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

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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.

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Capítol 4

Use of organic biomarkers to trace the transport of marine and terrigenous organic matter through the southwestern canyons of the Gulf of Lion

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Abstract

From October 2005 through October 2006 sediment traps were moored along the Lacaze-Duthiers and Cap de Creus submarine canyons and on the adjacent southern open slope in the Gulf of Lion (Northwestern Mediterranean). During the Winter 2006 (January-March), an intense Dense Shelf Water Cascading (DSWC) event was found to be a major driver of particle transport, increasing lateral advection of material at all stations. In this study, we assessed the sources and degradation of organic matter (OM) advected along canyons during both DSWC and quiescent conditions using specific organic biomarkers, including pigments, lignin phenols and amino acids. Three major events of fresh, marine OM inputs were detected during the study period. The largest one was in spring (March-May), with smaller events also observed in winter (December 2005) and summer (August 2006), suggesting that both spring blooms and sporadic blooms associated with wind-driven mixing affects carbon fluxes in this system. The DSWC event that partially overlapped the spring-bloom enhanced the overall transfer of OM down canyons. The lignin phenol data show no significant, along-canyon dilution and are consistent with constant advection of terrigenous material. In contrast, amino acid and chloropigment compositions indicate that part of the OM is degraded both prior to reaching the canyons and within the canyons themselves. Overall, our results illustrate the importance of both seasonal and sporadic pelagic and continental shelf/lateral events in controlling the exchange of organic matter across this margin.

Resum

Des d'octubre de 2005 fins a octubre de 2006, es varen fondejar trampes de sediment en el golf de Lleó (Mediterrànea nord-occidental) al llarg dels canyons submarins de Lacaze-Duthiers i Cap de Creus, així com al talus sud. Durant l'hivern de 2006 (gener - març), el major factor que controlà el flux de partícules a la zona d'estudi va ser una inetnsa cascada d'aigua densa (DSWC), el qual ocasionà un increment de l'advecció laterial a totes les estacións mostrejades. En aquest treball, es discuteix l'origen i la degradació de la material orgànica (OM) advectada a través dels canyons durant la DSWC així com també durant condicions de calma mitjançant l'ús de biomarcadors orgànics, els qual inclouen els pigments, els fenols derivats de la lignina i els aminoàcids. Principalment, es detcetaren tres esdeveniments de OM fresca i marina durant el període d'estudi. El més destacat tingué lloc a la primavera (març-maig), mentre que els altres dos varen ser observats a l'hivern (desembre 2005) i a l'estiu (agost 2006), els quals suggereixen que tant els "blooms" primaverals com els "blooms" esporadics associats a procesos de barreja d'aigua pel vent, afecten al flux de carboni en aquest sistema estudiat. L'esdeveniment de DSWC, que sol·lapà parcialment el "bloom" primaveral, afavorí la transferencia de OM fresca cap avall dels canyons. Les dades dels fenols derivats de la lignina no mostren una dilució al llarg dels transectes significant, i són, per tant, consistents amb una constant advecció de material terrestre. Per contra, la composició d'aminoàcids i cloropigments indica que part de la OM es degradadà abans d'arribar a les zones baixes del canyó, així com a través de la columna d'aigua. En resum, els nostre resultats il·lustren la importancia dels esdevenimnts pelàgics, tan estacionals com esporàdics, així com dels esdeveniments laterals o de plataforma, pel que fa al control de l'intercanvi de OM a través d'aquest marge.

Introduction

Along continental slopes, submarine canyons act as bypass zones connecting the shelf with the interior ocean. Lateral transport of organic matter (OM) along submarine canyons affects both biogeochemistry and ecology of deep sediments as canyons are fast track corridors for the transport of OM from land to deep sea (Weaver et al., 2004). Most of the particulate transfer occurs as a result of gravity-driven processes. Among these mechanisms, Dense Shelf Water Cascading (DSWC) has been suggested as the main driver affecting the shelf-slope exchange of particulate OM in the deep Mediterranean Sea. Among the objectives of the HERMES project (Hotspot Ecosystems Research on the Margins of European Seas) was the study of biogeochemical and physical drivers within the European canyons with the ultimate goal to understand the role that submarine canyons play in the shelf-slope transfer of material and the biogeochemical cycle of OM.

In previous publications, we presented the fluxes and bulk compositions of settling particles collected with nine sediment traps moored for over a year (October 2005-October 2006) along three transects in the Gulf of Lion (GoL). Traps were deployed along two of the major canyons of this margin, the Lacaze-Duthiers canyon (LDC) and Cap de Creus canyon (CCC), and on the adjacent southern open slope (SOS)

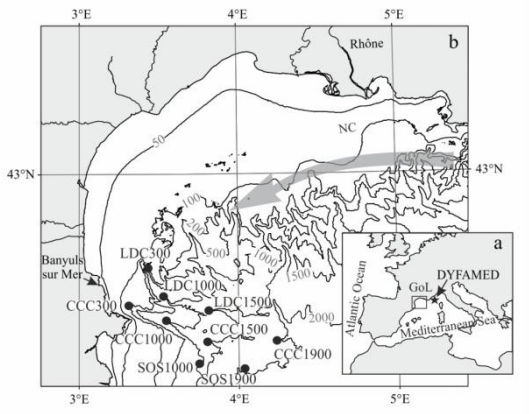

Fig. 4.1. a) Location of the Gulf of Lion (GoL) in the Western Mediterranean Sea and b) sediment trap mooring stations (black dots) along the tree transects studied: Lacaze-Duthiers Canyon (LDC) Cap de Creus Canyon (CCC) and their Southern Open Slope (SOS). Surface ocean circulation is represented by the Northern Current (NC grey arrow).

(Fig. 4.1). Previous publications included estimates of mass fluxes, calcium carbonate, opal, OC, lithogenic contents, as well as the elemental ratios and stable isotopic compositions of organic carbon and nitrogen (Sanchez-Vidal et al., 2008; 2009; Pasqual et al., 2010). Our results showed that the occurrence of a cascade of dense shelf water to the lower continental slope that occurred from January to March 2006 was a major physical forcing in enhancing particle flux throughout this region (Fig. 4.2a). Dense shelf water was traced using a strong negative near-bottom temperature anomaly and increased current speeds (Sanchez-Vidal et al., 2008; 2009; Pasqual et al., 2010). The lateral advection of homogenized material increased in all stations (from mid-canyon to canyon mouth and the open slope) by up to several orders of magnitude during DSWC events (Pasqual et al., 2010). The OC flux increased in association with the increment of the total flux even though it was diluted by lithogenic material. Although a large quantity of material was transported by the cascading waters, a significant part of the total mass flux in the deeper stations that occurred during quiescent conditions originated from autochthonous production in surface waters.

Deciphering the different components of the mass flux (e.g., horizontal vs. lateral fluxes) in this system is challenging due to the dynamic nature of canyon systems. Moreover, tracing the specific origin of the OM inputs (e.g, autochthonous vs. allocthonous) is difficult due to the wide range of possible sources, degradation and selective transport processes in canyons (Hedges et al., 1997). Two main questions remain from previous work: i) what are the sources of OM at different times and different locations and ii) what is the quality of the OM during these different periods at different locations. To address these questions, we analyzed the same sediment trap samples previously analyzed for bulk measurements (Pasqual et al., 2010) in order to reveal information on the sources and degradation state of organic materials. Specifically, we analyzed chloropigments, which are produced by phytoplankton and used as tracers of "fresh" marine OM (Lee et al., 2004), lignin-derived phenols, which are uniquely synthesized by vascular

plants and are used as tracers of land-derived OM (Hedges et al., 1997), and amino acids, which have both marine and terrestrial sources but can be used as tracers of the degradation state of OM (Dauwe and Middelburg, 1998; Ingalls et al., 2006). The aim of this work is to assess the sources and degradation of marine OM in settling particles along the southern canyons and open slope of the GoL and evaluate the inputs from terrigenous sources. Comparing fluxes, concentrations and OC-normalized yields of the pigments, amino acids and lignin phenols allow us to evaluate the temporal and spatial distribution of terrestrial and marine OM inputs and their overall cycling.

Regional setting

The inputs of terrigenous material to the continental shelf in the GoL have been the object of several studies (Bouloubassi et al., 1997; Buscail et al., 1995; Gought et al., 1993; Tesi et al 2007). Terrigenous materials from fluvial sources are deposited in the prodeltas primarily during autumn floods characteristic of the Mediterranean climatic regime and during spring floods due to the melt of the snow (Buscail et al., 1995). Prodelta and shelf sediments are exposed to continuous physical reworking that resuspends and exports the finest particles through to the adjacent continental margin (Buscail et al., 1995, Tesi et al 2007), often creating a multilayer nepheloid system (Monaco et al., 1990). Due to the general circulation patterns, these fine particles exit the shelf through the westernmost submarine canyons mainly during E and SE winter storms and DSWC events (Palanques et al., 2006) and accumulate on the seabed in the deeper parts of the Gulf (Bouloubassi et al., 1997). Aeolian inputs can also contribute terrigenous particles to offshore regions of the Mediterranean. Guerzoni et al. (1997) estimated that atmospheric particulate flux in the western Mediterranean is 27.4 mg m^{-2} d^{-1}. Saharan aerosols represent 90% of the atmospheric particulate fallout to the water column (Loye-Pilot et al., 1986). In addition, atmospheric inputs of nutrients such as nitrogen and iron cause sporadic phytoplankton production events during stratified and oligotrophic conditions (summer-autumn) (Migon and Sandroni, 1999).

Table 4.1. Abbreviation table of the different biomarkers analyzed.

Organic carbon	OC
Total pigments	pig
chlorophyll a	Chl a
phaeophorbide a	PPB
pyrophaeophorbide a	pyroPPB
Lignin	lig
Total hydrolyzed amino acids	aa
alanine	ALA
arginine	ARG
aspartic acid	ASP
β-alanine	BALA
β-glutamic acid	bGLU
γ-aminobutyric acid	GABA
glutamic acid	GLU
glycine	GLY
histidine	HIS
isoleucine	ILE
leucine	LEU
lysine	LYS
methionine	MET
ornithine	ORN
phenylalanine	PHE
serine	SER
threonine	THR
tyrosine	TYR
valine	VAL

Except for sporadic events, the spatial distribution of marine primary production in the GoL is controlled by the Northern Current that separates shelf waters directly influenced by the Rhône River from offshore waters that show seasonality in surface and deep chlorophyll concentrations associated with water mixing processes (Lefevre et al., 1997). Seasonal primary production in the southwestern GoL is characterized by spring blooms (Vidussi et al., 2000) and summer stratified oligotrophic waters followed by autumn blooms (Marty et al., 2008). The transfer of non-recycled particulate OM produced in the euphotic zone to deep waters is largely controlled by the intensity of seasonal pelagic production but also by local meteorology and hydrology (Marty et al., 1994; Mignon et al., 2002).

Material and methods

4.1.1 Sample collection and preparation

As described previously in detail (Pasqual et al., 2010), nine sediment trap moorings were deployed from mid October 2005 to late October 2006 along Lacaze-Duthiers and Cap de Creus canyons (LDC and CCC, respectively) and along the southern open slope (SOS) (Fig. 4.1). Each mooring was equipped with a PPS3 Technicap sequential sampling sediment trap 30 m above the bottom and an Aanderaa current meter 5 meters above the bottom. Sampling intervals were 15 days for traps and 30 minutes for current meters. Buffered formaldehyde in filtered seawater was used as a preservative. Limitations intrinsic to sediment trap flux estimates associated with trap hydrodynamics, swimmer intrusion and solubilization are discussed in Pasqual et al. (2010). Sediment traps experiments on the degradation of collected particles suggest that variable but potentially significant losses from sinking particles may take place (Buesseler et al., 2007 and references therein), especially in moored traps that are deployed for long periods of time (Lamborg et al., 2008).

After recovery, samples were processed according to Heussner et al. (1990). Samples were split into aliquots using a peristaltic pump robot to obtain 10-20 mg sub-samples, and freeze dried for the lignin analysis or filtered through pre-weighed glass-fiber filters for chloropigment and amino acid analyses.

4.1.2 Analytical methods

OC content was measured using an elemental analyzer (EA Flash series 1112 and NA 2100). Samples for organic carbon analysis were first decarbonatated using repeated additions of 100 µl 25% HCl with 60ºC drying steps in between until no further effervescence occurred. Organic matter (OM) content has been estimated as twice the total organic carbon content. Uncertainties were lower than 0.1% as determined from replicates of the certified estuarine sediment standard MESS-1.

Pigments and amino acids were analyzed following the same procedure described by Fabres et al. (2008). Chloropigments (chlorophyll a, pheophorbide a and pyropheophorbide a) were measured by reverse-phase high-performance liquid chromatography (HPLC) after extraction in acetone. Duplicate analyses of the same extract (n>3) agreed within ±2%. Total hydrolyzed amino acids (THAA) were analyzed by HPLC after acid hydrolysis and o-phthaldialdehyde (OPA) derivatization. In addition to standards of the non-protein amino acids, β-alanine (BALA) and γ-aminobutyric acid (GABA), the amino acids β-glutamic acid (BGLU) and ornithine (ORN) were also added individually to a standard mixture, and these latter compounds were also analyzed in samples. Duplicate analyses of THAA in the hydrolyzates of individual samples (n>3) agreed within ±11%. Lignin oxidation with CuO was performed on freeze-dried sediment trap samples. CuO oxidations were carried out according to Goñi and Montgomery (2000). Yields of individual lignin phenols were quantified by GC–MS using selective ion monitoring. Lignin phenol concentrations were estimated as the total weight in milligrams of carbon from vanillyl phenols (V; vanillin, acetovanillone, vanillic acid), syringyl phenols (S; syringaldehyde, acetosyringone, syringic acid), and cinnamyl phenols (C; p-coumaric acid, ferulic acid). Duplicate analyses of selected samples (n>3) of these compounds using the CuO technique were within ±10% of the measured value. Once the yields of all biomarkers were computed, we calculated the amount of carbon contributed by each compound based on their molecular formulas. Accordingly, all flux and concentration data are reported in units of mass of C represented by each biomarker class. The contribution of each compound to the total OC in the trap samples (%OC) is the quotient of the concentration in the sample divided by the organic carbon content of the sample.

4.1.3 Statistical Analyses

Principal Components Analysis (PCA) has been commonly used in the analysis of complex organic compound datasets (Ingalls et al., 2006; Goutx et al., 2007). PCA is a multivariate regression analysis that

reduces a large number of variables to a few principal components. We used it here to i) establish the relation of all the parameters included in this paper, both biomarkers, OC and total mass flux and ii) assess the variation in the amino acid composition of sinking particles collected at canyon and slope stations over time. It is a helpful tool for deciphering variability in large data sets (in our case, 25 variables x 188 samples = 4700 values). Prior to bulk data PCA, the data set was normalized by subtracting the mean of all values and dividing each variable by its standard deviation (e.g., Dauwe and Middelburg, 1998; Sheridan et al., 2002). A scree plot (of eigenvalues versus component number) was created to evaluate the importance of each eigenvalue (Xue et al., 2011). The first PCA principal component is the axis of maximum variation in the data set while the second one is equivalent to the axis of maximum residual variation. A "loading" (variable's contribution to the data set variability) and a "site score" (distance of the sample from the first principal component axis) are calculated for each variable and sample respectively. All PCA calculations were carried out using PSS Statistics 17.0 software.

Results

4.1.4 Pigments

Fluxes of total chloropigments peaked at two particular times at all stations (Fig. 4.3a). The first peak was during the first DSWC flushing in January, with a second peak associated with the spring bloom (March-May). The January DSWC peak was most notable in the middle canyon and slope stations (LDC1000, CCC1000 and SOS1000). The spring peak fluxes were in March through May depending on the canyon location and time with values up to 0.71 mg of pigment-derived carbon (C-pig) m^{-2} d^{-1} in CCC1000 and 0.28 mg C-pig m^{-2} d^{-1} in LDC1500. There was also a peak in pigment flux in summer (August) at the LDC and CCC upper canyon (300 m) stations.

The concentration of pigments in the sinking particles was highest in December just before the DSWC event, in spring (March-May) when the peak pigment concentration was associated with the peaks in flux, and in summer (August) in the lower LDC and CCC canyons (Fig. 4.3b). December values were quite high at LDC1500 (69.1 µg C-pig g^{-1}), CCC1500 (34.4 µg C-pig g^{-1}) and SOS1000 (21.8 µg C-pig g^{-1}). This trend agrees with measurements of OC (Fig. 4.2b) and

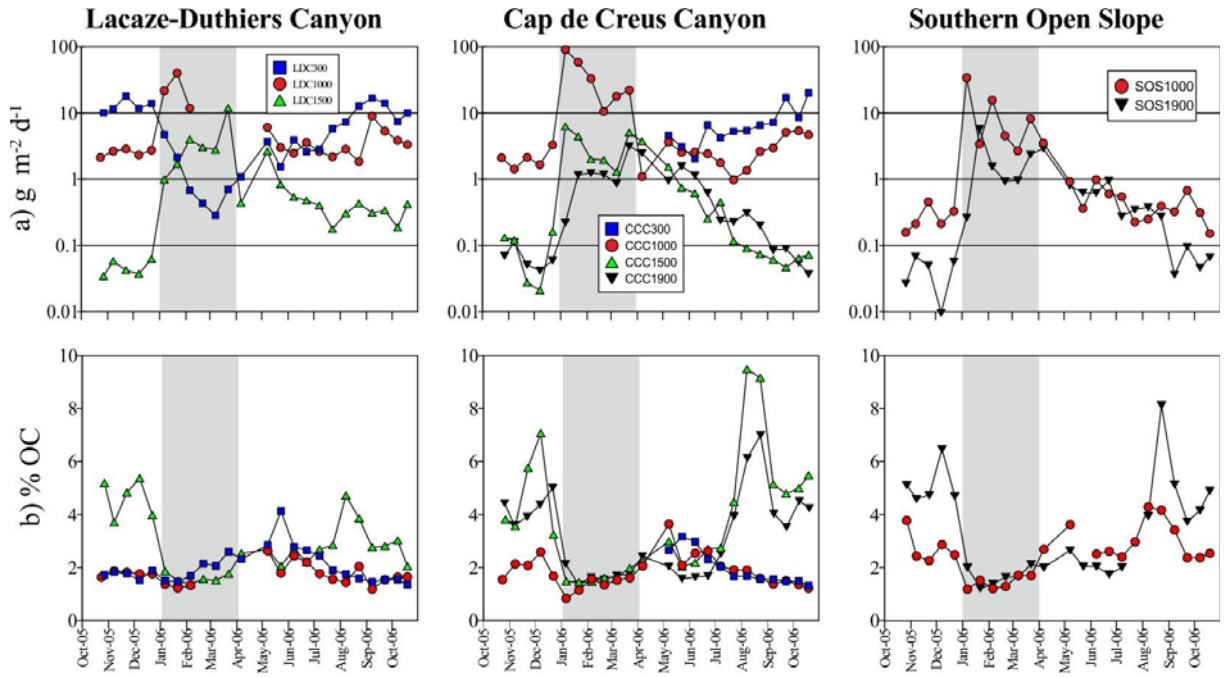

Fig. 4.2. Time-series data of a) total mass flux (g m^{-2} d^{-1}) and b) OC concentration in the trap sample (%). Note shaded area that highlights the DWCS period. Note shaded area that highlights the DSWC period. (OC analytical error is ±0.1%)

opal concentrations, which also were elevated at those times (Pasqual et al., 2010). In spring, the higher concentrations were more widely distributed among the stations, with values up to 43.0 µg C-pig g^{-1} in the LDC1500 during early April and 42.2 µg C-pig g^{-1} in the CCC1500 station during early May. In August a large enrichment was detected in the lower canyon stations (CCC1500, LDC1500 and CCC1900) reaching values of 54.2 µg C-pig g^{-1} at CCC1500 and 53.2 µg C-pig g^{-1} at CCC1900. The major contributions of chloropigments to the total pool of OC were detected during the same December, spring (March-May) and August periods already mentioned (Fig. 4.3c). Pigment contributions to the OC pool were generally highest in spring when they reached 0.12-0.2 % of the total carbon. These values are similar to the 0.1-1.5 % measured in May 2003 by Goutx et al. (2007) at 200 m water depth in the DYFAMED station (see location at Fig.1).

The dominant chloropigment in more than 80 % of the stations sampled was pyroPPB (Table 4.2), which is a zooplankton enzymatic alteration product of Chl a. Intact Chl a was often detected at the canyon head stations but only very occasionally seen in middle and lower canyon stations (Supplementary data).

4.1.5 Lignin

Fluxes of total lignin-derived compounds were higher at the canyon mouths, reaching up to 6 mg of lignin-derived carbon (C-lig) m^{-2} d^{-1} at CCC1000 (Fig. 4.4a). Temporal variability was similar to that of total

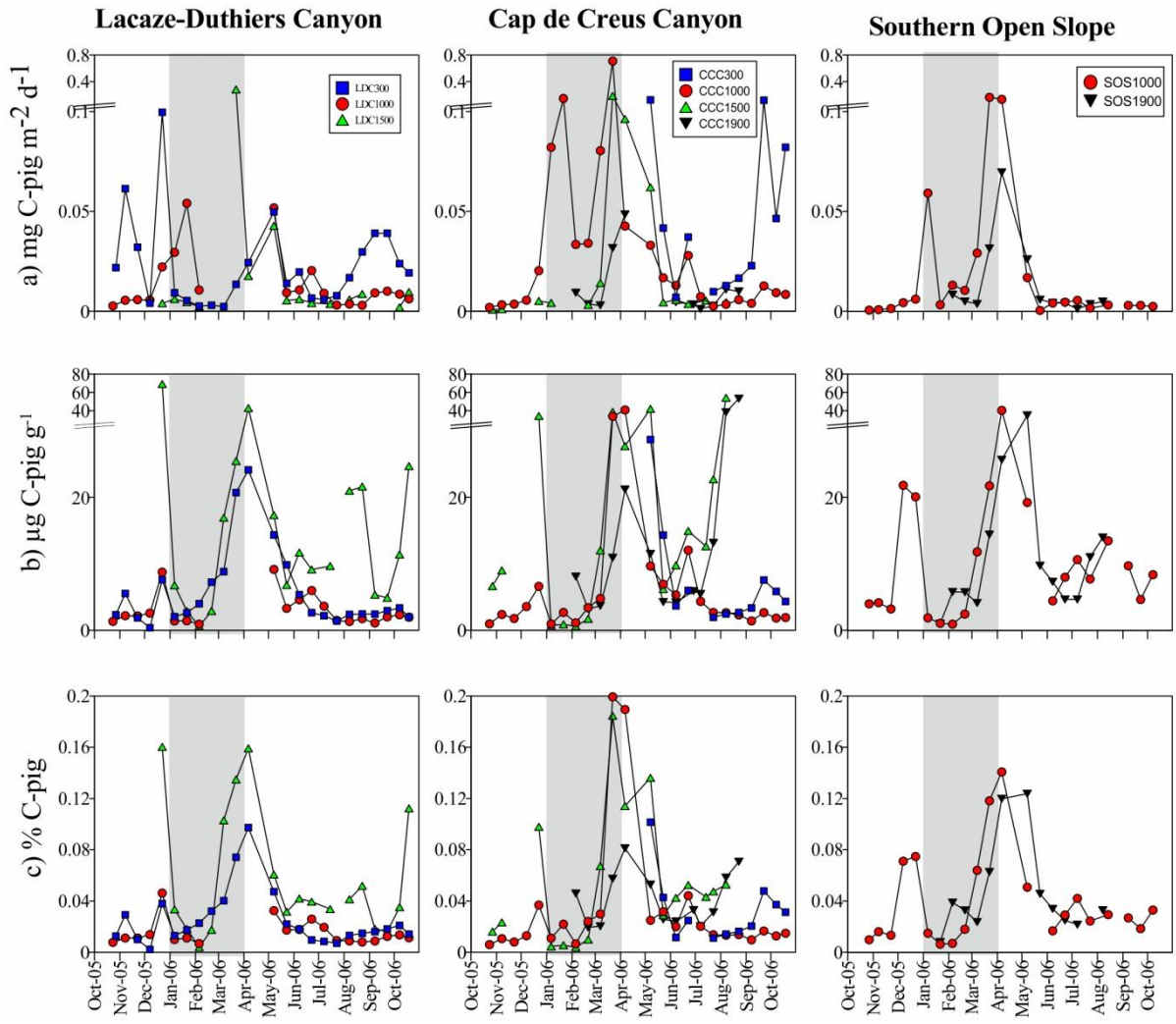

Fig. 4.3. Pigment time-series data from the sediment traps at the three study areas including a) flux of pigment-derived carbon (mg C-pig m^{-2} d^{-1}) b) concentration of pigment-derived carbon in the trap sample (µg C-pig g^{-1}) and c) contribution of pigment-derived carbon to the total OC in the trap samples (% C-pig). Note shaded area that highlights the DSWC period. (Pigment analytical error is ±2%)

mass flux (Fig. 4.2a) and was dominated by the DSWC event (Fig. 4.2a). Lignin-derived phenol concentrations in the sinking particles were significantly higher in summer after both the DSWC and spring bloom had passed, with values over 0.1 mg C-lig g^{-1} at all three locations (Fig. 4.4b). Upper and middle canyon stations, where complete data sets are available, showed peaks in lignin concentrations during May-July reaching values of 0.15 mg C-lig g^{-1} at the Lacaze-Duthiers canyon head. Slightly higher concentrations were found in the deeper canyon and open slope stations later in July. Lignin derived phenols contributed around 0.2-0.4% to the pool of total OC (Fig. 4.4c). There was a general increase in the lignin contribution to OC during June-July along the stations of both canyons, and a particularly high (0.8%) contribution during January in the middle Cap de Creus.

4.1.6 Amino acids

The fluxes of THAA showed contributions consistent with both terrestrial and marine inputs. Values were up to 17.1 mg of amino acid-derived carbon (C-aa) m^{-2} d^{-1} at LDC 1000 (Fig. 4.5a) in January during flushing by the DSWC, which was similar to the trends in lignin (Fig. 4.3a) and total mass fluxes (Fig. 4.2a). Smaller peaks occurred in spring (May), which were more comparable to the pigment flux patterns. Amino acid concentrations presented higher values in upper and middle canyon stations relative to the deeper canyon and open slope stations. For example, during the spring-summer period (from May to August), amino acid concentrations ranged from 13 to over 30 mg C-aa g^{-1} in the Cap de Creus upper and middle canyon station whereas the concentrations in the deep-

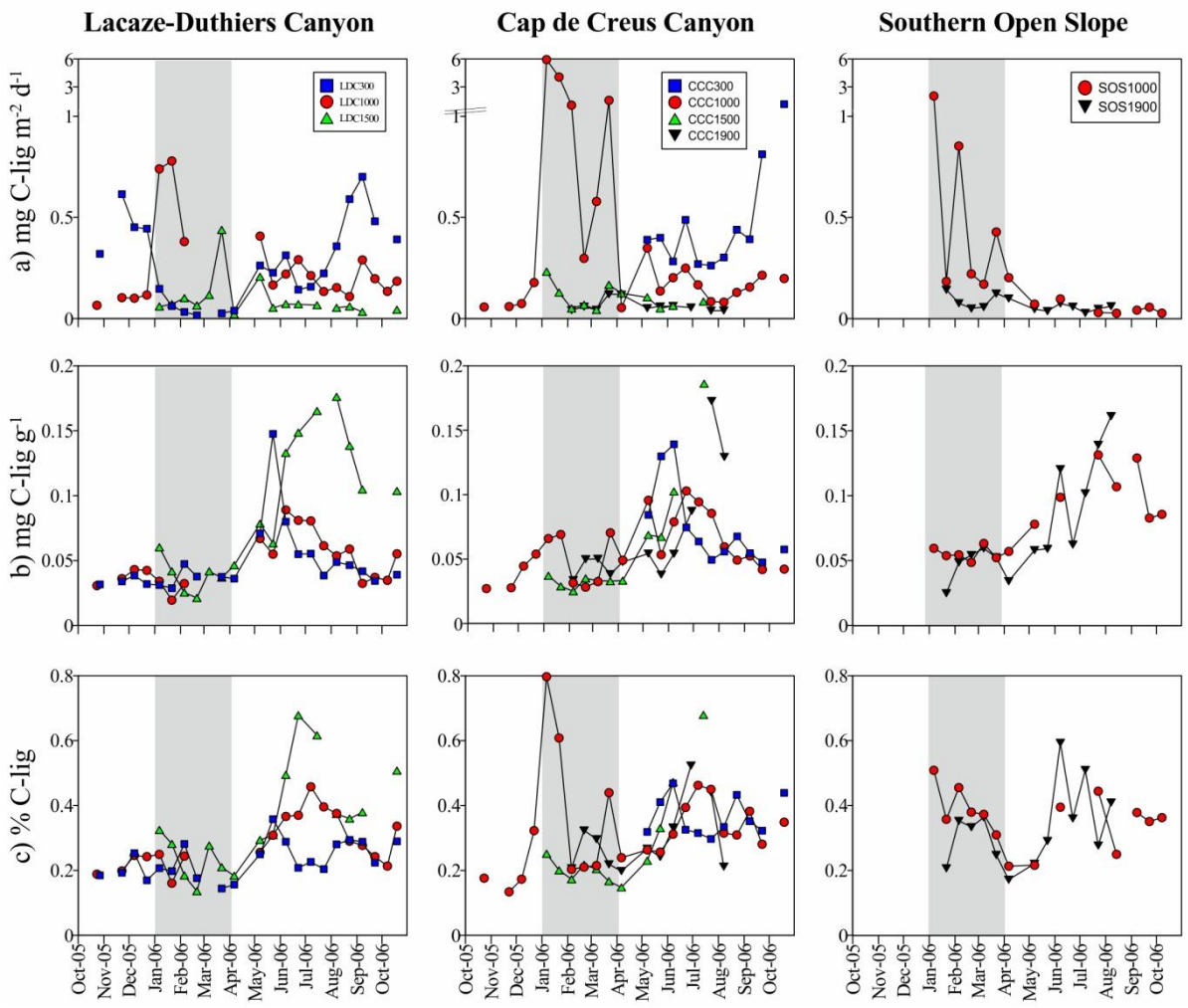

Fig. 4.4. Lignin phenol time-series data from the sediment traps at the three study areas including a) fluxes of lignin-derived carbon (mg C-lig m^{-2} d^{-1}) b) concentrations of lignin-derived carbon in trap samples (mg C-lig g^{-1}) and c) contribution of lignin-derived carbon to the total OC in trap samples (% C-lig). Note shaded area that highlights the DWCS period. (Lignin analytical error is ±10%)

Table 4.2. Mean relative contribution of amino acids and pigments analyzed to the total amino acids and pigments respectively. Statistics presented are number of samples (N) mean standard error of the mean (Std.) for each station studied.

Station		PPB	pyroPPB	Chl a	ASP	GLU	bGLU	SER	HIS	GLY	THR	ARG	BALA	ALA	GABA	TYR	MET	VAL	PHE	ILE	LEU	ORN
LDC300	N	21	21	21	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
	Mean	32,97	56,91	10,11	9,91	9,40	0,00	7,84	1,02	14,11	7,70	5,26	1,69	9,49	1,41	2,88	1,33	6,48	4,14	4,31	6,83	2,78
	Std.	4,03	3,40	3,09	0,42	0,31	0,00	0,32	0,06	0,97	0,18	0,13	0,10	0,35	0,44	0,14	0,19	0,28	0,18	0,16	0,16	0,69
LDC1000	N	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19	19
	Mean	40,69	59,00	0,32	8,50	7,71	0,00	8,24	0,86	16,69	7,77	5,35	2,00	10,14	0,79	2,44	1,16	5,79	3,68	3,80	6,17	4,97
	Std.	2,97	2,91	0,23	0,41	0,29	0,00	0,20	0,03	0,43	0,20	0,16	0,17	0,24	0,14	0,08	0,10	0,10	0,08	0,06	0,11	1,55
LDC1500	N	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16	16
	Mean	30,96	66,85	2,19	10,54	8,70	0,04	8,54	0,85	16,31	6,35	5,19	1,69	10,69	1,62	2,58	1,30	5,58	4,01	3,73	6,28	2,93
	Std.	3,99	3,92	1,21	0,74	0,29	0,04	0,15	0,05	0,60	0,28	0,21	0,10	0,26	0,30	0,05	0,09	0,32	0,19	0,25	0,24	0,58
CCC300	N	11	11	11	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	Mean	26,72	52,10	12,09	8,77	8,22	0,35	8,02	1,07	14,01	8,20	5,01	2,18	10,21	1,68	2,89	1,82	6,52	3,91	4,26	6,71	3,58
	Std.	4,34	5,74	3,77	0,28	0,12	0,07	0,11	0,03	0,38	0,10	0,10	0,13	0,11	0,38	0,07	0,19	0,20	0,08	0,15	0,15	0,44
CCC1000	N	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22
	Mean	39,39	57,91	2,70	10,83	8,46	0,01	8,75	0,94	15,65	6,79	5,40	1,77	10,64	1,34	2,63	1,37	6,10	4,06	4,06	6,36	1,66
	Std.	2,95	2,96	1,52	0,57	0,43	0,01	0,21	0,06	0,33	0,18	0,15	0,15	0,11	0,23	0,05	0,05	0,19	0,08	0,13	0,14	0,26
CCC1500	N	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11
	Mean	24,07	72,46	3,47	8,90	8,29	0,07	7,97	0,94	14,21	6,31	5,39	3,10	9,83	1,79	2,43	1,27	5,84	4,21	4,20	6,54	5,92
	Std.	5,43	6,41	3,47	0,37	0,23	0,05	0,27	0,05	0,56	0,12	0,13	0,42	0,20	0,33	0,09	0,10	0,21	0,22	0,18	0,18	0,79
CCC1900	N	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12
	Mean	29,55	70,45	0,00	19,20	11,35	0,12	7,07	0,50	16,25	3,85	3,49	2,19	11,94	4,80	2,25	1,16	3,08	2,82	1,94	4,83	0,49
	Std.	2,15	2,15	0,00	1,12	0,21	0,08	0,23	0,08	0,92	0,21	0,16	0,12	0,36	0,76	0,16	0,63	0,18	0,12	0,09	0,24	0,29
SOS1000	N	14	14	14	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12
	Mean	30,39	69,30	0,31	18,76	10,63	0,12	6,76	0,60	17,24	4,13	3,32	1,77	11,60	4,17	2,27	0,51	2,97	2,82	1,90	4,72	3,31
	Std.	4,38	4,36	0,31	1,12	0,41	0,06	0,21	0,05	0,90	0,16	0,14	0,44	0,37	0,83	0,17	0,06	0,20	0,13	0,11	0,19	2,07
SOS1900	N	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14
	Mean	30,38	67,00	2,62	19,93	11,02	0,02	7,27	0,58	18,49	3,96	3,36	1,64	12,16	3,33	2,23	0,53	2,85	2,79	1,92	4,81	0,90
	Std.	2,05	2,29	2,11	0,71	0,18	0,02	0,21	0,03	0,87	0,19	0,09	0,24	0,29	0,69	0,14	0,07	0,20	0,11	0,08	0,16	0,19
Total	N	140	140	140	136	136	136	136	136	136	136	136	136	136	136	136	136	136	136	136	136	136
	Mean	32,80	62,74	3,75	12,40	9,20	0,06	7,93	0,83	15,90	6,29	4,76	1,94	10,67	2,13	2,53	1,17	5,18	3,66	3,45	5,99	2,89
	Std.	1,27	1,33	0,77	0,43	0,15	0,01	0,09	0,02	0,26	0,15	0,09	0,08	0,12	0,18	0,04	0,07	0,14	0,07	0,10	0,09	0,34

est canyon station were all less than 10 mg C-aa g^{-1}. Higher concentrations were found later in summer (July-August) (Fig. 4.5b). The contribution of amino acids to the OC pool was notably lower at canyon mouth and open slope stations throughout the experiment with mean values around 5% (Fig. 4.5c).

The average amino acid composition of the settling particles from all stations was dominated by GLY (16.1 mol%), ASP (11.8 mol%), ALA (10.7 mol%), GLU (9.0 mol%), SER (8.0 mol%) and THR (6.4 mol%) (Table 4.2, See complete data set in supplementary data). These are the most common amino acids generally found in sediment trap samples (Lee et al., 2000). Using PCA (Fig. 4.6c), the first principal component (PC1) explained 43% of the variance. Amino acids (variables) with higher loadings on PC1 are VAL, ILE, ARG, THR, LEU and PHE whereas those with lower loadings are ASP, GLU, ALA, GABA and GLY. PC1 separates two groups of samples: slope and deep CCC stations on the left and all the others on the right. The second principal component (PC2) explained 17% of the variance. Amino acids with higher loadings on PC2 were GABA, TYR and GLU, while GLY, SER, LYS and ALA had lower loadings.

Discussion

Our data show that there are notable spatial and temporal differences in the input of marine and terrestrial OM to the canyons studied. In the following sections, we use lignin and pigment data from the sinking particles to differentiate between these marine and terrestrial components of the vertical flux. Amino acid biomarkers are used to investigate the degradation status of material sinking to various parts of the study region. The inferred sources and degradation state of the material being transported to the canyon are discussed in terms of what is known about sedimentation in this area.

4.1.7 Marine OC inputs

In marine environments, chlorophyll is produced by phytoplankton in the surface waters, but is quickly degraded relative to other organic compounds such as

lipids, amino acids and carbohydrates (Wakeham at el., 1997). The proportion of chlorophyll to its degradation products, pheophorbide and pyropheophorbide, is a good indication of its "freshness" (Lee et al., 2004). Land plants also produce chlorophyll, but because it is a relatively labile compound, by the time terrigenous OM reaches the sea it is typically devoid in intact chlorophyll.

INPUTS OF FRESH OM FROM SPRING BLOOMS AND DSWC. Chloropigment flux peaks were observed at the end of March, in April and early May at almost all stations, with values up to 0.7 mg C-pig m^{-2} d^{-1} at the CCC1000 station (Fig. 4.3a). Although there was a short gap in data collection during the trap recovery period in late April, fluxes during early May were consistent with a large spring pigment input. In these spring samples, pigments make their largest contribution to total OC, ranging from 0.08% in the CCC1900 up to 0.2% in the CCC1000 (Fig. 4.3b). Moreover, concentrations of pigments in the particles collected during that period are among the highest observed during the study period (Fig. 4.3c), consistent with a larger input of fresh marine OM at this time. Unaltered Chl *a* was detected in particles collected in March and May at both middle and lower canyons (Supplementary data), providing additional evidence for a pulse of fresh marine OM associated with the spring bloom reaching the deeper regions of both canyons. At the nearby DYFAMED station (Fig. 4.1), pigment fluxes measured by sediment trap during the MedFlux project were up to 35 µmol C m^{-2} d^{-1} (0.49

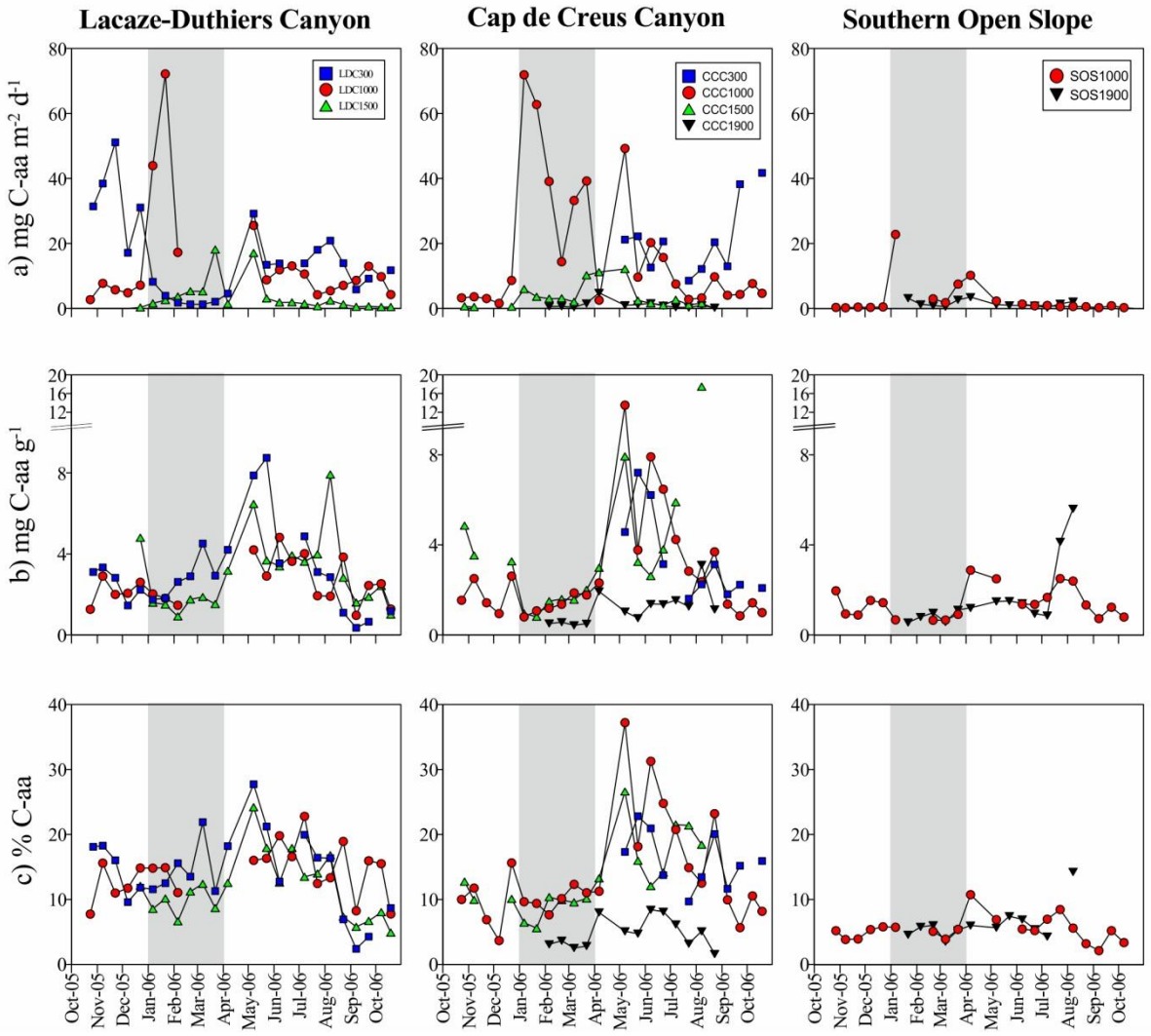

Fig. 4.5. Amino acid time-series data from the sediment traps at the three study areas including a) fluxes of amino acid-derived carbon (mg C-aa m^{-2} d^{-1}) b) concentrations of amino acid-derived carbon in trap samples (mg C-aa g^{-1}) and c) contribution of amino acid-derived carbon to the total OC in trap samples (% C-aa). Note shaded area that highlights the DWCS period. (Amino acid analytical error is ±10%)

mg C m^{-2} d^{-1}) at 200 m during the spring bloom but were generally much lower (Wakeham et al., 2009; Abramson et al., 2010). Lower values might be expected at the DYFAMED station, however, as it is located in the central zone of the Ligurian Sea in deeper waters (2500 m) that are isolated from coastal inputs (Marty et al., 2002). All data suggest that values found during spring indicate that relatively high quantities of fresh marine OM were settling in sediment traps during spring (March-May).

Earlier studies of bulk particle parameters (Fabrés et al., 2008; Sanchez-Vidal et al., 2009), were unable to determine whether the input of OM was from a surface water bloom that developed during March-April at the trap location, or from an earlier coastal bloom that developed from middle February to middle April 2006 (Fig. 4.7a) that was carried to the trap location by the second DSWC flushing event. Although these authors could not rule out direct pelagic input, Fabrés et al. (2008) and Sanchez-Vidal et al. (2009) suggested that when a DSWC event takes place in conjunction with increased phytoplankton productivity on the shelf, cascading waters advect fresh, newly-produced particles from the shelf down the canyons. In contrast to the enrichment in fresh marine OM during March-May, the first DSWC flushing in January is characterized by an increase in pigment flux in the stations located at 1000 m. Notably, samples collected during this peak in flux fail to show increases in overall pigment content (either sediment or carbon-normalized) (Fig. 4.3). These results indicate that the first DSWC event advected shelf materials to the middle canyon and slope stations that were relatively devoid of pigments and contained altered marine OM. Thus, the export fluxes down the canyons are controlled by the interactions between physical and biological forcings. The magnitude and timing of the pigment flux between March and May relative to the trend in primary productivity trends over the shelf inferred from satellite data (Fig. 4.7a) provide further evidence for these interactions.

WIND DRIVEN INPUTS OF FRESH OM. In addition to the peaks of fresh marine OM input observed during spring (March-May), there are other periods of the year (December 05 and August 06) that are characterized by inputs of OM that appear to have high concentrations of marine OM based on C-pig content (Fig. 4.2c). These samples are also enriched in amino acids (Fig. 4.5b). The pigment and amino acid trends coincide with elevated contents of OC, opal and CaCO3 and lower lithogenic contents (Pasqual et al., 2010) and lend support to the hypothesis that marine productivity in the euphotic zone is a major source of the particle flux during these periods.

Normally phytoplankton blooms, and resulting high Chl a values, do not occur in either coastal or open ocean surface waters in this region during December or August (Lefervé et al., 1997; Marty et al., 2002) (Fig. 4.7a). In summer, however, deep chlorophyll maxima are typical (Estrada et al., 1993) and might explain the origin of fresh material inputs during August. Several studies in the open Mediterranean Sea have suggested that in addition to normal seasonal pelagic production, there are other processes like wind events that control the fluxes of labile compounds (Goutx et al., 2000; Marty et al., 1994). Indeed, an increase of sinking flux has been associated with dust events (Zúñiga et al., 2007; Lee at al., 2009; Patara et al., 2009; Ternon et al., 2010), and with wind events that weaken the thermal stratification supporting secondary blooms (Goutx et al., 2000) or that promote the settling of material accumulated in the pycnocline (Martín and Miquel, 2010). Ternon et al. (2010) analyzed these results and concluded that efficient export of Saharan dust and particulate OC depend on the intensity of the Saharan dust events and on hydrological processes such as water mixing. Before both December and August periods there was a previous deposition of Saharan dust (in November and June-July, respectively) (Fig. 4.7c) that may have triggered the development of secondary localized blooms. In addition, both periods had persistent northern wind events (Fig. 4.7b). These results are consistent with rapid transmission of surface signals to deep water in areas characterized by weak horizontal advection (Goutx et al., 2000). Thus this vertical transfer of fresh OM due to wind induced OM inputs events should be considered in particle export models.

4.1.8 Terrigenous OM inputs

Lignin-derived phenols are uniquely synthesized by vascular plants, most of which inhabit the terrestrial ecosystems, and have been used extensively to trace the contribution and source of terrigenous OM in many environments (Opsahl et al., 1997; Goñi et al., 1998; Gordon and Goñi, 2003; 2004;). Lignin data presented here from the GoL canyons is consistent with a constant advection of land-derived organic material away from the coast and down the canyons (Fig. 4.4). As observed for total mass flux, the middle canyon displays the highest fluxes during the DSWC event, while during the other periods studied the maximum fluxes are in the canyon heads consistent with advection of shelf material (Fig. 4.4a). These data agree with Tesi et al. (2010), who analyzed samples from the 2004/05 DSWC and concluded that cascading supplied about 98% of the terrigenous OC to the Cap de Creus Canyon upper canyon (500 m water depth), although advection of terrestrial OC occurred throughout that study (October 2004-March 2005).

Peaks in lignin fluxes over time are matched by peaks in amino acid fluxes. In contrast to the concentration of amino acids, which decrease down canyon and slope during January-March 2006 (Fig. 4.5b), however, the concentration of lignin compounds is almost constant along the canyons during the DSWC (Fig. 4.4b). These trends differ from shelf observations where a decrease in the concentration (due to degradation or dilution with other OM pools) of lignin phenols is observed with increased distance from the river mouths (Gough et al. 1993; Tesi et al., 2007). Thus, it appears that once terrigenous OM reaches the canyon, it is flushed down by cascading waters rather efficiently compared to amino acids and pigments. The distinct behavior of lignin phenols relative to amino acids reflects their contrast in lability (e.g., Cowie and Hedges, 1992; Cowie et al., 1992) and is consistent with field studies that showed that lignin distribution in sediments is rather stable under most circumstances (e.g., Goñi, 1997; Gordon and Goñi 2003; 2004).

Sediment-normalized lignin concentrations reach maximum values during the summer time with the timing of these peaks varying spatially along canyons (Fig. 4.4b). 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. Although these fine materials represented a minor fraction of the total mass flux, it displayed a distinct chemical composition characterized by high lignin content. As a result, during quiescent conditions (mass fluxes $\approx$1 g m^{-2} d^{-1}) the material collected exhibited higher sediment-normalized concentrations of lignin phenols than during the cascading season.

4.1.9 Degradation state of the OM

Amino acids are the building blocks of protein molecules and are ubiquitous to all living organisms. Because most living organisms contain proteins made up of the same suite of amino acids, the molar ratios of individual amino do not yield very useful source information. Hence, with some exceptions (mainly bacteria) no single amino acid is unique to any particular source and there is sufficient variability within groups of organisms that no secondary compositional parameter (e.g. ratios of compounds) offers significant resolution of source types (Cowie and Hedges, 1992). However, because amino acids are among the most labile biochemicals in marine environments, their concentrations relative to OC and other more recalcitrant organic constituents have been used extensively as tracers of the degradation state of OM (Cowie et al., 1992; Dauwe and Middelburg, 1998; Lee at al., 2000; Fabres et al., 2008;). Overall, in systems dominated by algal inputs, higher abundances of amino acids are generally indicative of fresher OM (Lee et al., 2004). In our study, maximal amino acid fluxes were detected in January and March (Fig. 4.5a) associated with the advection of resuspended material due to the DSWC event, indicating that this event might be an important source of amino acids in the sediment traps, as it was for lignins. Indeed the significantly better correlation between amino acid and lignin fluxes than between amino acids and pigments suggest a common source

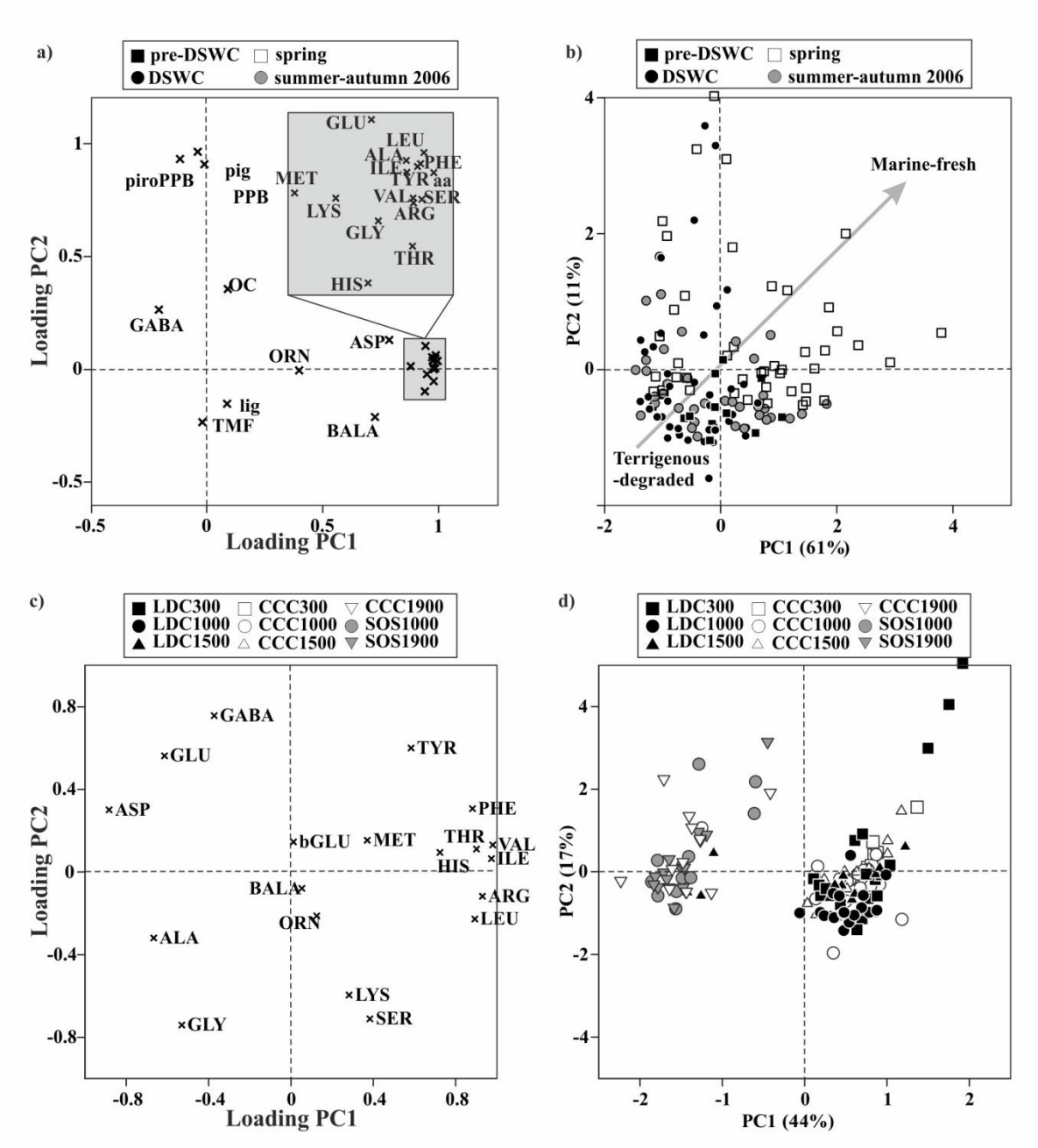

Fig. 4.6. Principal component analysis (PCA). a) Variable loadings plot and b) sample site score plot of total mass flux, organic carbon content (%), and the carbon-normalized content of derived carbon from pigments, amino acids and lignin. c) Variable loadings principal component plot and d) sample site score plot, of the relative abundance of each amino acids (%).

for the both amino acid- and lignin-derived carbon during the high flux periods (e.g. DSWC), which is most likely to be resuspended and advected shelf-sediment.

Based on these patterns, we might expect the presence of more degraded marine OM during DSWC flux events because materials transported along canyons under these conditions have had a longer residence time than OM derived from pelagic production. Indeed, the contributions of amino acids to the OC pool during the DSWC period are the lowest at almost all the stations (Fig. 4.5b) suggesting that more degraded OM dominates the particle flux (Lee et al., 2004). In contrast, during the spring bloom (April-May) higher inputs of amino acids coincide with peaks in pigment flux (Fig. 4.3a). Furthermore, the amino acid and pigment contents of particles collected during this period are consistently the highest, especially in the upper canyon stations. These compositions coupled with the presence of intact Chl a in the upper ca-

nyon traps (LDC300 and CCC300) (Table 2, supplementary dataset) indicate the efficient input of fresh marine OM to the canyon system following plankton blooms. The patterns in amino acid composition in the deeper sediment traps allow us to examine how these pulses of fresh marine OM are transported along the canyon system. Our results show that amino acids in the sinking particles generally decrease in concentration from the upper and middle to the lower canyon stations, canyon mouth and open slope (Fig. 4.5b). They also become a smaller portion of the pool of total OC along this transect (Fig. 4.5c). All these trends are consistent with the shelf region being the major source of fresh algal biomass to the margin and this material becoming increasingly degraded as it is transported down the canyons.

To test whether there is a statistical relation between the amino acid composition and other parameters analyzed (pigments, lignin, total organic carbon and total mass flux), a principal component analysis (PCA) was carried out (Fig. 4.6a, b). Specific amino acids (BALA, GABA and ORN) that are indicators of degradation processes and factors that are consistent with terrigenous sources (TMF and lignin) appear in the lower left quadrant while fresher, marine markers (OC, pigments and protein amino acids appear to the right along PC1 and in the upper half of the PCA plot. These trends suggest that most of the variability in samples shown in Fig. 4.6b follows a trajectory from fresh marine material in the spring to degraded terrigenous material during pre-DSWC and DSWC periods. Thus, the PCA reinforce our previous explanation of the sources and degradation of OM during the different periods.

Since PC1 is often used as a degradation index when amino acids are analyzed in sedimentary materials (Dauwe et al., 1999; Ingalls et al., 2006), we also performed PCA of the amino acid data set alone (Fig. 4.6b,c). PC1 is characterized by positive loadings of amino acids that are associated with fresh cell cytoplasm: VAL, ILE, ARG, LEU, THR, PHE, MET. In contrast, negative loadings are displayed by the acidic amino acids ASP and GLU, neutral amino acids ALA and GLY (which increase in relative abundance with depth, and presumably age; Lee et al., 2000) and the non-protein amino acid GABA (formed from the degradation of GLU (Lee and Cronin, 1982)) (Fig. 4.6c). In this data set, PC1 clearly separates the upper canyon stations in the “fresher” site from those in the

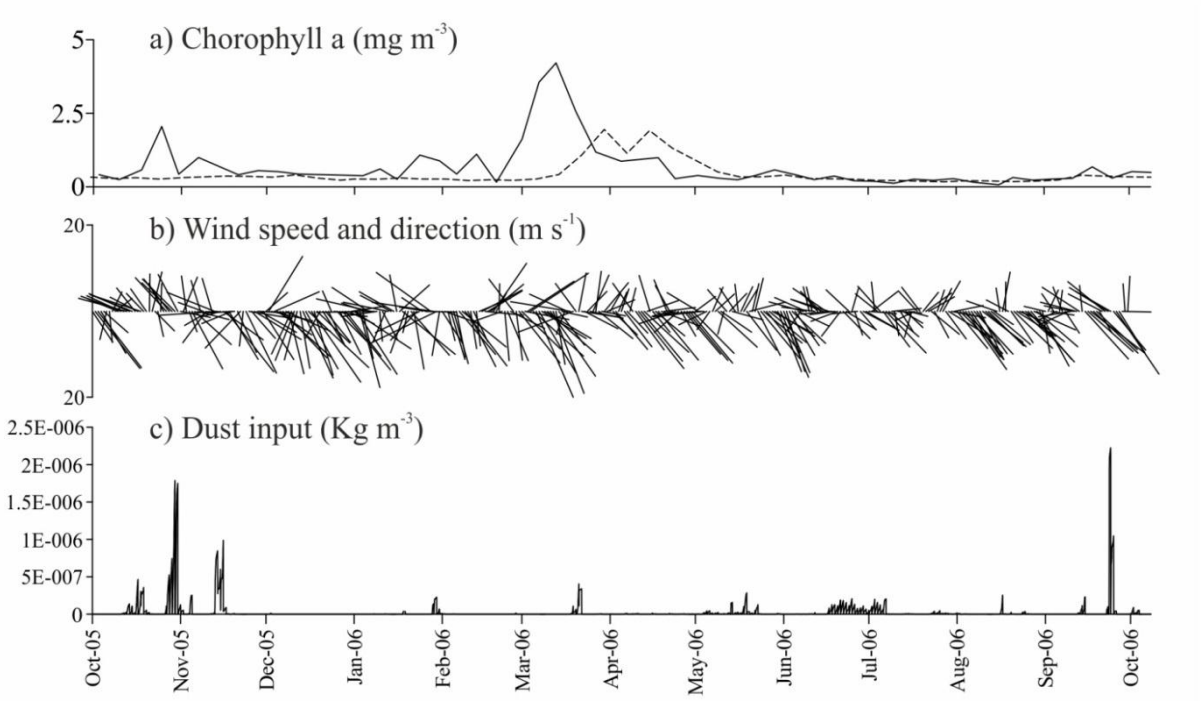

Fig. 4.7. a) Chlorophyll a concentration at coastal station and open-ocean (dotted line) b) wind speed and direction and c) total dust deposition obtained from the BSC-DREAM8b model (Nickovic at el. 2001; Perez et al. 2006) at 42.307833N 3.601000E.

lower canyon, canyon mouth and on the slope (Fig. 6d). These data indicate that particulate matter caught in the sediment traps is continuously mineralized during vertical and lateral transport resulting in increasing OM degradation further down the canyon and out onto the slope. Thus, the influence of the canyon environment is lost when the lower canyon widens and the morphological constrictions disappear.

Conclusions

The input of fresh marine OM to the sea floor along the southern canyons and open slope of the GoL is controlled by seasonal (spring blooms) and sporadic (wind-induced) primary production events in combination with continental shelf events (water downwelling and dense shelf water cascading). Land derived material is constantly advected throughout the continental slope. The timing of the dispersion of terrigenous material is controlled by the energetic conditions in the shelf that enhance the resuspension of sediment-associated terrigenous OM and its off-shore transport. Organic matter is degraded during its transport along the canyons but also in the water column before reaching the canyon mouth and open slope as indicated by trends in amino acid and chloropigment concentrations and compositions. The change in the quantity and quality of the OM transported down canyon likely has significant implications for the biogeochemistry and ecology of deep sea communities in this region of the GoL. Further work is needed to understand how the lateral (induced by continental shelf events) and vertical (seasonal or sporadic events) inputs of OM evolve to constrain the carbon cycle in this and other continental margins and associated deep basins.

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