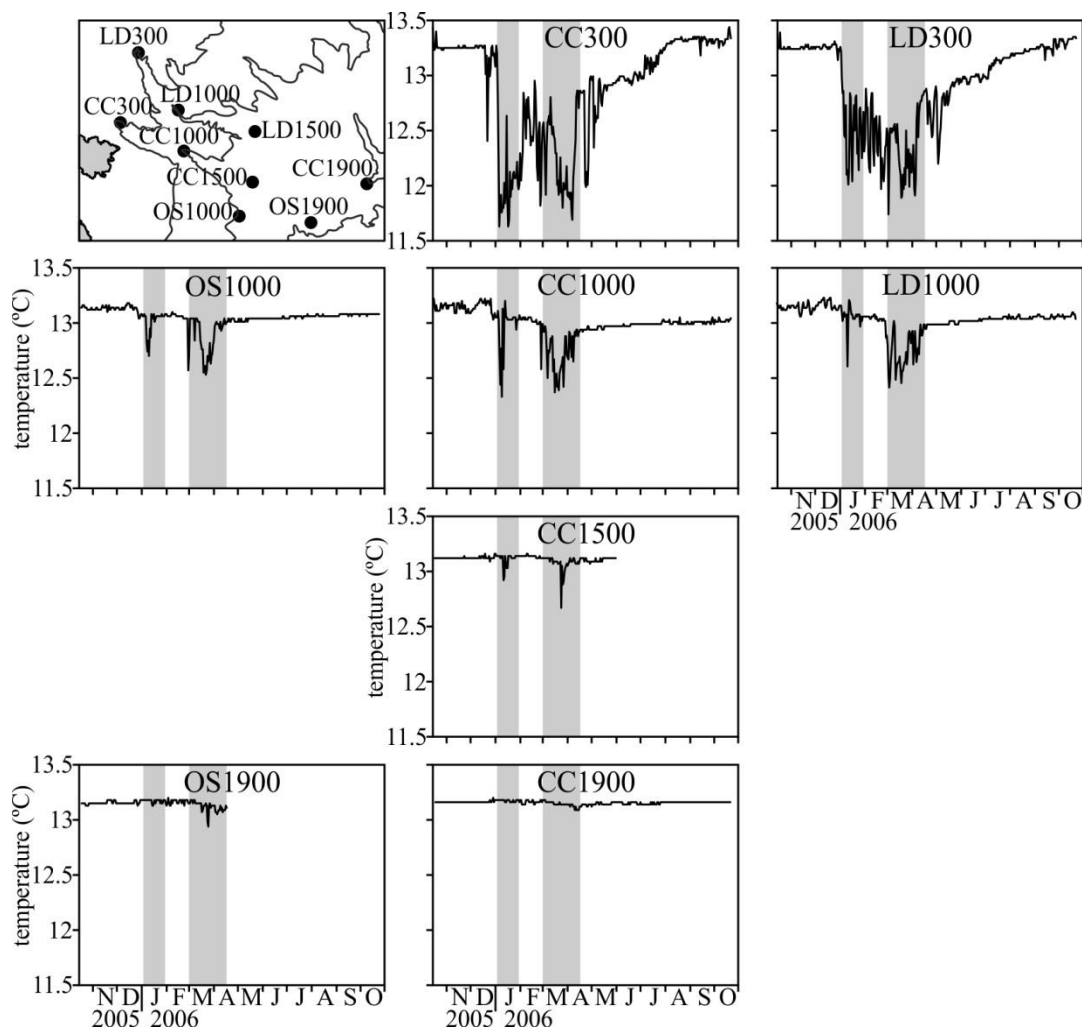
Fig. 3.6. Temporal evolution of near-bottom in situ temperature (ºC) at 5 meters above the bottom at the mooring stations. Grey bands show main pulses of dense shelf water.

Gulf of Lions display depleted $\delta^{13}C_{OC}$ values within the range of terrestrial organic matter derived from C3 vegetation. Kim et al. (2007) reported $\delta^{13}C_{OC}$ values of the Têt river suspended particulate matter ranging from -25‰ to -27.6‰ (mean value of -26.1‰), attributed predominantly to the contribution of soil organic matter, whereas Carlier et al. (2007) found a $\delta^{13}C_{OC}$ value for terrestrial plant detritus of -27.5‰. Besides, $\delta^{15}N$ values of soil and plant organic matter depend on a suite of ecosystem variables. One would expect terrestrial $\delta^{15}N$ signal to be lower than phytoplankton values, but environmental patterns and anthropogenic disturbances may vary $\delta^{15}N$ values. Carlier et al. (2007) found a $\delta^{15}N$ value for terrestrial plant detritus of -0.4‰ and Amundson et al. (2003) estimate soil $\delta^{15}N$ values at the northern Mediterranean Sea region ranging 4.7-7.6‰. Accordingly, suspended matter du-

ring the Têt river flood in November 2005 showed average values around 6‰ (P. Kerhervé unpubl.). Another characteristic of land plants is the predominance of nitrogen-free biomacromolecules over proteins (Hedges et al. 1997), which make plant tissues characteristically carbon-rich (N:C<0.06) vs. plankton (N:C>0.12). Furthermore, the tendency of vascular plant detritus to preferentially gain nitrogen during soil microbial decay increases the N:C ratio from the original plant value up to 0.12 (Hedges et al., 1997). Therefore, by plotting $\delta^{13}C_{OC}$ against N:C (Fig. 3.8A) and $\delta^{15}N$ (Fig. 3.8B) we can get a more incisive view of the source of sinking organic matter. Indeed, isotopic data of settling particles along with potential local sources reflect the mixed origin of settling particles during the reported period, which include, in different proportions, both terrestrial and marine organic
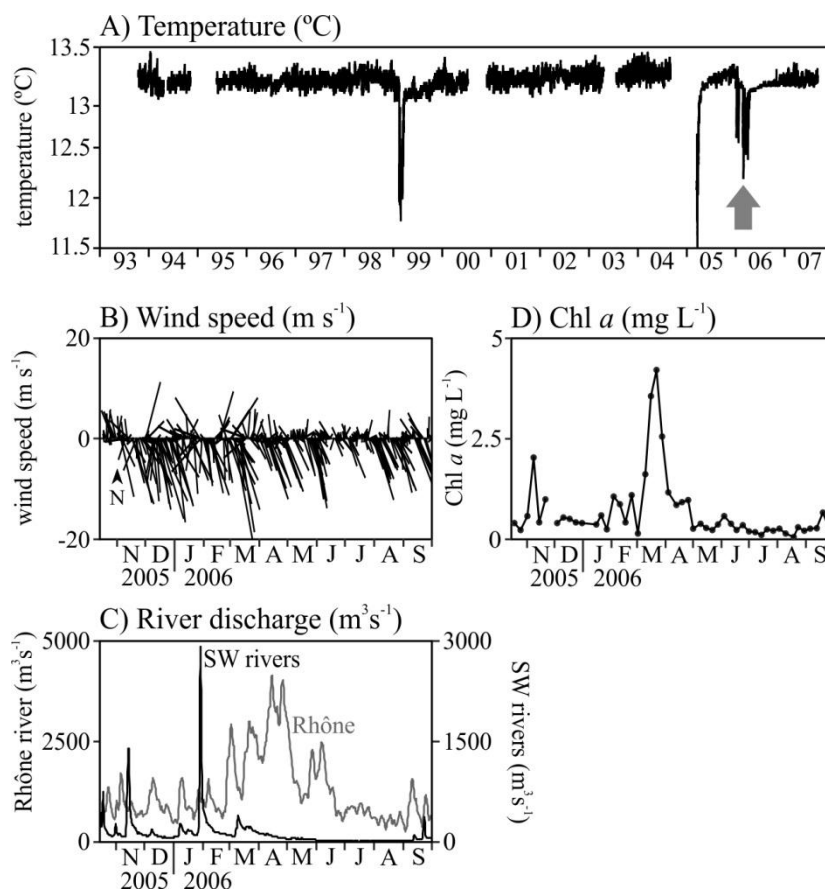

Fig. 3.7. (A) Temporal evolution of near-bottom in situ temperature (ºC) at 30 meters above the bottom at the LD1000 station from 1993 to 2007 (extended from Durrieu de Madron et al. 2005 and Canals et al. 2006). Negative temperature anomalies indicate major DSWC events reaching >1000 m depth, the grey arrow shows the studied event. (B) Daily averaged wind speed obtained from the Meteo-France Aladin atmospheric model (42ºN, 5ºE). (C) Temporal evolution of the water discharge (m s^{-1}) from the Rhône (grey line), and from the sum of the SW rivers (Hérault, Orb, Aude, and Têt; black line). Data from the French national data bank (HYDRO) and the Compagnie National du Rhône (CNR). (D) Surface (3 m) Chlorophyll a (Chl a, µg L^{-1}) concentration at the SOLA monitoring station, located 1 km off Banyuls sur Mer (42.48°N, 3.13ºE). Data provided by Service d'Observation en Milieu LIToral (SOMLIT).

matter.

The analysis of the temporal evolution of $\delta^{13}C_{OC}$, $\delta^{15}N$ and N:C (Figs. 3.4, 3.5) helps to better elucidate the sources of settling organic matter. Both $\delta^{13}C_{OC}$ minimum in early January 2006 and maximum in April 2006 were recorded concomitantly with the large OC fluxes attributed to off-shelf transport by DSWC (Figs. 3.2, 3.3). Accordingly, abrupt highs in $\delta^{15}N$ were recorded in early January 2006, and lows in $\delta^{15}N$ were recorded in April 2006, which suggests that particulate organic matter carried by the first and the second pulses of year 2006 cascading currents originated from different sources.

Settling particles during January 2006 display isotopic compositions consistent with a relevant contribution of terrestrial organic matter sources, in particular at the upper Cap de Creus canyon course, which shows the lowest (-25.5‰) and highest (6.6‰) $\delta^{13}C_{OC}$ and $\delta^{15}N$ values, respectively (Figs. 3.4, 3.5). Since none of the rivers from the Gulf of Lions drainage basin were flooding during early January 2006 (Fig. 3.7C), it is likely that this terrestrial material originates from resuspension of previously deposited riverine material (i.e., winnowing of the inner shelf deposits). Recent studies have related depleted $\delta^{13}C_{OC}$ values of western shelf sediments to increased deposition of terrestrial organic matter during high river discharge events (Kim et al. 2006, 2007), which can be remobilized and deposited as secondary (and successive) flood deposits during DSWC (Bourrin et al. 2008). The strong currents in January 2006 eroded and transported these flood deposits from the shelf towards the deep basin, with their terrestrial signal progressively decreasing along the path of cascading waters due to reducing transport capacity of the dense shelf water plume and mixing with resuspended canyon floor sediments (Sanchez-Vidal et al. 2008). The depleted N:C values recorded at the upper canyon course (0.08-0.09) (Fig. 3.4) suggest a major influence of relatively undegraded flood deposits from the inner-shelf, which contrasts with the high N:C ratios (>0.17) of degraded mid-shelf sediments in the Gulf of Lions found by Tesi et al. (2007). The increased river discharge recorded in mid-November 2005 (with increased solid transport at the onset of the wet season, Serrat et al. (2001)) in

the western rivers Têt, Aude, Orb, and Hérault (Figs. 1, 7C) is most likely the origin of this terrestrial material initially deposited on the inner-shelf and later transported downslope by DSWC. In particular, the Têt river discharged up to 236 m^{-3} s^{-1} in mid-November, a value 20 times higher than the average annual water discharge (Ludwig et al. 2004).

In contrast, the higher $\delta^{13}C_{OC}$ values (-21.9‰ to -23‰) of particles settling during the second pulse of cascading waters in late March-April 2006 indicates that, though particles were advected by the strong currents associated with cascading of dense waters, newly produced particles by primary producers remained a significant source of organic matter. Indeed, the occurrence of intense and widespread phytoplankton blooms in spring is a well-known feature in the study area (Lèfevre et al. 1997; Bosc et al. 2004), as also shown by high chlorophyll a values (up to 4.2 μg Chl a L^{-1}) in coastal surface waters in March 2006 (Fig. 3.7D). Transient nutrient inputs due to increased Rhône river discharge in March-April 2006 (Fig. 3.7C) may have also favoured phytoplankton blooming (Lèfevre et al. 1997), even thought no terrestrial $\delta^{13}C_{OC}$ signal reached the western end of the Gulf (Fig. 3.4). At the same time, a negative nitrogen isotopic composition shift (with values down to 0.0‰) was recorded at the whole study area. This might be a direct signal of marine organic matter production by phytoplankton under nitrate-replete conditions at the onset of the spring phytoplankton bloom (Fig. 3.7D). In the initial phase of the bloom, when nitrate in the euphotic zone was abundant, the $\delta^{15}N$ of phytoplankton biomass was low relative to that of nitrate because of the preferential uptake of nitrate containing the lighter isotope (^{14}N). As nitrate was consumed, the residual nitrate became enriched in ^{15}N, and the $\delta^{15}N$ of phytoplankton increased as it took up this nitrate (Altabet and Deuser 1985; Altabet 1996). The $\delta^{15}N$ -enrichment of marine organic matter after nutrient depletion was nicely recorded in the material collected by sediment traps, which, after a minimum in early April 2006 shows a $\delta^{15}N$ increase during late April-May-June 2006 at the whole study area where values up to 3.9‰ were reached (Fig. 3.5). This value is rather close to the mean $\delta^{15}N$ of deep water nitrate in the western

Mediterranean Sea, 3.4‰ (Pantoja et al. 2002), and the phytoplankton $\delta^{15}N$ value at the end of a spring bloom, 4.4‰ (Harmelin-Vivien et al. 2008). All observations suggest that organic matter deposited at the continental shelf during this spring phytoplankton bloom was quickly resuspended in response to the strong currents, being transported and deposited again further offshore as shown by the high OC and TN fluxes recorded by sediment traps. The sequence of isotopic fractionation during nitrate uptake by plankton during the spring bloom propagated into rapidly sinking particles, which were resuspended and transferred to the deep basin by cascading waters. Thus, transferred particulate matter contained the trace of nutrient utilization by phytoplankton in surface waters. This downslope transport of chlorophyll-rich shelf waters is further supported by the formation of a 200-500 m thick layer with increased fluorescence recorded at >1500 m of water depth basinwards in April 2006 (data not shown), similar to the findings by Canals et al. (2006). In addition, settling particles from surface waters above sediment traps may have contributed to the increased marine organic matter signal at the lower canyon course and deep slope stations (i.e., Sta. CC1900, OS1900).

Though down-slope export of organic matter of shelf origin predominates in winter and spring 2006, particles settling out of the overlying waters remain an important source of organic matter, with maximum OC (up to 9.5 wt. %) and TN (up to 1.1 wt. %) contents linked to low $\delta^{15}N$ (minimum of 1‰) and minimum flux intensity in August 2006 at the more offshore stations (1500-1900 m of water depth). Shelf waters showed minimum Chl a values in summer 2006 (Fig. 3.7D), indicating the absence of phytoplankton blooms near the coast during this season. Also, offshore water column stratification may have inhibited nitrate entrainment from below to the surface layer, as supported by nutrient depletion in summer observed over a 9-year record (Marty et al., 2002). As both $\delta^{13}C_{OC}$ and $\delta^{15}N$ values and the absence of fluvial inputs (Fig. 3.7C) argue against the arrival of material from the continent, it is most likely that this OC and TN-rich and particularly $\delta^{15}N$ -depleted particulate matter was partially produced from the addition of isotopically

depleted N under the influence of diazotrophic activity (i.e., di-nitrogen (N_2) fixation, Karl et al. (2002)). Indeed, the productivity limitation by nitrate depletion may be overcome by organisms capable of converting dissolved N_2 into fixed N (see review in Mahaffey et al. 2005). Over the last decades, several studies based on N to P ratio anomalies (Béthoux and Copin-Montégut 1986), nitrogen fixation experiments (Garcia et al. 2006; Sandroni et al. 2007) and $\delta^{15}N$ measurements in the water column (Kerhervé et al. 2001; Pantoja et al. 2002) and the sediment (Sachs and Repeta 1999; Struck et al. 2001) have revealed the relative importance of nitrogen fixation in the western Mediterranean Sea, both at present and in the past. However, while it is well known that most of the nitrogen fixation in the global ocean is carried out by the marine colonial cyanobacteria Trichodesmium and/or unicellular N_2-fixing cyanobacteria and bacterioplankton in pico- and nanoplankton communities (Zher et al. 2001), direct evidence of N_2 fixing organisms in the Mediterranean Sea is still lacking. If fixation is mediated by the cyanobacteria Synechococcus (Mutsui et al. 1986), which are quite abundant in the study area (Jacquet et al. 1998), and/or by diatoms hosting nitrogen-fixing bacterial symbionts (Villareal 1991), remains unknown.

Nitrogen fixation would produce N that is roughly -3‰ to 1‰ relative to atmospheric N_2 (Carpenter et al., 1997 and references therein). The relatively low $\delta^{15}N$ found on settling particles in August 2006 when compared to typical values of marine phytoplankton in the study area (4.4‰, Harmelin-Vivien et al., 2008) does not enable us to understand which organisms are responsible for N_2 fixation but suggest that diazotrophs contribute to some extent to isotopically depleted N. This is consistent with the high rates of N_2 fixation observed in the NW Mediterranean Sea in August by Sandroni et al. (2007). N_2 fixation may have thus contributed to organic matter input to surface waters during stratified summer conditions in the studied area. Therefore, despite cross-slope exchange mechanisms that can result in opposite $\delta^{15}N$ imprints on settling particles (January 2006 vs. April-May 2006), our observations suggest $\delta^{15}N$ can be used to reconstruct past productivity from the sediment record of the NW

Mediterranean Sea. At present, settling particles during the spring bloom (high flux) have a $\delta^{15}N$ signal of 0-2‰ explained by isotope discrimination during nitrate uptake by phytoplankton, and those settling during summer oligotrophic conditions (flux minima) display a $\delta^{15}N$ signal of 1-3‰ attributed to the contribution of diazotrophic activity to organic matter production. If we assume no diagenetic alteration at moderate to high flux rates (Altabet et al. 1999), nitrogen isotopes can indeed be used to indicate past sources of organic matter and the extent of nutrient utilization by phytoplankton.

3.1.4 Implications for the deep export of carbon

Our study adds to the growing evidence that physical exchange processes such as DSWC are responsible for a large transfer of particulate matter from the continental shelf of the Gulf of Lions to the deep Mediterranean basin. The strong temperature and current speed anomalies recorded in 2006 were the signals of the occurrence of a major 4-month long cascading event down to the continental rise, with current speed maxima recorded at the onset (early January) and at the end (March) of the event. Both cascading pulses of

dense shelf water coincided with maxima OC and TN fluxes recorded by the sediment traps, which supports off-shelf transfer of large quantities of organic matter. In contrast, minimum OC and TN flux intensity associated to marked increases of OC and TN contents recorded during the following months reflect the escape of particles from surface waters. In order to evaluate the importance of the different sources as inputs of organic matter a simple $\delta^{13}C_{OC}$-based binary mixing model has been applied assuming marine $\delta^{13}C_{OC}$ = -20.1‰ (Harmelin-Vivien et al. 2008) and terrestrial $\delta^{13}C_{OC}$ = -26.5‰ (Kim et al. 2007) endmembers. $\delta^{15}N$ is not considered in the estimation because of the overlapping $\delta^{15}N$ values of vascular plant detritus, soil organic matter and marine algae during bloom and non-bloom conditions (Fig. 3.8), complicating a direct assessment of the contribution of each of these organic matter sources to the total organic matter flux. Overall, up to 84% of the OC settling at the CC1000 station during the first pulse of cascading waters in January 2006 was of terrestrial origin, as was up to 73% at the CC1900 station, or 65% at the LD1000, OS1000, and OS1900 stations (Fig. 3.9). This is translated in maximum values of up to 564 mg terrestrial OC m^{-2} d^{-1} (or more than 1 g terrestrial organic matter m^{-2} d^{-1} if organic matter content is estimated as twice
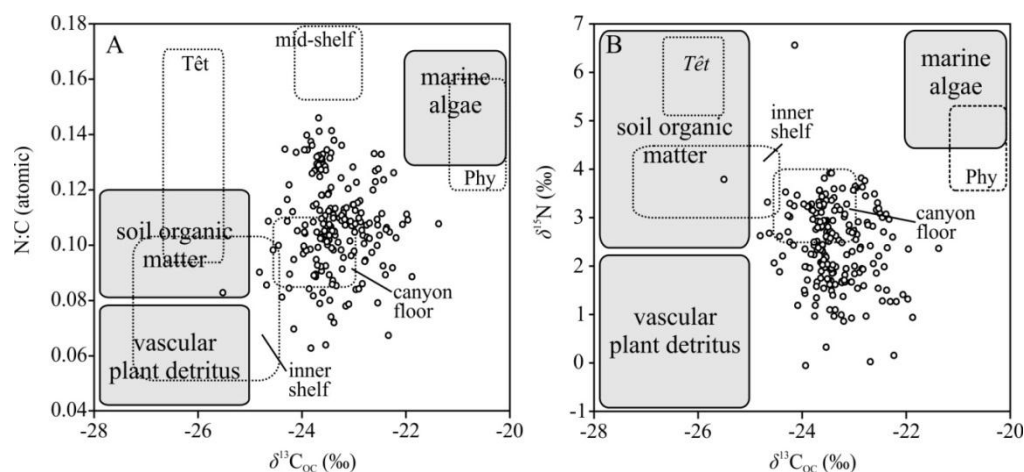

Fig. 3.8. (A) Plot of $\delta^{13}C_{OC}$ vs. N:C atomic ratio of settling particles along with potential sources (marine algae, C3 soil organic matter, and vascular plant detritus). Compositional range of values from Meyers (1994), Goñi and Hedges (1995), and Hedges et al. (1997). Local source values of the Gulf of Lions are also displayed: Phy is phytoplankton data from Harmelin-Vivien et al. (2008); inner-shelf (Têt and Rhône prodeltas) and mid-shelf are surface sediments data from Kim et al. (2006, 2007) and Tesi et al. (2007); canyon floor are surface sediments below mooring lines analysed following the same methodology as settling particles (this study); Têt suspended particulate matter is from Kim et al. (2007). (B) Plot of $\delta^{13}C_{OC}$ vs. $\delta^{15}N$ of settling particles along with potential sources. Compositional range of values from Altabet (1996) and Amundson et al. (2003). Local source values displayed: Phy is phytoplankton data from Harmelin-Vivien et al. (2008); canyon floor are surface sediments (0-1 cm) below mooring lines analysed following the same methodology as settling particles (this study); inner-shelf (Têt and Rhône prodeltas surface sediments) and Têt suspended particulate matter data is from P. Kerhervé unpubl.

the organic carbon content). As discussed in previous sections, this terrestrial organic matter was most likely introduced to the inner shelf by the increased river discharge recorded in mid-November 2005 in the western Gulf of Lions rivers, and later resuspended and transported by cascading waters to the deep basin. In contrast, particle settling during the second pulse of cascading waters in early spring show a higher contribution of marine sources, with up to 72% of the organic carbon of marine origin or up to 385 mg marine OC m^{-2} d^{-1}. In fact the simultaneous high Chl a concentrations recorded in shelf waters in late winter supports marine organic matter production under bloom conditions concurrent with the second DSWC pulse. While lateral input of organic matter from the adjacent shelf predominated during wintertime, biogenic particles escaping from surface waters represent the major source of organic matter during low-energy and low-flux periods that prevail during summertime. Moreover, indirect evidences from stable-isotopic values suggest that N_2 fixation contributes to fuel C fixation and thus organic matter export.

The downslope transport to the deep NW Mediterranean basin of organic matter of different origin (i.e., terrestrial and marine) might alter within a couple of months the quality of the sedimentary organic matter deposited on the sea floor and thus the dynamics of the ecosystems. In fact recent findings have shown that the strong currents associated with intense cascading events displace the deep-sea living resource Aristeus antennatus from the normal fishing grounds. However, despite this initial effect, the large transport of organic matter associated with cascading might favour the nutritive conditions of the adult populations resulting in a large increase in recruitment and juveniles, and a repopulating of the initial fishery grounds the following years (Company et al. 2008). Thus, the abrupt change in the quantity and the quality of particulate organic matter along with physical and chemical conditions may have immediate effect on the benthic ecosystems, which may respond distinctly depending on their ability to use each specific organic matter source.
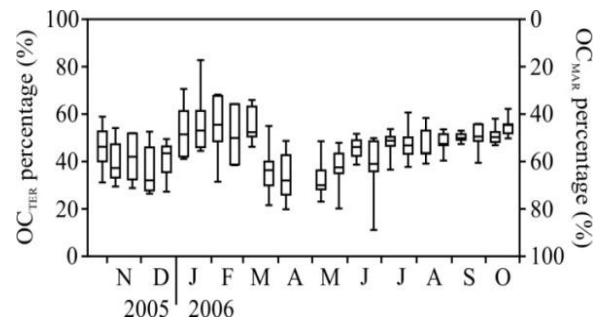

Fig. 3.9. Box plot showing the temporal evolution of terrestrial (left axis) and marine (right axis) organic matter at all stations obtained following a mixing model. The caps at the end of each box indicate the extreme values, the box is defined by the lower and upper quartiles, and the line in the center of the box is the median.

Acknowledgements