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

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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

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Capítol 5

Composition and provenance of terrigenous organic matter transported along submarine canyons in the Gulf of Lion (NW Mediterranean)

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Abstract

Previous projects in the Gulf of Lion have analyzed the path of terrigenous compounds in the Rhone deltaic system, the continental shelf and the canyon heads. In this study we present results focused on the GoL slope to further assess the particulate exchange with the interior ocean. Experimental design consisted in nine sediment traps deployed along the Lacaze-Duthiers and Cap de Creus submarine canyons (from the canyon heads to the canyon mouth) and the southern open slope during 1 year. Sediment trap materials were analyzed by CuO oxidation to investigate spatial and temporal variability in the yields and compositional characteristics of lignin-derived phenols.

Sediment trap data indicate that the Dense Shelf Water Cascading event that took place in winter 2006 dominates overall particle fluxes in both canyons. During the DSWC period land-derived material is not significantly enriched in lignins and main changes in lignin composition are the relative enrichment in vanillyn phenols in the middle Cap de Creus canyon and upper open slope samples. Lithogenic-normalized lignin contents were higher during late spring and summer at all stations, when overall particle fluxes are relatively low. During these periods, lignin compositions were characterized by elevated cinnamyl to vanillyl phenol ratios, a trend that is consistent with elevated inputs of pollen. Our results suggest large differences in the sources and transport processes responsible for terrigenous material transport along canyons, ranging from export of fluvial and shelf sediments during winter to atmospheric dust inputs during spring and summer.

Resum

Projectes anteriors portats a terme en el golf de Lleó (GoL) han analitzat la trajectòria dels components terrestres al sistema deltaic del Roine, a la plataforma continental i a les capçaleres dels canyons. En aquest estudi, es presenten resultats centrats en el talús del GoL per tal de incrementar el coneixement de l'intercanvi de partícules entre la plataforma i l'interior de l'oceà. El disseny experimental ha consistit en el fondeig de 9 línies instrumentades al llarg dels canyons submarins de Lacaze-Duthiers i Cap de Creus i al talús del sud, durant 1 any. El material de les trampes de sediment va ser analitzat amb una oxidació alcalina amb CuO per tal d'investigar la variabilitat temporal i espacial del contingut i composició dels fenols derivats de la lignina.

Les dades de les trampes de sediment indiquen que una cascada d'aigua densa de plataforma (DSWC) va tenir lloc a l'hivern de 2006, i va dominar la majoria dels fluxos en els canyons. Durant la DSWC, el material terrestre no està enriquit en lignina, i els principals canvis en la composició de la lignina fan referència a l'enriquiment en fenols de vanil·lina de les mostres de la zona mitjana del canyó de Cap de Creus i del talús. Els continguts de lignina varen ser majors al final de la primavera i a l'estiu a totes les estacions, quan els fluxos de partícules esdevingueren menors. Durant aquests períodes, la composició de lignina es va caracteritzar per presentar una ràtio del fenols cinnamil/vanil·lines elevada, una tendència que és consistent amb inputs elevats de pol·len. Els nostres resultats suggereixen grans diferències en l'origen i els processos de transport responsables del transport de material terrestre al llarg dels canyons, variant d'aportacions d'origen fluvial i de plataforma durant l'hivern cap a unes aportacions atmosfèriques durant la primavera i l'estiu.

Introduction

The delivery, cycling and fate of terrigenous organic matter (TOM) to the oceans are important, but poorly understood, processes that affect the global carbon cycle (Falkowski et al., 2000; Sarmiento and Sundquist, 1992; Hedges et al., 1992). Much of the particulate TOM delivered to the oceans is composed of the degraded remains of continental primary production, including materials that have significant alteration during pedogenesis (Goni et al., 1998; Hatten et al., 2010; Blair et al., 2010). As a consequence, the 65% of the particulate organic matter delivered by rivers, approximately $0.15 \cdot 10^{15}$ g C yr^{-1} (Hedges et al., 1997), is thought to be relatively refractory and potentially can accumulate in marine sediment depocenters (e.g., Hedges, 1992; Goni et al., 2008; Tesi et al., 2007).

While the fate of TOM in deltas and shelves has been studied in some detail in different margins (Bianchi et al., 2002; Goni et al., 2000), much less is known about its transport further offshore. Studies of sediment and particle dynamics in the Gulf of Lion investigated the connections between the shelf and the deep basin in this region of the Northwestern Mediterranean (Bouloubassi et al., 1997). Specifically, our group has studied particle transport along the Lacaze-Duthiers and Cap de Creus submarine canyon system where the most active off-shelf export of GoL material takes place (Palanques et al., 2006). Findings from previous analyses have resulted in several publications describing the physical controls on particle exports and organic carbon sources and degradation (Pasqual et al., 2010; 2011; Sanchez-Vidal et al., 2008; 2009). During the sampling period, main particle flux forcing was a Dense Shelf Water Cascading event that took place in winter 2006. The strong downcanyon currents during the DSWC event eroded and transported material quickly basinwards inducing significant particle fluxes increase.

The objectives of this paper are to evaluate temporal and spatial changes in the contribution and compositions of TOM exported offshore and use these data to evaluate TOM provenance transport processes within and among canyons. With these goals in mind, we characterized the composition and sources of TOM in samples collected by sediment traps located along two canyons by measuring a variety of biomarker compounds (i.e., lignin phenols and cutin acids). These compounds are uniquely synthesized by vascular land plants and have been used extensively to trace the contribution and source of terrigenous organic matter in many environments (e.g., Goñi et al., 1990; 1998; 2000; 2008; Gordon et al., 2003; Gough et al., 1993; Opsahl et al., 1997). We use these markers in combination with bulk geochemical characteristics of the trap materials (e.g., siliciclastic content) to gain insight into the sources and pathways of TOM inputs in this system.

Background

Starting in 1983 with ECOMARGE program (Monaco et al., 1990), several multidisciplinary experiments (e.g., EUROSTRATAFORM, HERMES, HERMIONE) have focused on studying the cycle of particulate matter in GoL. Insights into the biogeochemistry of the region has progressively increased as a result of these investigations, which have also shed new light on the physical drivers of the system (see Monaco et al., 1990; Raimbault et al., 2003; Durrieu de Madron, 2008). Several studies have investigated the major inputs of terrestrial material to GoL and lead

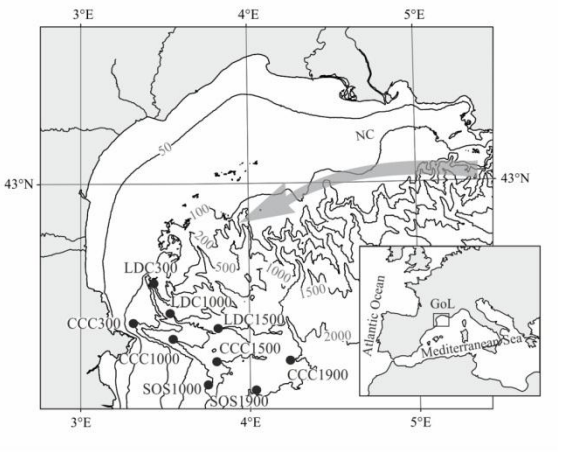

Fig. 5.1. Location of the Gulf of Lion (GoL) in the Western Mediterranean Sea and sediment trap mooring stations (black dots) along the tree transects studied: Lacaze-Duthiers Canyon (LDC) Cap de Creus Canyon (CCC) and their Southern Open Slope (SOS). Surface ocean circulation is represented by the Northern Current (NC grey arrow).

to significant advances in our understanding TOM cycling in the region (Gought et al., 1993; Buscail et al., 1995; Bouloubassi et al., 1997; Tesi et al 2007; Kim et al., 2010).

The continental shelf of the GoL, receives inputs from Rhône River, which accounts for 90% of the total annual freshwater and sediment flux (Bourrin et al., 2006), and from several smaller rivers to the southwest (Fig. 5.1). The major input of terrestrial material to the prodeltas occurs during fall floods typical of the Mediterranean climatic regime and during spring floods caused by snowmelt (Buscail et al., 1995). In the nearshore, sediments are exposed to a continuous physical reworking that resuspend and export finest particles through benthic nepheliod layers to the adjacent continental margin (Buscail et al., 1995, Roussiez et al., 2005; Tesi et al 2007) creating a multilayer nepheliod system (Monaco et al., 1990). Fine sediments on the continental shelf are advected by the mean anticlockwise near-bottom flow, and exit the shelf through the westernmost submarine canyons mainly during E and SE winter storm and DSWC events (Palanques et al., 2006).

The continental slope of the GoL is incised by several submarine canyons. Sediment trap studies have documented significant increases in near-bottom sediment transport through the westernmost canyons (Lacaze-Duthiers and Cap de Creus canyons) when storm-induced downwelling conditions are coupled with DSWC. Under these conditions, resuspended sediments are transported as bottom turbidity layers (Palanques et al., 2006; Bonnin et al., 2008), which lead to further erosion of canyon floor sediments (Canals et al., 2006, Puig et al., 2008). As result of these lateral adjective transport processes, the deep North Western Mediterranean basin is likely to be a significant sink for terrestrial organic matter originating from both, riverine transport and atmospheric deposition (Gough et al., 1993; Bouloubassi et al., 1996). The aim of the work presented here is to specifically investigate the transport of TOM between the continental shelf and the deep basin and fill a gap in our current understanding of carbon fluxes and cycling in this system.

Methods

Sampling has been described in detail in Pasqual et al. (2010). Our strategy consisted in the deployment of instrumented moorings at different sites along both the Lacaze-Duthiers and Cap de Creus canyons (LDC and CCC, respectively), including at upper (300 m), middle (1000 m) and lower (1500 m) canyon areas and at the canyon mouth were both canyons converge (1900 m). We also deployed moorings along the southern open slope (SOS) at 1000 and 1900 m water depth (Fig. 5.1). The sampling period was from mid October 2005 to late October 2006. Each mooring was equipped with a PPS3 Technicap sequential sampling sediment trap (12 collecting cups, 0.125 m^2 opening and 2.5 height/diameter aspect ratio for the cylindrical part) at 30 m above bottom and an Aanderaa current meter (RCM7/8/9) at 5 meters above the bottom. In addition, the LDC1000 mooring included an extra trap and current meter placed 500 meters above the bottom (LDC1000-500 mab). The sediment traps were programmed to collect samples in individual cups for 15-day periods whereas the current meters collected data at 30-minute intervals.

The receiving cups of the traps were filled up before deployment with a buffered 5% (v/v) formaldehyde solution in 0.45 μm filtered seawater. Virtually all traps functioned according to the sampling plan, with the exceptions being failures of the rotating motors of the CCC300 trap and of the LDC1000 trap during six- and two-month periods of the deployments. In addition, early January 2006 the sediment sampling bottle from the CCC1000 trap overfilled and the excess material probably entered into the following cup during the rotation of the carrousel, resulting in consecutive flux values that were under- and over-estimates, respectively. Given the implicit limitations and uncertainties of sediment traps associated to trap hydrodynamics, swimmer intrusion and solubilisation processes that may bias the particle fluxes (Gardner et al., 1997; Buesseler et al., 2007 and references therein), the flux estimates obtained from the traps and hereafter presented should be regarded as semi-quantitative data.

5.1.1 Sample treatment

After recovering, samples were stored in dark at 2-4ºC until they were processed in the laboratory according to the procedure described by Heussner et al. (1990). Samples were (i) split into aliquots using a high precision peristaltic pump robot to obtain 10-20 mg sub-samples, (ii) filtered through glass-fibre preweighted filters for carbon and nitrogen analysis and 0.45 µm pore size cellulose membranes for total mass determination and biogenic Si analysis, (iii) rinsed with distilled water and, finally, (iv) dried at 40ºC during 24 h for dry weight determination. The precision of mass estimates, as measured by the coefficient of variation was 4.1%.

5.1.2 Elemental analyses

Total and organic carbon, and total nitrogen contents were measured using an elemental analyzer (EA Flash series 1112 and NA 2100) according to the procedure of Nieuwenhuize et al. (1994). Samples for organic carbon analysis were first decarbonatated using repeated additions of 100 µl 25% HCl with 60ºC drying steps in between until no effervescence occurred. Organic matter (OM) content has been estimated as twice the total organic carbon content, and carbonate content was calculated assuming all inorganic carbon is contained within the calcium carbonate ($CaCO_3$) fraction, thus using the molecular mass ratio 100/12. Uncertainties were lower than 0.1% as determined from replicates of the certified estuarine sediment MESS-1. Biogenic Si was analyzed using a two-step extraction with 0.5 M Na_2CO_3 (2.5 hours each) separated after filtration of the leachate. Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used to analyze Si and Al contents in both leachates, and a correction of the Si of the first by the Si/Al

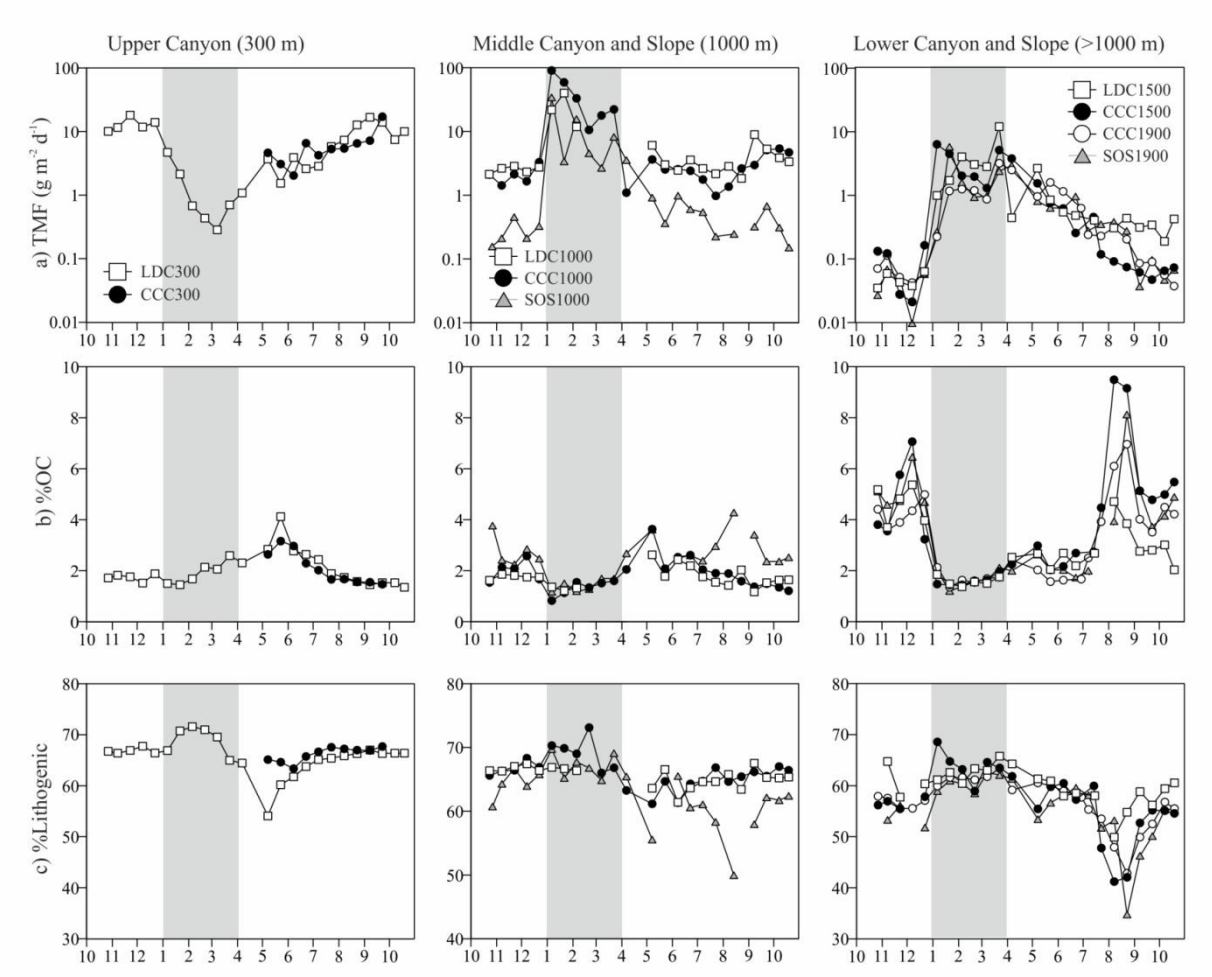

Fig. 5.2. Time-series data of a) total mass flux (g m^{-2} d^{-1}), b) OC concentration in the trap sample (%) and c) lithogenic concentration in the trap sample (%).

relation of the second one was applied to obtain the opaline Si concentration (Fabres et al., 2002). Corrected Si concentrations were transformed to opal after multiplying by a factor of 2.4 (Mortlock and Froelich, 1989). Analytical precision of opal measurements was 4.5%. The siliciclastic fraction was calculated assuming % siliciclastic = 100 - (% OM + % $CaCO_3$ + % opal).

5.1.3 CuO oxidation

Oxidations with alkaline CuO were performed on sediment trap according to Goñi and Montgomery (2000). An amount of sample containing 2 - 5 mg of OC was oxidized in pressurized Teflon vessels containing 8% NaOH, CuO and $Fe(NH_4)SO_4$ at 152ºC for 90 min under an oxygen-free atmosphere. Known amounts of recovery standards (trans-cinnamic acid and ethylvanillin) were added after the oxidation. After separating the hydrolysate from the solids by centrifugation, the alkaline solution was acidified to pH 1 with concentrated HCl and extracted with ethyl acetate. The organic solvent was evaporated and the samples redissolved in pyridine. The CuO oxidation products were derivatized with BSTFA + 1% TCMS at 60^{o}C for 10 min prior to chromatographic analysis. The yields of lignin and cutin oxidation products were quantified by gas chromatography-mass spectrometry (GC–MS) using an Hewlett Packard 6890 GC linked to a 5973 Mass Selective Detector using selective ion monitoring (see Goñi et al., 2009 for details). The yields of lignin phenols were calculated using five-point calibration curves derived from periodically injected mixtures of commercial standards of different concentrations (Goñi et al., 2009). The yield of cutin acids (for which commercial standards were not available) were quantified using the calibration curve of trans-cinnamic acid. We report the different CuO oxidation products as sums of distinct compound categories, including vanillyl phenols (VP; vanillin, acetovanillone, vanillic acid), syringyl phenols (SP; syringealdehyde, acetosyringone, syringic acid), cinnamyl phenols (CP; *p*-coumaric acid, ferulic acid) and cutin acids (CA; 16-hydroxyhexadecanoic acid, hexadecanedioic acid, 18-hydroxyoctadecenoic acid, 8,16-dihydxoxyhexadecaonic acid, 9,16-dihydroxyhexadecanoic acid, 10,16-dihydroxyhexadecanoic acid, 7-hydroxyheaxadecanedioic acid and 8-hydroxyhexadecanedioic acid). Ratios of these compounds are used to characterize distinct sources of TOM (e.g., Hedges and Mann, 1979; Goni and Hedges, 1990).

Results

5.1.4 Bulk Compositions

In previous publications we have presented the total mass fluxes, as well as organic carbon, opal, calcium carbonate and lithogenic contents and fluxes of samples obtained during the sediment trap deployments between October 2005 and October 2006 (see Pasqual et al., 2010; 2011). Examination of these data revealed distinct spatial and temporal trends in the magnitude and composition of the materials collected by the traps deployed along the two canyons (LDC and CCC) as well as the open slope (SOS). We identified three distinct periods when physical and biological processes affected the materials collected by the sediment trap. Dense shelf water cascading (DSWC) occurred from January to April of 2006, leading to lateral advection of materials, which dominated the mass fluxes into sediment traps during that period. From April to May, a significant algal bloom characterized the surface waters of the region, which occurred as the DSWC period subsided. Sediment traps samples after the DSWC period were characterized by notably lower total mass fluxes and higher biogenic contents. The final period of the deployment (mid-July to October 2006) was characterized by non-DSWC and non-bloom conditions when advection of shelf material to the upper and middle canyon nevertheless appeared to be active due to increasing wave regime. Pulses of organic carbon, opal and calcium carbonate materials were observed during this period at the deeper stations and open slope, which we interpreted as resulting from pelagic fluxes (Fig. 5.2). It is in the context of these interpretations that we investigate the magnitude and composition of the TOM component, using specific biomarkers (lignin and cutin products) as a tracers.

5.1.5 CuO products

ORGANIC-CARBON NORMALIZED YIELDS. The OC-normalized yields of lignin-derived vanillyl, syringyl and cinnamyl phenols, and cutin-derived hydroxyl fatty acids (Fig. 5.3) in sediment trap samples displayed marked spatial and temporal differences. Lignin-derived vanillyl phenols (VP) ranged from 0.47 to 6.96 mg g^{-1} OC. Maximum values were detected in the middle Cap de Creus canyon (CCC1000) and upper open slope (SOS1000) stations, where the VP yields reached 6.96 and 3.81 mg g^{-1} OC respectively during early-January sample. The peaks in VP yields coincided with peaks in mass flux during DSWC event. At the open slope stations values remained relatively high (up to 1.95 mg g^{-1} OC) during January, February and March 2006. The yields of syringyl phenols (SP) were comparable to VP, ranging from 0.69 to 4.76 mg g^{-1}

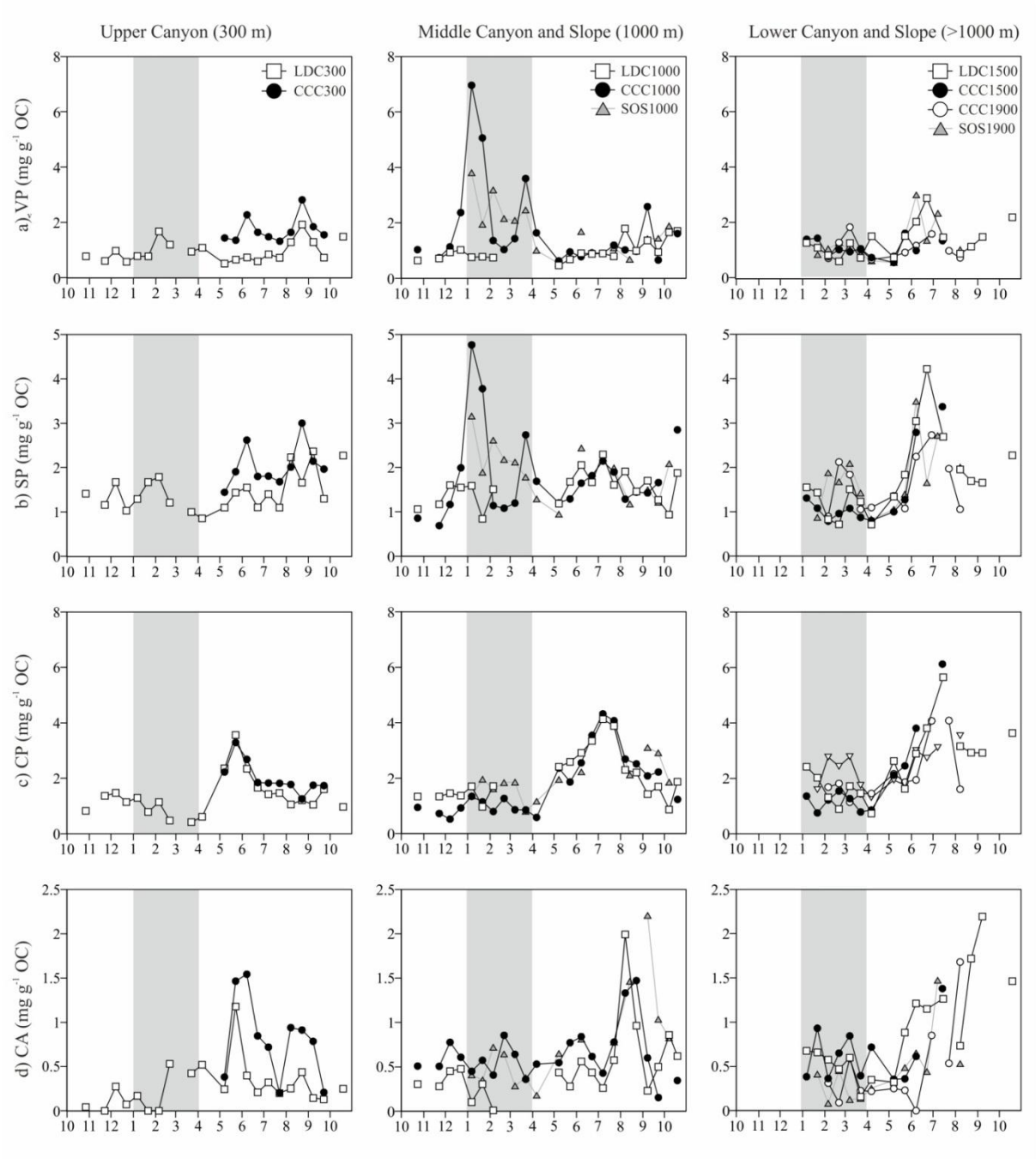

Fig. 5.3. Organic carbon (OC)-normalized time-series data from the sediment traps at the different water depth ranges 300 m, 1000 m and >1000 m of: a) vanillyl phenols (VP) (mg g^{-1} OC) b) syringyl phenols (SP) (mg g^{-1} OC), c) cinnamyl phenols (CP) (mg g^{-1} OC) and d) cutins (mg g^{-1} OC).

OC. As with VP, maximum SP values were measured during the DSWC pulses in the CCC1000 and SOS1000. In contrast to VP, SP yields at 1900 stations (CCC1900 and SOS1900) during the DSWC event increased in concentration up to 2 mg g^{-1} OC. Stations at the lower canyon, slope stations and at the canyon mouth displayed maximum SP values during June - July. Cinnamyl phenols (CP) yields ranged from 0.42 and 6.12 mg g^{-1} OC. In contrast with VP and SP, the maximum concentration of CP were detected at the lower section. CP had a generalized peak in yields during July 06 (except in upper canyon stations detected at May 06) up to 6.12 mg g^{-1} OC at the lower Cap de Creus stations. Cutin acids (CA) displayed two peaks in OC-normalized yields. In May, there was an increase in the upper canyons and the middle water column sediment trap located at the middle Lacaze-Duhiers canyon. Moreover, a more generalized peak

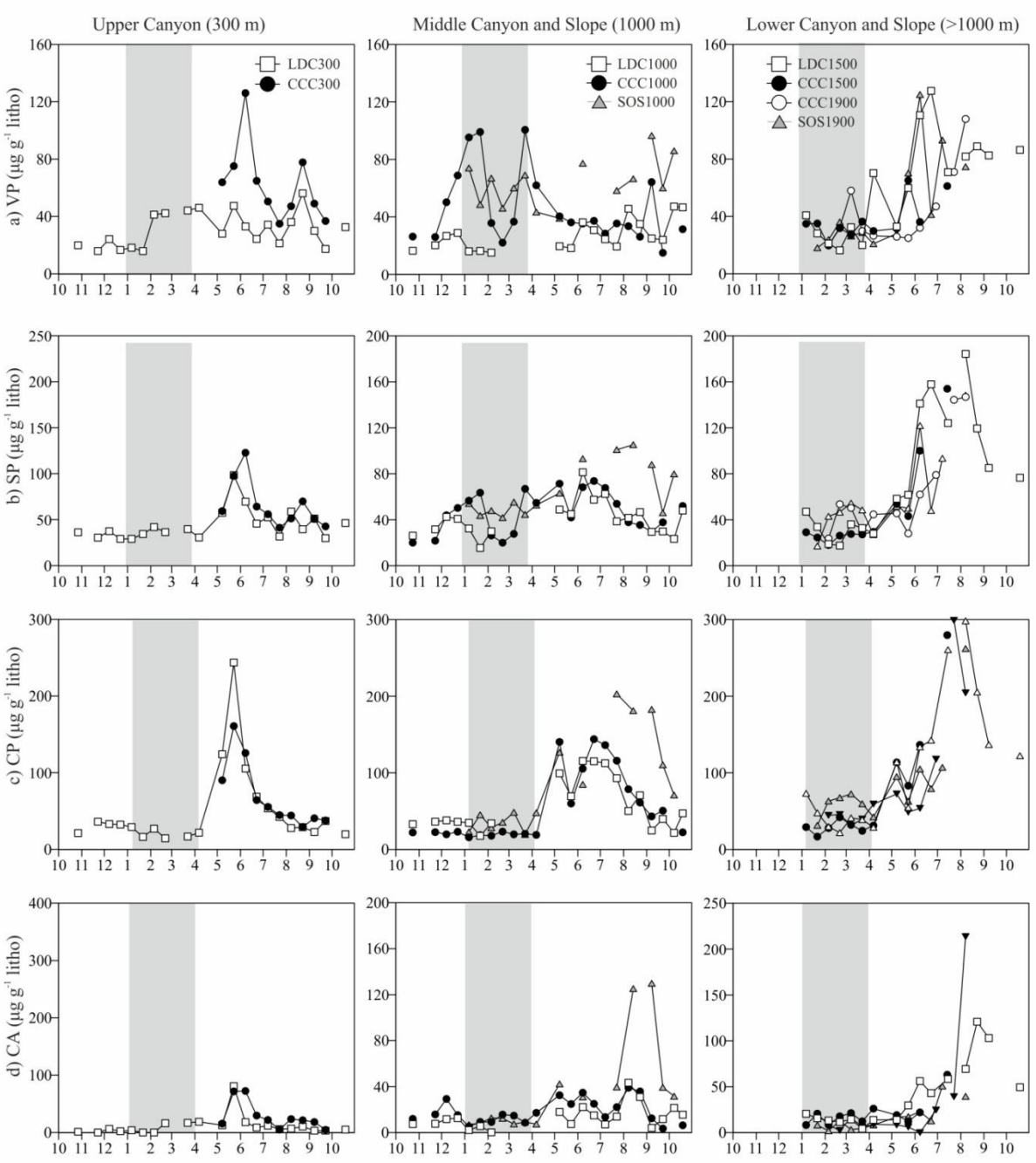

Fig. 5.4. Lithogenic (litho)-normalized time-series data from the sediment traps at the different water depth ranges 300 m, 1000 m and >1000 m of: a) vanillyl phenols (VP) (µg g^{-1} litho) b) syringyl phenols (SP) (µg g^{-1} litho), c) cinnamyl phenols (CP) (µg g^{-1} litho) and d) cutin acids (CA) (µg g^{-1} litho).

was detected during August-September 06 (except in the LDC300 station).

Overall, sediment trap samples displayed lignin-derived phenols yields that were comparable to values measured in surface sediments from the mid-shelf mud belt (0.10-0.60, 0.11-0.46 and 0.03-0.12 for VP, SP and CP respectively) (Tesi et al., 2007). Combined, lignin-derived products ranged from 2.16-13.07 mg g^{-1} OC, a range that was virtually identical to that found in the Cap de Creus upper canyon during 2004-05 deployment (Tesi et al., 2010) (Table 5.1). The yields of lignin-derived phenols in the Gulf of Lion are comparable to those found in surface sediments from the Gulf of Mexico (Goñi et al., 1998; Gordon et al., 2002) and higher than the yields found in sediment traps in the the Cariacco Basin (mean values were 0.54, 0.35 and 0.23 mg g^{-1} OC for VP, SP and CP), an upwelling region in the Caribbean Sea where most of the OM sinking through the water column is of autochtonous marine origin (Goñi et al., 2009).

LITHOGENIC NORMALIZED YIELDS. Variations in OC-normalized lignin and cutin acid products yields reflect changes in the contributions and compositions of both marine and terrigenous organic matter. To investigate changes in terrigenous contributions independently from variations in marine organic matter, we calculated the yields of these terrigenous biomarkers normalized to the mass of lithogenic materials in each sample. Because both terrigenous biomarkers and lithogenic (siliclastic) contributions reflect inputs from land, ratioing the two allows us to specifically determine whether or not there are differences in the nature of these allothonous materials in the sediment traps samples.

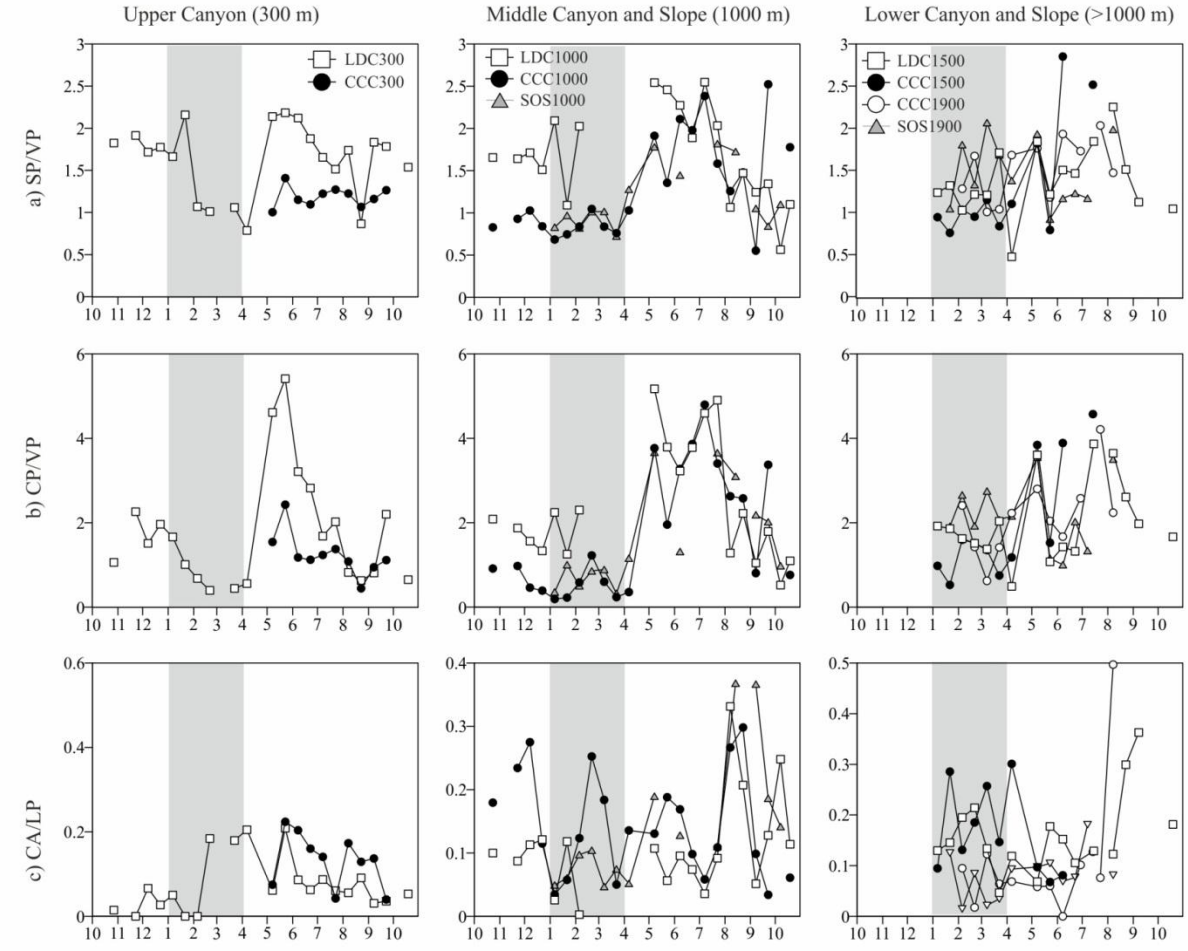

Fig. 5.5. Time-series data from the sediment traps at the different water depth ranges 300 m, 1000 m and >1000 m of: a) the ratio of syringul phenols and vanillyl phenols (SP/VP), b) the ratio of cinnamyl phenols and vanillyl phenols (CP/VP) and c) the ratio of cutin acids and lignin-derived phenols (CA/LP).

Table 5.1. Lignin derived phenol concentration detected in different experiments.

Study	Zone	Regime	Lignin-derived phenols	
			mg 100 mg^{-1}OC	ug g^{-1}DW
Gough et al., 1993	Gulf of Lion	River Rhone and Delta	1.29 - 2.08	
		Gulf of Lion Shelf	0.14 - 2.95	
		NW med. Slope	0.16 - 0.88	
		NW med. Basin	0.031	
Tesi et al., 2007	Gulf of Lion	Rhone prodelta	4.07 - 2.30	
		Mid shelf mud belt	1.16 - 0.25	
Tesi et al., 2010 sediment traps	Gulf of Lion	Inner shelf	1.77 - 2.62	
		Mid shelf	1.16 - 3.07	
		Outer shelf - canyon head	0.14 - 0.79	
		Upper slope CCC	0.74 - 1.54	
		Upper slope LDC	0.23 - 0.28	
		pre-DSWC CCC	0.39 - 0.71	
		DSWC	0.25 - 1.30	
		post-DSWC	0.28 - 0.52	
Gordon et al., 2002	Gulf of Mexico	River SS	2.23 - 3.22	
		Attchafalaya delta and bay	3.45 - 4.06	
		Shoal stations	0.56 - 0.57	
		Inshore stations	1.36 - 2.73	
		Offshore stations	0.96 - 1.26	
Goñi et al., 2008	Gulf of Mexico	Shelf	1.37 - 0.50	
		Slope	0.37 - 0.81	
Goñi et al., 2009 sediment traps	Cariaco Basin	Upwelling season	0.100 ± 0.013	
		Stratified season	0.123 ± 0.021	
		Rainy season	0.130 ± 0.020	
		Dry season	0.090 ± 0.010	
Gough et al., 1993	North East Atlantic	Celtic shelf	0.012	
		Hatton Rockall basin	0.055 - 0.120	
		Porcupine Abisal Plain	0.006 - 0.011	
Schmidt et al., 2009	NW Iberian margin	Mudbelt		43.05 - 189.26
		Inner/mid-shelf		6.89 - 153. 54
		Outer shelf		5.70 - 104.13
		Continental slope		6.51 - 24.85
This study	Gulf of Lion	Southwestern margin	0.21 – 1.307	31 - 296

Lithogenic-normalized (Litho.-normalized) yields of VP, SP and CP, as well as CA are presented in figure 5.4. As was the case with OC-normalized yields, we observed notable temporal and spatial differences in the concentration of the different compound types phenols. VP ranged from 14.98 to 193.46 μg g $litho^{-1}$. Maximum values were detected at lower Lacaze-

Duthiers canyon and during June and canyon mouth. VP were specially high in the middle Cap de Creus stations and upper Open Slope during the DSWC flushing. SP yields were close to VP, (15.55 - 244.83 μg g^{-1} litho) and displayed a similar behaviour than the vanillyl ones except in the middle open slope stations where during the DSWC event no significant peaks in their concentration were measured.

Unlike VP and SP, the litho-normalized yields of CP were markedly elevated from May to September at all stations, with differences among stations concerning the specific period of peak concentration. For example, CP yields were highest during late May in the Upper canyon stations (e.g., 250 μg g^{-1} litho in the LDC400) whereas they peaked in late-June in the middle canyons stations. In October 06 values stabilized at same values as for the ones previous to the spring 06 (<50 μg g^{-1} litho). Deeper stations showed the highest litho-normalized CP yields in July (CCC1500, CCC1900 and SOS1000 stations) and August (SOS1900). Cutins present to period of high yields in May-June in the upper canyon stations and in the middle water depth trap and a generalized increase in August (except for the LDC300 stations).

In addition to the temporal variations in litho-normalized yields, we measured a general increase in the overall yields of all terrigenous biomarkers with increasing water depth. The concentration of lignin-derived phenols present in general an increasing trend when increasing water depth. Exceptions to that are the vanillyl pehnols yields during the DSWC event and in the CCC300 during spring-summer time.

BIOMARKER RATIOS. Different types of vascular plant tissues display contrasting lignin and cutin compositions), that have been used to trace changes in the sources of these materials (Hedges and Mann, 1979; Goni and Hedges, 1990, Goni and Eglinton, 1996; Goni and Thomas, 2000). In order to further investigate specific changes in the sources and composition of TOM we calculated a variety of biomarker ratios (e.g., SP/VP, CP/VP, CA/VP) for the different sediment trap samples (Fig. 5.5) there are presented. Because angiosperm (flowering) plants synthesize lignin that contains both SP and VP and whereas gymnosperm (conifer) plants do not have the ability to synthesize SP, the SP/VP ratio can provide information about the vegetation sources of lignin in sediment samples. In contrast to woody tissues, nonwoody tissues of vascular plants, such as leaves, needles, grasses, bark, pollen, yield elevated amounts CP resulting in elevated CP/VP ratios. Hence, CP/VP ratios have been used to trace contributions from non-woody tissues in field samples. Cutin acids are synthesized by vascular plants to make up the cuticular covering of soft tissues (e.g., leaves, needles). Thus, CA/VP ratios also provide information regarding woody vs. non-woody inputs of TOM. SP/VP ratio ranged from 0.40 and 2.77 with a mean value of 1.35 CP/VP ratio ranged from 0.17 and 5.13. Temporal variability in lignin-derived phenols ratios is driven by the presence of two peaks at all stations in May and in July-August when CP/VP ratio was >3 at all stations.

Discussion

5.1.6 TOM transport along canyons.

Lignin is a macromolecule that has been used as a tracer of TOM in marine environments (Keil et al., 1998; Tesi et al., 2008, 2010; Goñi et al., 2009; 1998; Schmidt el at., 2010; Hernes et al., 2010; Gordon et al., 2003). In the GoL lignin phenols are transported from Rhone prodelta to the southwestern area of the shelf along the main sediment transport pathway (Buscail et al., 1994; Gough et al., 1992; Tesi et al., 2010). Along this pathway, small rivers to the southwest provide additional TOM contributions that account for 10-20% of the total sediment entering the GoL. The data presented in this work from the Lacaze-Duthiers and Cap de Creus canyon systems in combination with the data from previous studies in the Rhone River (Gough et al., 1993), the prodelta and mid-shelf mud deposit (Tesi at el., 2007) and the Cap de Creus canyon head (Tesi et al., 2010) allow to track land derived material path in the Gulf of Lion from the major source of terrigenous material (the Rhone River) up to the lower slope (Table 5.1).

All four sediment trap deployments studies detected a decrease in the concentration of LP from the

Table 5.2. Mean values and standard error of the mean (SE) of vanillyl phenols (VP), syringyl phenols (SP), cinnamyl phenols (CP) and the sum of the lignin-derived phenols (μg g^{-1} litho), SP/VP, CP/VP, Vd/Vl and Sd/Sl ratios. Values are calculated for each period: pre-DSWC (October - December 05), DSWC (January - March 06), post-DSWC (April - mid-July 06) and summer (mid-July - October 06) at the different studied stations.

Station	Period		VP	SP	CP	LP	SP/VP	CP/VP	Vd/Vl	Sd/Sl
LDC300	pre-DSWC	Mean	19.19	33.36	30.60	82.49	1.76	1.65	0.53	0.80
	(N=4)	SE	1.90	2.08	3.27	3.48	0.08	0.27	0.02	0.10
	DSWC	Mean	32.35	36.33	20.61	86.20	1.31	0.80	0.58	0.77
	(N=5)	SE	6.28	2.24	3.05	7.24	0.25	0.23	0.03	0.05
	post-DSWC	Mean	33.51	55.13	94.17	180.81	1.68	2.80	0.45	0.63
	(N=7)	SE	3.84	8.91	28.30	38.76	0.20	0.62	0.04	0.05
	Summer-Autumn	Mean	34.44	45.17	27.19	103.24	1.44	0.95	0.53	0.77
	(N=5)	SE	6.28	4.95	2.97	6.56	0.19	0.30	0.03	0.03
LDC1000	pre-DSWC	Mean	23.06	35.28	35.78	92.47	1.54	1.62	0.46	0.65
	(N=4)	SE	2.87	3.87	1.06	7.11	0.04	0.17	0.02	0.06
	DSWC	Mean	15.83	26.00	28.82	69.56	1.65	1.83	0.52	0.51
	(N=3)	SE	0.39	5.27	5.59	11.27	0.35	0.38	0.03	0.07
	post-DSWC	Mean	24.78	55.61	100.78	180.91	2.27	4.20	0.40	0.56
	(N=6)	SE	2.97	6.23	7.33	15.22	0.12	0.30	0.04	0.03
	Summer-Autumn	Mean	37.29	36.52	42.33	112.21	1.03	1.20	0.52	0.68
	(N=6)	SE	4.42	4.19	7.36	12.34	0.12	0.22	0.02	0.04
LDC1500	DSWC	Mean	26.49	31.03	42.13	97.44	1.18	1.58	0.49	0.58
	(N=6)	SE	3.73	4.55	7.22	14.98	0.10	0.11	0.01	0.05
	post-DSWC	Mean	78.70	95.18	122.45	286.02	1.24	1.80	0.48	0.41
	(N=6)	SE	14.12	21.50	33.19	57.49	0.21	0.57	0.04	0.09
	Summer-Autumn	Mean	84.97	116.34	190.73	380.96	1.38	2.26	0.43	0.49
	(N=4)	SE	1.67	24.50	40.18	67.98	0.31	0.50	0.05	0.03
CCC300	post-DSWC	Mean	69.23	73.52	90.13	223.29	1.08	1.32	0.41	0.59
	(N=6)	SE	12.71	12.43	18.44	38.42	0.06	0.18	0.05	0.06
	Summer-Autumn	Mean	53.58	53.00	37.93	137.06	1.01	0.77	0.52	0.67
	(N=5)	SE	6.86	4.51	2.45	8.12	0.05	0.11	0.03	0.04
CCC1000	pre-DSWC	Mean	42.84	34.00	21.90	93.01	0.80	0.61	0.43	0.43
	(N=4)	SE	10.36	7.67	0.75	15.97	0.03	0.14	0.07	0.08
	DSWC	Mean	64.90	43.53	19.31	117.43	0.72	0.44	0.46	0.40
	(N=6)	SE	15.11	8.59	1.03	20.56	0.05	0.14	0.02	0.02
	post-DSWC	Mean	39.28	61.68	102.94	200.63	1.66	2.91	0.45	0.53
	(N=7)	SE	4.02	4.41	17.76	19.78	0.19	0.56	0.03	0.04
	Summer-Autumn	Mean	34.07	38.52	51.15	119.86	1.42	1.89	0.49	0.58
	(N=5)	SE	8.20	3.69	9.36	7.98	0.34	0.52	0.03	0.10
CCC1500	DSWC	Mean	30.83	25.45	28.67	80.87	0.84	0.98	0.54	0.46
	(N=6)	SE	2.62	1.61	3.42	4.66	0.05	0.15	0.11	0.10
	post-DSWC	Mean	44.77	76.10	128.81	246.18	1.73	2.85	0.41	0.45
	(N=5)	SE	7.60	22.79	41.64	68.78	0.41	0.71	0.04	0.07
CCC1900	DSWC	Mean	38.31	40.40	38.23	113.24	1.12	1.22	0.39	0.46
	(N=5)	SE	7.14	5.93	3.26	9.17	0.15	0.31	0.04	0.11
	post-DSWC	Mean	37.92	67.28	108.48	213.27	1.70	2.56	0.35	0.56
	(N=6)	SE	7.43	16.95	39.46	63.29	0.13	0.37	0.03	0.10
	Summer-Autumn	Mean	108.02	146.86	204.44	430.18	1.36	1.89	0.29	0.28
	(N=1)	SE	.	.	.	.	.	.	.	.
SOS1000	DSWC	Mean	60.82	47.93	33.37	134.12	0.80	0.59	0.49	0.52
	(N=6)	SE	4.66	2.31	4.82	5.74	0.05	0.11	0.02	0.04
	post-DSWC	Mean	54.51	77.50	115.64	241.66	1.44	2.23	0.45	0.53
	(N=4)	SE	8.65	11.60	33.29	44.89	0.14	0.66	0.05	0.06
	Summer-Autumn	Mean	77.35	79.77	136.29	282.22	1.05	1.82	0.44	0.43
	(N=4)	SE	8.45	12.43	27.51	37.71	0.18	0.39	0.06	0.07
SOS1900	DSWC	Mean	26.66	41.95	58.89	126.93	1.56	2.22	0.41	0.62
	(N=5)	SE	2.96	6.47	7.19	16.03	0.20	0.21	0.04	0.06
	post-DSWC	Mean	63.15	65.36	81.92	201.32	1.16	1.70	0.44	0.24
	(N=6)	SE	16.62	14.35	10.44	36.03	0.16	0.40	0.03	0.11
	Summer-Autumn	Mean	134.08	196.57	256.43	564.11	1.63	2.40	0.38	0.51
	(N=2)	SE	59.38	48.26	5.67	78.99	0.36	1.11	0.07	0.16

river mouths southwestward following the GoL sediment dispersal system (Gough et al. 1993; Tesi et al., 2007). The physical reworking of the prodelta superficial sediments cause a first sorting of the land-derived material and the finest fraction associated with soil-deived OM is selectively transported along the main

sediment dispersal system (Tesi et al., 2007). This process is active in other prodelta regions such as Tet river (Buscail et al., 1994). By the time it reaches the southern end of the GoL, the concentration of lignin-derived phenols has lowered up to 1/3 of the Rhône River and Rhône prodelta concentration. This has been associated either to degradation of the land-derived compounds or to the dilution with other organic matter pools.

As indicated by Tesi et al. (2010), lignin concentrations in stations from the upper canyons to the lower slope are comparable to the values determined for surface sediments in mid-shelf mud-belt. This finding is not unexpected, given the fact that during DSWC periods, which dominate material transport, most of the materials advected along the canyons likely originate from those areas. Therefore, in the GoL, lignin-containing materials funneled from mid-mud shelf regions through the submarine canyons to the lower slope undergo little dilution or alteration compared to the changes observed between the rivers mouth up to the outer shelf. Measurements of sediment samples from the GoL northeastern slope, outer shelf and deep Balearic basin in contrast with the data from this experiment (Table 1) suggest that the canyon system studied, Lacaze-Duthiers - Cap de Creus, and their southern open slope, funnels material relatively enriched in LP in comparison with northern or southern slope materials. Moreover, deep basin samples from these areas displayed the lowest lignin-phenols yields, which suggest that TOM is being diluted or degraded by the time it reaches such deep environments.

Advection of land-derived OM down the Lacaze-Duthiers and Cap de Creus canyons appears to occur throughout the study period, even though the quantities and compositions change with physical forcings. Similar findings were observed at the Cap de Creus canyon head during the October 2004-March 2005 sediment trap deployment (Tesi et al. (2010), in sediment traps studies from the Bari canyon (Tesi et al., 2008) and in sediment traps from the Cariacco Basin (Goñi et al., 1998). The persistent inputs of terrigenous materials in these different locations suggest continuous and steady supply of highly altered TOM to the sea floor under variable physical and geomorphologic regimes.

Enrichments in litho-normalized yields of VP, SP and CP basinwards are observed (Fig. 5.6a) associated with lower ratios from the acid and aldehyde syringyl and vanillyl phenols (except ccc1900 syringyl ones), (Fig. 5.6c). Large ratios indicate a highly degraded state for the lignins as the oxidative degradation of lignin sidechains by certain microorganisms, such as white-rot fungi, often produce characteristically elevated [Ad/Al]>0.4 (Hedges at al., 1998; Goñi et al., 1993). Moreover, it is detected an increase of CP/VP and SP/VP ratios with water depth (LDC 1500 m does not follow that trend), wich indicates a change in the vegetation sources. Keil et al., 1998 also detected an increase in CP/VP and SP/VP rations in the deeper stations of the Washington coast indicating an enhancement of nonwoody inputs (or preservation) at more off-shore sites. Indeed, the increase in SP/VP and CP/VP ratio has been observed in several regions such as the Galician margin (Schmidt et al., 2010) and the Gulf of Mexico (Goñi et al., 1998). However, it is worth mentioning that both microbial degradation and sorting processes can affect SP/VP and CP/VP ratios. Therefore the variability of these ratios does not necessarily reflect a different TOM source. Indeed, our results might also suggest that TOM material deposited basinwards during our experiment is relatively more enriched in less degraded nonwoody material than the one that settles at shallower canyon stations. Alternatively, fine material relatively rich in cinnamyl and syringyl phenols, could be preferentially transported offshore

5.1.7 Temporal contrasts in TOM inputs

The temporal resolution of this experiment (15 days) allows us to evaluate the TOM compositional trends between the different periods defined in Pasqual et al., 2010: pre-DSWC, DSWC, post-DSWC bloom and finally summer-autumn 06.

THE DENSE SHELF WATER CASCADING. During the DSWC CP and SP yields at deeper stations (Table 2) are lower that during post-DSWC and summer time suggesting the advection of a CP and SP-poor materi-

al. But concerning the samples from where we have a complete time series, LDC300, LDC1000, CCC1000, the DSWC did remobilizated a terrestrial material with the same CP and SP load than during pre-DSWC and summer-autumn 2006 period, and is during the "post-DSWC/Bloom" period when the material is especially enriched in lignin-derived phenols as in the case of deeper stations. That suggests that material laterally advected during the DSWC event has the same LP yields that the one that is advected during autumn downwelling processes.

Indeed, major differences during the DSWC period are associated with the VP yields rather than SP or CP. VP phenols increase with the advection of shelf material at middle canyon and slope stations (CCC1000 and SOS1000). During the 2006 DSWC the Lacaze-Duthiers canyon station registered an increase in mass fluxes as in the Cap de Creus canyon but latter and with lower values (Pasqual et al., 2010). It was also suggested that the SOS1000 was affected by the dense shelf water plume that spread out the canyon. Data presented in this study indicates that at 1000 m water depth Lacaze-Duthiers station the yields of VP and SP are significantly lower than at the same water depth in the Cap de Creus and slope station (Table 2). Plus to the yields, CP/VP and SP/VP ratios in the Lacaze-Duthiers are significantly high. Thus, data indicate a different source of land derived material. In the LDC, the source of TOM may be outer shelf sediments which have higher SP/VP and CP/VP (Tesi et al., 2010) whereas the inner shelf sediments may be sources of TOM to the CCC, which is what we may expect since the CCC head is very close to the coast.

The digenetic state of lignin can be estimated from the ratio of acid to aldehyde vanillyl and syringyl LP (Ad_v/Al_v and Ad_s/Al_s respectively). The decay of lignin by terrestrial fungi and other lignin-degrading organisms has been shown to increase that ratio (Hedges at al., 1998; Goñi et al; 1993; Opsahl and Benner, 1995). In this study, Lacaze-Duthiers canyon head transect present higher ratios from the acid and aldehyde syringyl and vanillyl phenols (Table 2), that would indicate a more degraded terrestrial organic matter. Lignin content in sediments is relatively stable on continental shelves and slopes relative to

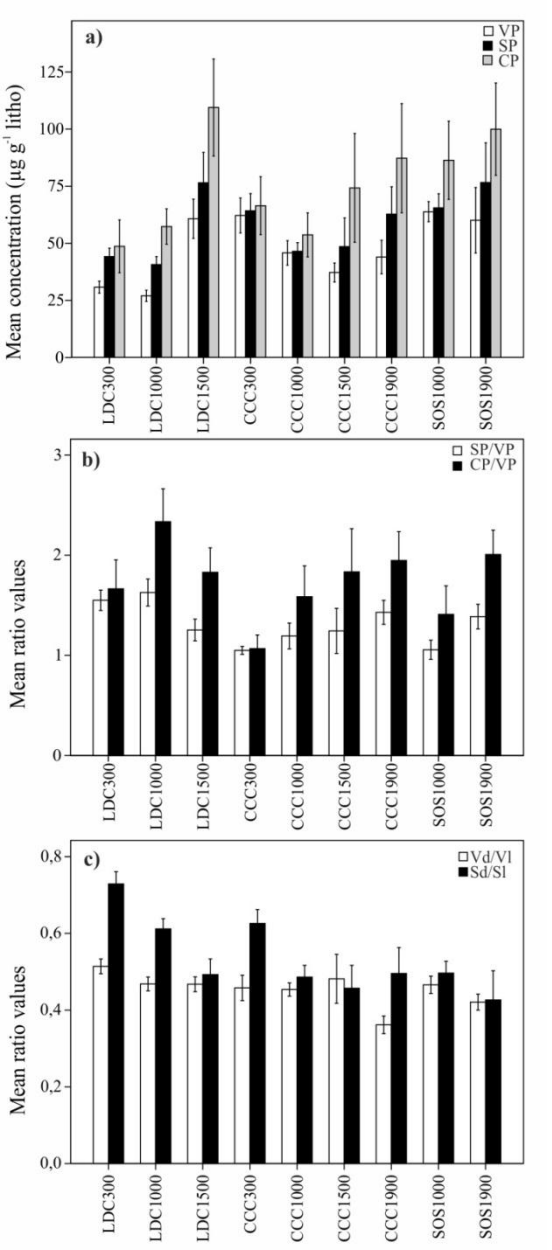

Fig. 5.6. a) Mean concentration (μg g^{-1} litho) of vanillyl phenols (VP), syringyl phenols (SP), and cinnamyl phenols (CP) of sediment traps particles at each station. b) Mean ratio values of the ratio of syringul phenols and vanillyl phenols (SP/VP) and the ratio of cinnamyl phenols and vanillyl phenols (CP/VP). c) Mean ratio values of vanillic acid to vanillin (Vd/Vl) and syringic acid to syringealdehyde (Sd/Sl).

more reactive biochemical compounds (i.e., lipids, amino acids) (Goñi et al., 1998). Other studies have shown lignin to be stable in sediments for thousands of years (Ishiwatari and Uzaki, 1987; Goñi, 1997). Even the degradation was in marine environment or in aerial one, the terrestrial material settled at Cap de Creus canyon middle canyon during the DSWC is different in nature that the one that settles at the middle

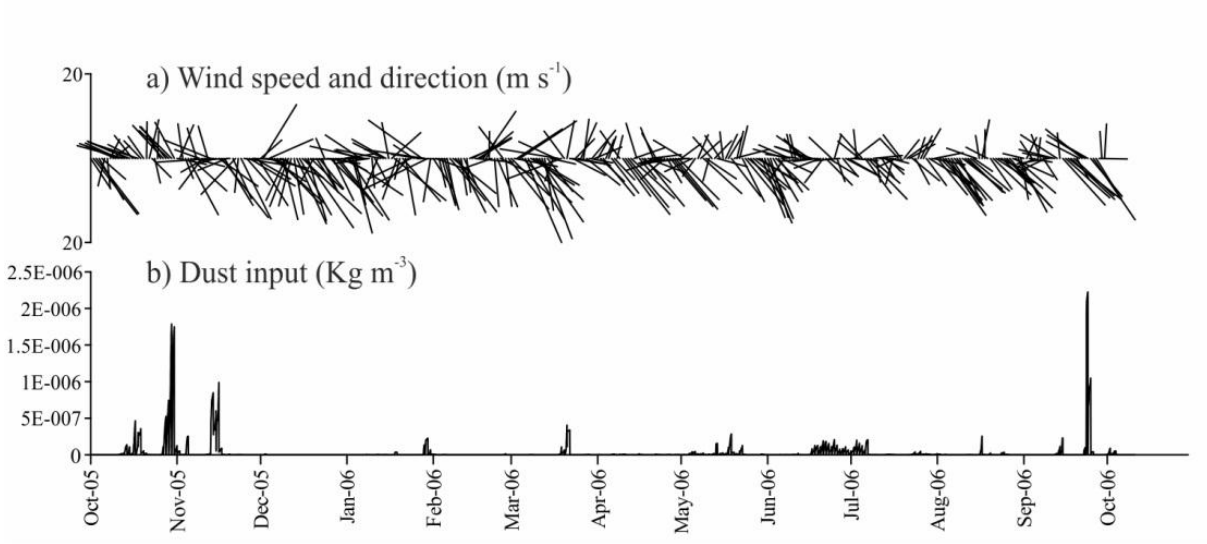

Fig. 5.7 a) Wind speed (m s^{-1}) and direction. b) total dust deposition obtained from the BSC-DREAM8b model.

Lacaze-Duthiers canyon at the same time. All data together suggests that a fresher land derived material is funneled through the Cap de Creus and thus a higher degree of linkage between the Cap de Creus canyon and the shelf.

ATMOSPHERIC INPUTS OF TOM?. The ratio of CP to VP (C/V) has been used to distinguish contributions from woody and nonwoody plant tissues. Elevated CP/VP ratios (give range from literature) are typical of gymnosperm needles, angiosperm leaves and grasses. In our study, we measured unusually high CP/VP ratios (from 2.75 up to 5) at all stations in early May and July (except at upper canyon ones, CCC300 and LDC300) (Fig. 5.5b). The only tissues analyzed to date that yield such high CP/VP ratios upon CuO oxidations are pollen samples from different angiosperm and gymnosperm species (Hu et al., 1999; Keil eta al., 1998; Goni et al., unpublished data). Indeed, pollen grains are known to be among the sedimentary organic matter the most resistant to microbial degradation and thus may also be important lignin contributors from sediments (Keil et al., 1998). After the CP/VP peak detected in July, a relatively high CA/LP contents is detected in August. Cutins are present in aereal soft tissues of vascular plants and its information is potentially complementary to phenols ratios. These extremely high CP/VP ratio and CA concentrations where observed in no-cascading condition and during particularly low mass fluxes indicating negligible advection from the continent (Fig. 5.2a). Pasqual et al. (2011) explained that during June-July physical forcings (such as waves, currents and river discharge) that enhance the transfer of shelf material basinwards were the lowest favouring the settling of particles in suspension in intermediate or bottom nepheloid layers under such relatively quiescent conditions. That was formulated to explain the timing of these maximum peaks in LP concentrations during the summer time (in the upper canyon, the peak is observed in May, in the middle canyon in June, and the in lower canyon and upper slope in July whereas in most of the distal stations peaks were detected in August). These trends suggest the settling of fine particle relatively rich in lignin that were initially mobilized during cascading season and subsequently moved down canyons. Tesi et al., (2010) suggests that the relative proportion of lignin-cutin derived in lateral fluxes in CdC canyon strictly depends on the sediment grain-size due to the selective sorption of CA on surface of fine particles. Consequently the down canyon transport of TOM would be driven by sediment sorting associated with transport mechanisms.

But the fact that CP/VP and CA peaks are detected at all stations at the same time with no time lag may be indicating that the inputs of TOM with that particular signal (high CP/VP) are triggered by a different transport process, rather than lateral advection. One explanation could be the atmospheric inputs of materials during May and June-July months when the study area was affected by dust inputs (Fig. 5.7). The

importance of the aerial transport of pollen from continent to marine and distal regions have been highlighted in several studies (Izquierdo et al., 2010; Franzén et al., 1994) and known as "yellow snow" events when pollen yellowish the dust. Indeed, it is kwon that at offshore locations the atmospheric inputs represent the major source of terrigenous particles and OM Estimates of atmospheric flux in the western Mediterranean indicate values of 27.4 mg m^{-2} d^{-1} (Guerzoni et al., 1997) being the Saharan aerosols the 90% of the atmospheric particulate fallout to the open water column (Loye-Pilot et al., 1986).

Conclusions

Our results suggest large differences in the sources and transport processes responsible for terrigenous material transport along canyons. Lignin-derived phenols signal at studied stations is conditioned by the DSWC event, responsible of the major part of the inputs of lignin at submarine canyons. The terrigenous organic matter that is advected during the DSWC event through the Cap de Creus canyon and Open slope is fresher that the one that is advected through the Lacaze-Duthiers canyon suggesting higher degree of linkage between the southern parts of the Gulf with the Shelf during those high energetic conditions. The temporal resolution obtained with sediment traps allows detecting punctual terrigenous organic matter inputs during low energetic conditions (i.e. atmospheric inputs during summer time). As a consequence, it was detected that TOM material deposited basinwards was relatively more enriched in less degraded nonwoody material than the one that settles at shallower canyon stations.

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