D..**Juan Luis Gómez Pinchetti**...SECRETARIO DEL DEPARTAMENTO DE .....Biología.... DE LA UNIVERSIDAD DE LAS PALMAS DE GRAN CANARIA

CERTIFICA,

Que el Consejo de Doctores del Departamento en sesión extraordinaria tomó el acuerdo de dar el consentimiento para su tramitación, a la tesis doctoral titulada **"New insights into POC dynamics in the subtropical northeast Atlantic Ocean"** presentada por el/la doctorando D. Iván Julio Alonso González y dirigida por el Dr. Javier Arístegui Ruiz y el Dr. Antoni Calafat Frau.

Y para que así conste, y a efectos de lo previsto en el Art° 73.2 del Reglamento de Estudios de Doctorado de esta Universidad, firmo la presente en Las Palmas de Gran Canaria, a Octubre de 2010.

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TÍTULO DE LA TESIS: **"New insights into POC dynamics in the subtropical northeast Atlantic Ocean"**

Tesis Doctoral presentada por D. Iván Julio ALONSO GONZÁLEZ

Dirigida por:	Javier ARÍSTEGUI RUIZ	-	ULPGC
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El Director **El Codirector** **El Doctorando**

Las Palmas de Gran Canaria, Diciembre de 2010

A mis padres y Verónica...

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"... dejé esa roca llorando. Es que dejaba en ella raíces en la roca y raíces de roca".

Miguel de Unamuno, Fuerteventura, 1924

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Abstract

The capacity of the ocean to sequester atmospheric carbon (CO_2) depends to a large extent on the dynamics of biogenic carbon in the water column. However, most current global and regional estimates of carbon balances are solely based on particles collected with drifting and moored sediment traps. As a consequence, construction of ocean carbon budgets has long been guided by the simplification introduced by sediment traps, which give a 1D vision of the whole picture. In this thesis we have assessed a quantitative analysis of the flux magnitude and the mechanisms of transport of the whole particle spectrum (suspended, slowly-sinking and sinking particles). The distribution of particulate organic carbon (POC), the shape of the particle settling velocity spectrum, the magnitude of the vertical and lateral POC fluxes, the eddy-induced POC fluxes and the carbon respiration were studied in the northeast Atlantic Ocean. We found that, at least during half of the year, more than 60% of total POC is contained in slowly-settling particles (0.7-11 m d^{-1}). Lateral POC fluxes are found to be 2 or 3 orders of magnitude higher than vertical fluxes depending on water masses, indicating a more relevant horizontal versus vertical flux of POC per unit area. From a biogeochemical point of view, this work reveals that suspended POC supports between 65% and 74% of plankton respiration, highlighting a low contribution of sinking POC (<20%). Thus, the coupling between sinking POC and respiration in the water column is much weaker than has traditionally been assumed. Taken together, these findings help to explain the apparent imbalance between the carbon sources and the oxygen utilization rates in the mesopelagic waters when accounting only for the vertical sinking POC collected with sediment traps, and indicate that prokaryotic activity is linked to suspended POC rather than to vertical POC flux. Regarding to the eddy-induced POC fluxes, we find that, mesoscale eddies enhance POC export 2-4 times relative to non-eddy conditions. The dominance of $CaCO_3$-rich organisms over diatoms, the more efficient ballasting by $CaCO_3$, and hence the lower zooplankton grazing activity are suggested to be the major factors controlling organic matter export within eddies. We also provide evidence that the material transferred during the late-winter bloom is mainly recycled in the mesopelagic zone, whereas cyclonic eddies during the stratified period enhance carbon sequestration, highlighting the important role of these features on the regional water column biogeochemistry.

Resumen

La capacidad del océano para secuestrar carbono atmosférico (CO_2) depende en gran medida de la dinámica del carbono biogénico en la columna de agua. Sin embargo, la mayoría de las estimas regionales y globales actuales de los balances de carbono están únicamente basadas en partículas recogidas con trampas de sedimento a la deriva o fijas. En consecuencia, la elaboración de los balances de carbono ha estado ampliamente condicionada por la simplificación introducida por las trampas de sedimento, las cuales dan una perspectiva 1D de la visión total. En esta tesis nosotros hemos desarrollado un análisis cuantitativo de la magnitud de los flujos y los mecanismos de transporte del espectro total de particulas (suspendidas, de sedimentación lenta y que sedimentan). La distribución del carbono orgánico particulado (POC), la forma del espectro de velocidades de sedimentación de las partículas, la magnitud de los flujos verticales y laterales de POC, los flujos inducidos por los remolinos y la remineralización del carbono fueron estudiadas en el Océano Atlántico noreste. Encontramos que, al menos durante la mitad del año, más del 60% del POC total está contenido en partículas de sedimentación lenta (0,7-11 m d^{-1}). Los flujos laterales de POC son de 2 a 3 órdenes de magnitud superior a los verticales dependiendo de las masas de agua, lo que indica que el transporte lateral es más relevante por unidad de área que el vertical. Desde un punto de vista biogeoquímico, este trabajo revela que el POC suspendido soporta entre el 65% y el 74% de la respiración del plancton, poniendo de manifiesto una baja contribución por parte del POC que se hunde (<20%). Por tanto, el acoplamiento entre el POC que se hunde y la respiración en la columna de agua es mucho más débil que lo que tradicionalmente se piensa. En conjunto, estos resultados ayudan a explicar el aparente imbalance entre las fuentes de carbono y las tasas de utilización de oxígeno en las aguas mesopelágicas cuando sólo se tienen en cuenta los flujos verticales de POC recogidos con trampas de sedimento, e indican adems que la actividad procariota está más ligada al POC suspendido que al que se hunde. Con respecto a los flujos inducidos por remolinos, encontramos que, los remolinos mesoescalares aumentan la exportación de POC entre 2 y 4 veces con respecto a la condición de no remolino. El predominio de organismos enriquecidos en $CaCO_3$ sobre diatomeas, el "lastrado" más eficiente por parte del $CaCO_3$, y por tanto la menor presión por parte del zooplancton son sugeridos como los mayores factores de control sobre la exportación de materia orgánica en los remolinos. También proveemos evidencias de que el material transferido durante el bloom tardío de invierno es principalmente reciclado en la zona mesopelágica, mientras que los remolinos ciclónicos durante el periodo de estratificación aumentan el secuestro de carbono, resaltando así la importancia de estas estructuras en la biogeoquímica de la columna de agua a nivel regional.

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Chapter 1

INTRODUCTION

1.1 GENERAL INTRODUCTION

1.1.1 Organic matter in the ocean

Primary Production (PP) by phytoplankton cells is considered the main source of organic matter in the ocean [Mopper and Degens, 1979]. These microscopic flora play a key role in the ocean carbon cycle by converting inorganic carbon into organic matter through photosynthesis. Other minor, but locally important inputs of organic matter, in addition to primary production by marine plankton and macrophytes, include terrestrial inputs by rivers, atmosphere deposition, resuspension of organic matter from marine sediments, hydrothermal emissions, chemoautotrophy, and direct oil spills. On the contrary, ocean respiration (R) is the process whereby heterotrophic organisms obtain energy through oxidation of organic matter and converted back it into its inorganic constituents. Since organic matter cycling rely on the balance of these two processes, PP and R are widely accepted as critical factors controlling the carbon cycle in the ocean [Arístegui et al. 2005]. However, the mechanisms controlling the distribution of organic matter in the water column have received less attention presumably because of their difficulty in quantifying such processes *in situ*. Understanding how these mechanisms of transport operate is crucial for quantitative prediction of organic matter fluxes and pathways in different environments.

An essential aspect to try understand the mechanisms involved in the carbon transport is to identify the different carbon pools presented in the water column. Traditionally, organic matter in the ocean has been operationally divided into two different pools according to filtration techniques. Organic matter passing through glass-fiber filters with an effective pore size of about 0.2-0.7 μm is assumed to be dissolved organic matter (DOM), while material retained is considered particulate organic matter (POM). Another key issue affecting carbon dynamics in the water column is the organic matter composition. DOM in surface waters consists of a mixture of very old, refractory DOM and a smaller fraction of young, labile DOM [Benner, 2002] produced in situ by plankton communities. In tropical and subtropical areas, most of the bioavailable DOM fraction is mineralized at surface and upper mesopelagic waters contributing little to deep-water prokaryotic metabolism or carbon storage in the dark ocean. Indeed, DOC exported with the overturning circulation accounts for only 10-20% of the global apparent oxygen utilization in the dark ocean [Arístegui et al. 2002; Hansell and Carlson, 20xx]. This supports the current view that microbial life in the deep ocean is mainly driven by the organic particulate pool [Honjo 1996; Bendtsen et al. 2002; Arístegui et al. 2009]. Regarding to the particulate pool, organic composition of POM is dominated by phytoplankton derived compounds [Lee et al. 2004]. However, during its travel to deeper levels, organic matter undergoes alteration of its original composition due to heterotrophic activity. Such alteration of the original signature is particle size-dependent, thus the interest of determine the different size classes of particles.

Particles carrying organic carbon in the ocean are part of a size continuum [Verdugo et al. 2004], however, they are operationally divided by oceanographers into two distinct classes attending to its properties: i) suspended particulate organic carbon (POC_{susp}), and ii) sinking particulate organic carbon (POC_{sink}). The differentiation between these fractions is essential since each of them present a different behavior in the water column. POC_{susp} is assumed to comprise particles ranging from 0.7 to 50 μm while POC_{sink} those generally larger than about 50 μm [McCave, 1975; 1984]. POC_{susp} dominates the standing stock of particulate matter in the ocean [McCave, 1975; Kepkay 2000], although, surprisingly, our knowledge of its biogeochemical significance is scarce. This lack of information has been due to the fact that researchers have traditionally focused on sinking particulate organic carbon [Suess, 1980;

Boyd and Trull, 2007]. On the contrary, the transfer of organic carbon produced in surface waters to the deep ocean via POC$_{sink}$ is critical, on a large scale, to the removal of climatically active elements, such as carbon dioxide from the atmosphere.

Recent evidence suggest that the behavior of particles in the water column is not only dependent of particle size, but also of the difference between its average density and that of the surrounding water [Burd and Jackson, 2009]. Thus, particle settling velocity is thought to be the key issue influencing vertical fluxes and carbon remineralization, although little is known about its spatio-temporal variability. Particle settling velocity determines whether organic carbon undergoes lateral or vertical transport, travelling within or across water masses, respectively. Therefore, an interesting question arises: *What is the regional and temporal variability in the shape of the particle settling velocity spectrum?*

1.1.2 Balance between synthesis and destruction of particulate organic carbon in the epipelagic waters

In the global ocean and in steady state, the amount of photosynthetically fixed organic matter by autotrophic organisms has to be balanced by the organic matter consumption by heterotrophic organisms. Nevertheless, regional studies on plankton metabolism suggest a regional variability in the metabolic balance between autotrophic and heterotrophic processess. Indeed, several experiments on plankton metabolism conducted in the subtropical Northeast Atlantic Ocean have reported that this is a net heterotrophic ecosystem [Duarte et al. 2001; González et al. 2001; Serret et al. 2002]. A possible explanation to this imbalance is that gross primary production could be underestimated due to methodological issues [Robinson and Williams, 2005]. Duarte et al. [2001] suggest that the organic carbon needed to support this imbalance must be supplied by external inputs (e.g., lateral transport and atmospheric deposition). Another possibility reported by other authors is that these rates may be biased by its different time scale as well as its different spatio-temporal variability, especially PP [del Giorgio et al. 1997; Arístegui and Harrison, 2002; Karl et al. 2003; Williams et al. 2004]. South of the Canary Islands, Arístegui et al. [2003] suggest that the high respiration rates measured in the Canaries are fueled by mesoscale eddies and external inputs of organic matter.

Despite the apparently consistency of this anomaly, an heterotrophic metabolic imbalance (P<R) can hardly be explained when particles are collected below the euphotic zone, if we take into account only the carbon production and export from the surface ocean. As an example, Table 9.1 shows the results of a study conducted in the subtropical northeast Atlantic (unpublished data) where we looked at mesoscale and regional trends in both plankton metabolism and POC_{sink} fluxes obtained from in vitro changes in dissolved oxygen and free floating sediment trap deployments, respectively.

Table 1.1: Integrated daily rates (mmol O_2 m^{-2} d^{-1}) of gross primary production (GPP), net community production (NCP) and community respiration (R) from the August cruise (RODA I). Depth of integration, 120 m. POC flux (mmol C m^{-2} d^{-1}) at the base of the euphotic zone (150 m).

Station	Lat. N	Long. W	GPP	NCP	R	P/R	POC flux
1	29.42	20.02	58.8	-47.3	106.5	0.55	5.53
2	28.75	18.27	112.2	-7.2	119.2	0.94	6.06
3	27.59	17.33	89.2	-16.4	105.5	0.85	13.09
4	27.58	15.60	113.5	-7.7	121.0	0.94	6.38
5	27.71	16.00	73.0	-11.6	84.7	0.86	9.63

As can be observed, NCP rates were always negative during RODA I cruise (August, 2006). Therefore, we might expect that the POC export from the euphotic zone is negligible. Nevertheless, these stations presented considerable POC export rates ranging from 5.5 to 13 mmol C m^{-2} d^{-1} rising the question of the origin of the organic matter below the euphotic zone. This conundrum leads us to the second question we would like to answer in our study: *Are we correctly interpreting carbon balances in surface waters by just looking at the* *in situ production rates?*

1.1.3 Carbon balance in the mesopelagic waters

Over the last two decades several evidences indicate that mesopelagic prokaryotes represent a major metabolic component of the ocean [see review by Arístegui et al. 2009]. According to the classical view of the biological pump, prokaryotic assemblages in the mesopelagic waters are supplied with particulate organic matter largely formed in the surface waters and transported down into the ocean via sinking particles. This is corroborated by the finding that dissolved organic carbon (DOC) contributes only 10-20%, at a global scale, to the remineralization rates in the dark ocean [Arístegui et al. 2002]. Nevertheless, sinking POC collected with current sediment traps does not explain the remaining 80-90% of oxygen utilization rates in the dark ocean [Reinthaler et al. 2006; Steinberg et al. 2008; Baltar et al. 2009]. This apparent imbalance is one of the most exciting unresolved paradoxes in the ocean carbon cycle and indicates either the existence of alternative mechanisms to fulfill the high carbon demand of the mesopelagic waters or that metabolic activity in the dark ocean is being over-estimated. The calculation of the conversion factors used to estimate metabolic rates in the deep waters present several uncertainties [Burd et al. 2010], so over-estimation of the metabolic rates would be possible. However, estimates of bacterial metabolic activity in deep NW Mediterranean waters are suggested to be greater at in situ pressures compared with those made under decompressed conditions [Tamburini et al. 2003], indicating that unaccounted carbon sources must exist [see Burd et al. 2010 for more details].

One of these unaccounted carbon sources could be the presence of low-sinking or suspended organic carbon (POC$_{susp}$) udersampled with current sediment traps. The majority of particulate organic matter in the water column is formed by suspended, neutrally buoyant particles [Kepkay 2000; Verdugo et al. 2004], although, paradoxically, the mechanisms of advective transport and remineralization of POC$_{susp}$ are barely known [Bauer and Druffel, 1998], in contrast to sinking POC [see review in Boyd and Trull 2007]. Recently, Baltar et al. [2009] found a significant correlation between suspended POC and potential respiration in the bathypelagic waters of the subtropical Northeast Atlantic. Nevertheless, POC_{susp} concentrations at depth have been reported to be inadequate to support sustained metabolic demand since a new supply of POC_{susp} would be required to keep up with the demand (Steinberg et al. 2008). *Is therefore any mechanism able to supply enough* POC_{susp} *to fulfill the metabolic carbon demand in the mesopelagic waters?*

1.1.4 Impact of mesoscale eddies on organic carbon fluxes

Eddies are known to have a major impact on upper ocean biogeochemistry by fuelling pulses of nutrients to the euphotic zone [Oschlies and Garçon, 1998] and enhancing biological activity [Falkowski et al. 1991; Sweeney, 2001; McGillicuddy et al. 2007]. However, our knowledge about the impact of eddies on the planktonic metabolic balance and subsequent carbon export is limited to a few studies and reported contradictory results. Regarding to the plankton metabolism, González et al. [2001] concluded that the organic carbon deficit within the North Atlantic Subtropical Gyre should increase between 14% and 52% in the absence of mesoscale structures. Maixandeau et al. [2005], working in the northeastern Atlantic basin, reported that the spatial variability of the biological processes in winter was controlled by mesoscale structures. In a more recent mesoscale study conducted in the Sargasso Sea, the authors provided new data suggesting that the type and age of the sampled eddy are important factors controlling the sign of the net community production [Mouriño and McGillicuddy, 2006]. Despite these important studies, our knowledge about the complex mechanisms that control the organic matter synthesis and respiration within eddies is scarce.

In relation to organic carbon fluxes within eddies, a limited number of studies have showed direct evidence of enhanced POC export mediated by mesoscale eddies [e.g. Sweeney, 2003; Bidigare et al. 2003; McGillicuddy et al. 2007]. However, recent interdisciplinary programs (E-Flux (North Pacific) and EDDIES (North Atlantic)) focused on the effects of eddies on carbon export have shown unexpected results. Surprisingly, both programs concluded that the studied eddies did not enhance carbon flux, although they increased the flux of biogenic silica [e.g. Benitez-Nelson and McGillicuddy, 2008; Maiti et al. 2008]. These new findings highlight our lack of knowledge about the mechanisms that control POC export out of the euphotic zone within mesoscale eddies.

Most sediment trap studies within eddies have measured bulk properties of the fluxes, such as total carbon and nitrogen, while individual compounds have received less attention. Although total carbon and nitrogen are useful, knowledge of the specific compounds provides more precise information on lability, interaction with other elements, and mechanisms of degradation [Lee et al. 2000; Sheridan et al. 2002; Ingalls et al. 2006]. Here we have tried to resolve some of the uncertainties related with the role that eddies can play in the transport of organic matter to the dark ocean: *Can we elucidate what are the factors controlling carbon export within eddies using biomarkers? Can eddies change the composition of the exported organic matter? Can eddies enhance carbon sequestration in the deep ocean or they are surface structures with poor biogeochemical relevance?*

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1.2 THESIS OBJETIVES AND ORGANIZATION

The general aim of this thesis was to deepen our understanding of the particulate organic carbon (POC) dynamic in the subtropical northeast Atlantic ocean, as well as to determine the biogeochemical significance of the two fractions accounting for total POC (non-sinking and sinking POC). To achieve this goal, several specific objectives were tackled. Basically, we tried to respond to the questions raised in the general introduction:

- 1. *What is the regional and temporal variability in the shape of the settling velocity spectrum?*

- 2. *What is the contribution of suspended POC to the carbon demand in the dark ocean? Is there any mechanism able to supply enough* POC_{susp} *to fulfill the metabolic carbon demand in the mesopelagic waters?*

- 3. *What is the degree of coupling between suspended POC and respiration?*

- 4. *Can we elucidate what are the factors controlling carbon export within eddies using biomarkers?*

- 5. *Can eddies change the composition of the exported organic matter?*

- 6. *Can eddies enhance carbon sequestration in the deep ocean?*

$\ast$ To address the first question, we deployed a mooring in the Canary Current region over a 1.5-year period. This mooring accommodated Indented Rotating Sphere Carousel (IRSC) sediment traps [Peterson et al., 2005] at 260 m, with the capacity of separating particles into discrete classes as a function of their sinking velocity. In order to know the potential biogeochemical role of each settling velocity fraction, we performed analysis of amino acid and chloropigment fluxes and compositions. **(Chapter 2)**

This work has resulted in the following publication:

- *"Role of slowly settling particles in the ocean carbon cycle"* published in **Geophysical Research Letters (GRL)**.

∗ To try to resolve the apparent carbon imbalance in surface and mesopelagic waters (questions 2 and 3), two chapters are presented. In the first study, to answer question 2, we estimated the horizontal transport and consumption, from surface to 3000 m depth, of suspended particulate organic carbon (POC) collected with oceanographic bottles. The analysis was performed through a box model approach, with physical boundaries extending from 20° to 29° 10'N and 20° 35' to 26°W (1000 x 600 Km) in the Canary Current region. **(Chapter 3)**

∗ In the second study, to answer question 3, the spatio-temporal variability in the epipelagic and mesopelagic respiration through the enzymatic activity of the electron transport system (ETS) in microplankton was analyzed. This study was conducted along two zonal sections (21°N and 26°N) extending from the northwest African costal upwelling to the open ocean waters of the subtropical North Atlantic. **(Chapter 4)**

These works have resulted in the following publications:

- *"Lateral POC transport and consumption in surface and deep waters of the Canary Current region: A box model study"* published in **Global Biogechemical Cycles (GBC)**.

- *"Spatio-temporal variability of water column respiration in the Canary Basin: the role of suspended particulate organic carbon"* submitted to **Journal of Marine Systems (JMS)**

∗ In order to elucidate the factors controlling carbon export within eddies we report, together with total POC/PON fluxes, mesoscale and regional trends in amino acid (THAA) and chloropigment compositions and fluxes obtained from free floating sediment trap deployments in the northeast Atlantic Ocean. **(Chapter 5)**

This work has resulted in the following publication:

- *"Regional and temporal variability of sinking organic matter in the subtropical northeast Atlantic Ocean: a biomarker diagnosis"* published in **Biogeosciences (BG)**.

∗ To address the specific objectives number 5 and 6, we measured POC, amino acid and chloropigment fluxes and compositions in samples collected from a mooring deployed in the area of generation of cyclonic eddies south of the Canary Islands over a 1.5-year period. The effects of the presence of an eddy were investigated from surface down to 1000 m.**(Chapter 6)**

This work has resulted in the following publication:

- *"Increased carbon sequestration by mesoscale eddies in the northeast Atlantic Ocean"* submitted to **Proceedings of the National Academy of Sciences, (PNAS)**.

Part I

Particle settling velocity spectrum

CHAPTER 2

Role of slowly settling particles in the ocean carbon cycle

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Abstract

Here we present results from sediment traps that separate particles as a function of their settling velocity, which were moored in the Canary Current region over a 1.5-year period. This study represents the longest time series using "in situ" particle settling velocity traps to date and are unique in providing year-round estimates. We find that, at least during half of the year in subtropical waters (the largest ocean domain), more than 60% of total particulate organic carbon is contained in slowly settling particles (0.7-11 m d^{-1}). Analyses of organic biomarkers reveal that these particles have the same degradation state, or are even fresher than rapidly sinking particles. Thus, if slowly settling particles dominate the exportable carbon pool, most organic matter would be respired in surface waters, acting as a biological source of CO_2 susceptible to exchange with the atmosphere. In the context of climate change, if the predicted changes in phytoplankton community structure occur, slowly settling particles would be favored, affecting the strength of the biological pump in the ocean.

KEYWORDS: Particle settling velocity, Lateral transport, carbon balance

Contents

2.1 Introduction

Sinking particles have been traditionally considered the most important vehicle by which the biological pump sequesters carbon in the ocean interior [Buesseler et al., 2007a]. This is corroborated by the finding that dissolved organic carbon (DOC) contributes only 10-20%, at a global scale, to the remineralization rates in the dark ocean [Arístegui et al., 2002]. Nevertheless, sinking POC collected with current sediment traps does not explain the remaining 80-90% of oxygen utilization rates in the dark ocean. This apparent imbalance (between carbon supply and consumption) is one of the most exciting unresolved paradoxes in the ocean carbon cycle. It indicates either the existence of unaccounted sources of organic carbon, an overestimation of the metabolic activity in the dark ocean, or an underestimation of the vertical particle flux.

Sediment trap collection efficiency depends on the behavior of the traps with respect to hydrodynamic conditions as well as on particle properties [Buesseler et al., 2007b]. Several efforts have been carried out to address the hydrodynamic effects on traps (see reviews by Gardner [2000] and Buesseler et al. [2007b]). However, intrinsic particle properties have received less attention presumably because of their difficulty in quantifying such characteristics in situ. Particle settling velocity is thought to be a key issue influencing vertical fluxes and carbon remineralization, although little is known about its spatio-temporal variability.

Settling velocities are particle size-dependent, and hence are affected by plankton community structure and its physiological state [Boyd and Newton, 1995; Guidi et al., 2009]. Additionally, mineral components can play a direct role in regulating the settling velocity of particles via the ballast effect [Armstrong et al., 2001; Ploug et al., 2008]. Recent studies predict a global replacement of diatoms by smaller phytoplankton cells induced by an increase in ocean stratification and nutrient depletion as climate changes [Bopp et al., 2005]. In that scenario, the higher percentages of small versus large particles would result in slower average settling velocities, making determining the regional and temporal variability in the shape of the particle velocity spectrum of great interest.

Here, with the aim of addressing this challenge, we have measured total mass and POC fluxes, amino acid and chloropigment fluxes and compositions, as well as the particle settling velocity spectrum, in the mesopelagic waters of the Canary Current region.

2.2 Methods

2.2.1 Sampling

We deployed a mooring south of the Canary Islands during three 6-month periods (from June 2005 to December 2006). In the first two (Periods I and II) the mooring was located at 27° 29' 57"N; 016° 15' 19"W, 3600m bottom depth. Rough sea conditions forced the mooring deployment closer to the islands during Period III (27° 30' 4"N; 15° 44' 32"W, 2500m bottom depth). The mooring accommodated Indented Rotating Sphere Carousel (IRSC) sediment traps [Peterson et al., 2005] at 260m, with the capacity of separating particles into discrete classes as a function of their sinking velocity. Using a protocol similar to that described by Lee et al. [2009], one of the traps was programmed to collect particles in a time-series mode (TS), while the other two were programmed to collect particles based on their settling velocities (SV). In situ SV separation was accomplished by rotating the IRS once each day and then rotating the sample carousel, corresponding to a minimal settling velocity for each sample tube of >980, 490-980, 326-490, 196-326, 140-196, 98-140, 49-98, 22-49, 11-22, 5.4-11, and 0.68-5.4 m d^{-1}.

All sediment trap cups were poisoned with mercuric chloride released 'in situ' into each cup from a small vial containing 14 mg $HgCl_2$ in a solid pellet of NaCl. Upon recovery, samples were visually checked and the supernatant removed. Swimmers were rarely present, but when so (only in the TS trap) were handpicked under a dissecting microscope. A high precision peristaltic pump was then used to obtain subsamples through repeated splitting of the raw samples. Subsamples for total mass, POC, PON, chloropigment and amino acid analyses were filtered onto pre-combusted GF/F filters.

2.2.2 POC and Biomarker Analysis

The carbon analyses were performed with a Perkin-Elmer 2400 CHN elemental analyzer. DOC sorption onto GF/F filters ($<3.5\%$ of the POC signal) was subtracted from samples to avoid overestimation of POC.

Chlorophyll a, pheophytin a, pheophorbide a, and pyropheophorbide a were determined using reverse-phase High Performance Liquid Chromatography (HPLC) [Lee et al., 2000; Wakeham et al., 2009].

Amino acidsweremeasured by HPLC on the same filters analyzed for pigments, using pre-column *o*-pthaldialdehyde (OPA) derivatization after hydrolysis [Lee et al., 2000; Wakeham et al., 2009].

2.2.3 Integrated Mass Flux Density Calculation

Integrated Mass Flux Density Calculation (IMFD) is the mass of any constituent per square meter of trap area integrated over the length of the deployment time and divided by the width of the SV interval, which is defined here as the dimensionless $\log_{10}$ of the ratio of the highest and lowest settling velocities in each SV interval ($\log_{10}(\mathrm{SV}_{max})$ - $\log_{10}(\mathrm{SV}_{min}) = \log_{10}(\mathrm{SV}_{max}/\mathrm{SV}_{min})$) [Armstrong et al., 2009].

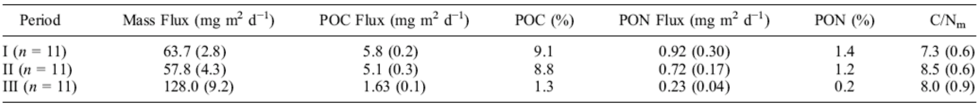
2.3 Results

2.3.1 Fluxes and Current Velocity Variability

From June to December 2005 (Period I) the time average (6-months) mass flux was 63.7 mg m^{-2} d^{-1} while the mean particulate organic carbon (POC) flux was

5.8 mg C m^{-2} d^{-1}, yielding a %POC of 9.1 (Table 2.1). These average values were almost the same in December 2005 to June 2006 (Period II). However, from June to December 2006 (Period III) the average mass flux was two fold higher than Periods I and II, while mean POC flux and %POC were lower (Table 2.1).

Table 2.1: Average (±1 SD) fluxes and contribution (%) of POC and PON to the total mass for each period. I, June 2005 to December 2005; II, December 2005 to June 2006; III, June 2006 to December 2006.



Period	Mass Flux (mg m^2 d^{-1})	POC Flux (mg m^2 d^{-1})	POC (%)	PON Flux (mg m^2 d^{-1})	PON (%)	C/N$_m$
I (n = 11)	63.7 (2.8)	5.8 (0.2)	9.1	0.92 (0.30)	1.4	7.3 (0.6)
II (n = 11)	57.8 (4.3)	5.1 (0.3)	8.8	0.72 (0.17)	1.2	8.5 (0.6)
III (n = 11)	128.0 (9.2)	1.63 (0.1)	1.3	0.23 (0.04)	0.2	8.0 (0.9)

Figure 2.1 shows the seasonal variability of POC fluxes, glycine (mol%) and current velocity. POC fluxes during Period I ranged from 2.8 to 10.3 mg C m^{-2} d^{-1} (Figure 2.1a), while during Period II fluxes were low, 2-3 mg C m^{-2} d^{-1}, except in March, when values reached 24 mg C m^{-2} d^{-1} (Figure 2.1b). During Period III POC fluxes were lower than in the first two periods, ranging from 0.45 to 4.1 mg C m^{-2} d^{-1} (Figure 2.1c). Average (15 days) current velocities during Period I ranged from 5 to 12 cm s^{-1}, yielding an average current velocity for the whole period of 7.18±2.1 cm s^{-1} (Figure 2.1a). During Period II, current velocities ranged from 6.5 to 14 cm s^{-1} (Figure 2.1b), yielding a higher average current velocity (10.2±2.3 cm s^{-1}) compared to Period I.

2.3.2 Particle Settling Velocity Spectrum

In spite of the different locations, during both Periods I and III, time-integrated mass flux densities (IMFD) calculated from SV sediment traps exhibited an exponential tail at lower settling velocities (0.7-11 m d^{-1}) that explains 68-75% of total mass flux and a smaller Gaussian portion at the higher end of the SV spectrum (Figures 2.2a and 2.2c). In contrast, the settling velocity spectrum from Period II presented a different shape, with a

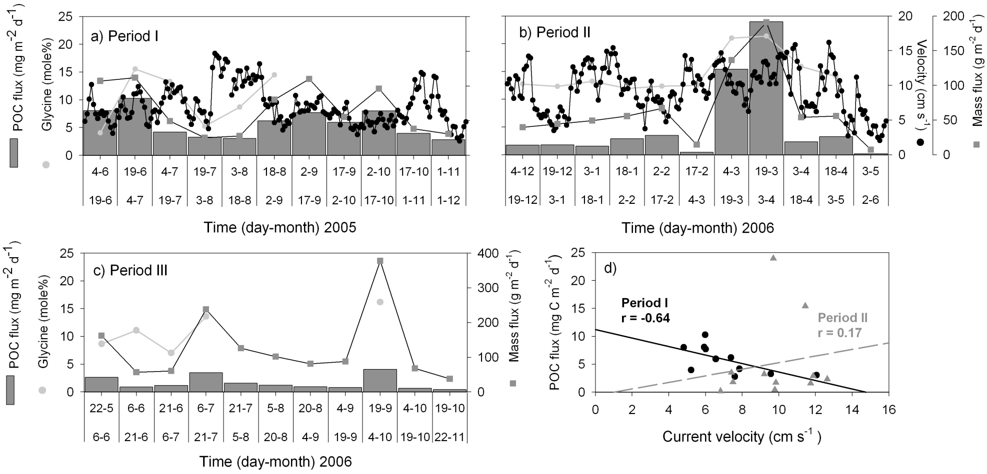


Figure 2.1: Seasonal variability of variables measured with IRSC sediment traps. Mass flux (grey squares); POC fluxes (grey bars); mol% glycine (grey dots); current velocity measured with current meters at 275 m depth (black dots). (a) Period I: from June 2005 to December 2005. (b) Period II: from December 2005 to June 2006. (c) Period III: from June 2006 to December 2006. (d) POC flux versus current velocity for periods I and II.

peak of rapidly settling particles (>326 m d^{-1}) that explains 41% of total mass flux and a roughly constant IMFD over the other SV groups (Figure 2.2b).

The relative contribution (in %) of each of the velocity classes of particles to the total POC flux also exhibited different distributions between periods I-III and period II. Periods I and III showed a bimodal distribution with the highest amount of total POC (62%) in the slowest settling velocity groups (0.7-11 m d^{-1}), and lower amounts (~25% of total POC) in the highest settling velocity classes (>326 m d^{-1}). Each of the intermediate SV groups (11-326 m d^{-1}) contained less than 5% of total POC (Figures 2.2a and 2.2c). On the contrary, during period II most of the total POC (53%) collected by SV traps was in the highest settling velocity classes (>326 m d^{-1}). Each of the other SV groups represented less than 10% of total POC (Figure 2.2b).

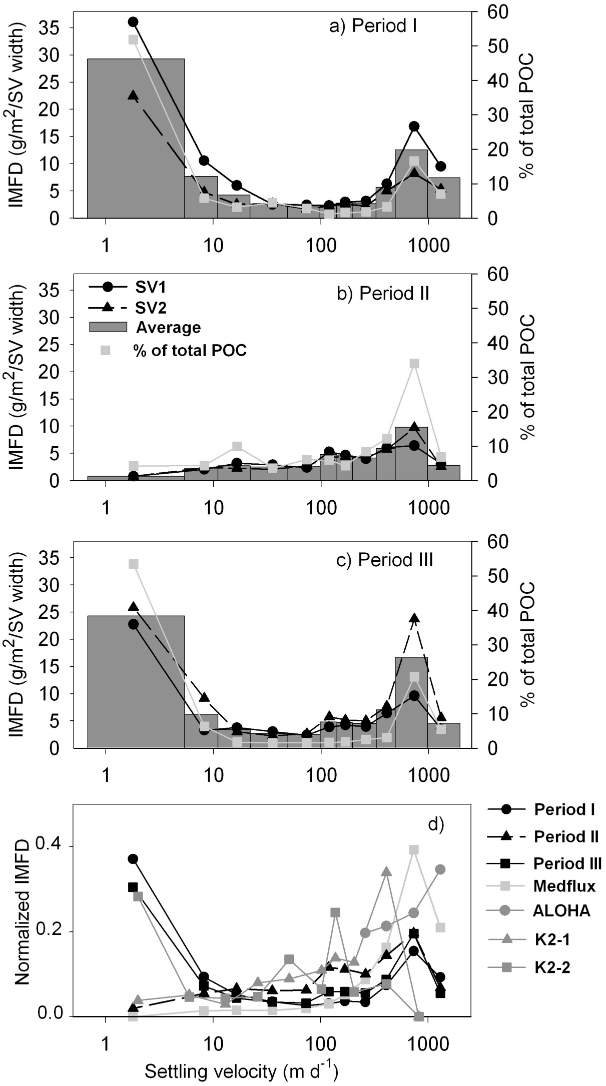
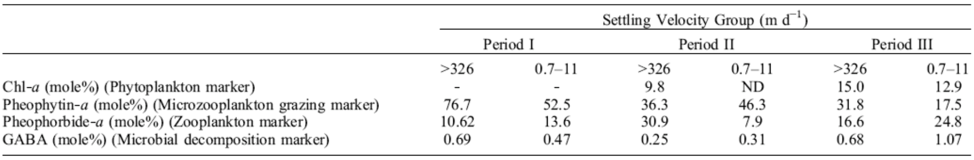


FIGURE 2.2: Settling velocity groups. Time-integrated mass flux density (IMFD) versus particle settling velocity for (a) period I, (b) period II, and (c) period III. Black lines correspond to each of the SV traps (SV1 and SV2), grey bars stand for the average of SV1 and SV2 and grey lines stand for the relative contribution (in %) of each of the velocity-classes of particles to the total POC flux. See Figure 3.1 for period dates. (d) Mass flux density normalized to total mass flux, for the RODA, Medflux and VERTIGO deployments.

To evaluate the degradation state of these two different classes of settling particles we selected four biomarkers: chlorophyll-a, pheophytin-a, pheophorbide-a and -aminobutyric acid (Table 2.2). During Period I, biomarkers indicated that the dominant slowly settling particles were fresher than the rapidly settling particles (the latter enriched in pheophytin and Gaba mole%), whereas the opposite pattern was found during Period II. Additionally, glycine, a diatom indicator, was used to evaluate the contribution of this phytoplankton group to the carbon fluxes. During period II, mole% glycine and POC flux follow a similar behavior characterized by a directly proportional relationship ($r^2 = 0.84$; $p < 0.05$).

Table 2.2: Pigment and amino acid biomarkers used to evaluate the degradation state of the two different settling velocity groups (>326 and 0.7-11 m d^{-1}). See Table 2.1 for period dates. Dash indicates not determined; GABA, -aminobutyric acid; ND, not detected.



	Settling Velocity Group (m d^{-1})					
	Period I		Period II		Period III	
	>326	0.7–11	>326	0.7–11	>326	0.7–11
Chl-*a* (mole%) (Phytoplankton marker)	-	-	9.8	ND	15.0	12.9
Pheophytin-*a* (mole%) (Microzooplankton grazing marker)	76.7	52.5	36.3	46.3	31.8	17.5
Pheophorbide-*a* (mole%) (Zooplankton marker)	10.62	13.6	30.9	7.9	16.6	24.8
GABA (mole%) (Microbial decomposition marker)	0.69	0.47	0.25	0.31	0.68	1.07

2.4 Discussion

2.4.1 Effect of Current Velocity on POC Fluxes

Previous laboratory and field analysis regarding the effects of flow velocity on the collection efficiency of sediment traps have shown conflicting results (see reviews by Gardner [2000] and Buesseler et al. [2007b]). Here we report new results that fuel this controversy, but may represent a step forward in understanding the complex mechanisms that control sediment trap collection efficiency. Our observed correlations between flow velocity and POC flux also show contradictory results (Figure 2.1d). Period I shows a decrease in POC flux with increased flow velocity (Pearson's $r = -0.64$, $p < 0.05$), while during Period II no statistically difference was found. This change in the flux-flow velocity relationship could be explained by the modifications that the ecosystem undergoes with time. Period I is dominated by slow sinking particles which are susceptible to lateral advection, while Period II is dominated by fast sinking particles that are presumably less affected by current velocity. According to these results, particle-settling velocity is a key factor controlling the hydrodynamic biases affecting sediment traps, in agreement with Gust and Kozerski [2000].

2.4.2 Particle Settling Velocity Spectra

The analysis of the temporal evolution of near-surface Chl-a and depth of the mixed layer (MLD) and euphotic zone (Ze) reveal that the depth interval between the bottom of the MLD and the depth of the sediment trap is higher during Periods I and III (when slow sinking particles dominate), suggesting that these particles were passively collected, rather than mixed down from surface to the trap depth (see Appendix 2.5).

A comparison of the sinking rate spectra observed here with those obtained using IRSC traps at approximately the same depth (∼300 m) in the subarctic K2, subtropical ALOHA (North Pacific) and DYFAMED (Mediterranean) stations reveals important findings (Figure 2.2d). The DYFAMED station showed particle-sinking spectra similar to our Period II, characterized by a Gaussian portion of fast settling particles, which dominate sinking fluxes, and a tail of slowly settling particles [Armstrong et al., 2009]. More interesting is the fact that these studies were carried out in the same season as our Period II. This suggests that a large fraction of the surface primary production generated during the late-winter bloom (Figure 2.3) is rapidly (∼1 month) exported to the dark ocean via fast-settling particles. This phenomenon is induced by a higher contribution of large phytoplankton cells and zooplankton fecal pellets to the sinking flux as indicated by the contributions of glycine (Figure 2.1b) and pheophorbide to the organic matter (Table 2.2).

On the other hand, the SV spectra at both Pacific stations, determined in the same season that our Periods I and III (ALOHA, June 2004 and K2, July 2005) showed a contribution of slowly settling particles (2-13 m d^{-1}) to the total POC flux ranging from 15 to 50% [Trull et al., 2008]. In addition to this significant contribution, the authors indicated that the addition of brine solution into the cups could have affected the entry of slowly settling particles. In our case, we used $HgCl_2$ diffusers within the cups, thus avoiding such problems [Peterson et al., 2005]. Moreover, the short rotation cycle of the IRSC valve (6 hours) used at the Pacific stations limited the minimum-settling rate that can be resolved to 2 m d^{-1} (versus 0.68 m d^{-1} with the 24 h cycle used in our study). Taking into account all these factors, it is reasonable to think that slowly settling particles could be a major fraction of the mass flux in those stations. Overall, these studies suggest that particle settling velocities in the ocean vary seasonally and with location, with profound implications for carbon sequestration in the deep ocean.

2.4.3 Implications of Slowly Settling Particles Dominating the Size Spectrum

Our results give evidence that slowly settling particles dominated the carbon flux in our study during summer and autumn. In such a situation, sediment traps may miss a fraction of the exported POC in the smallest particles. Thus, if vertical carbon fluxes derived from sediment traps are used to construct budgets for different biogeochemical processes, strong imbalances may arise. Indeed, recent studies have reported important discrepancies between the mesopelagic metabolic carbon demand (MCD) of planktonic communities and the vertical carbon supply [Steinberg et al., 2008; Baltar et al., 2009]. We suggest that this "apparent" mismatch between MCD and vertical POC fluxes would presumably be less noticeable when fast-sinking particles dominate the flux and/or current velocities are low, as lateral transport would be relatively less important. The consumption of the undersampled slowly settling carbon pool could be therefore an additional mechanism buffering this imbalance by uncoupling MCD from vertical fluxes. However, considering the slow sinking rate of these particles, the effect of this undersampled carbon pool would be restricted to the upper mesopelagic waters (the place where the MCD is higher and the major decrease in molecularly-characterized material occurs) [Baltar et al., 2009; Lee et al., 2004].

Biomarkers indicate that the slowly settling particles have the same degradation state, or are even fresher, than the rapidly settling particles during the summer-autumn (Table 2.2). This observation raises the questions of how can a carbon pool that sinks at 1-10 m d^{-1} be very labile? Could it be that slow sinking particles are in fact broken parts of larger particles, which were formed during rotation of the IRS ball? To test if the signal of fresh particles in a slow velocity class reflects these biases in the SV trap, we performed a principal components analysis (PCA) to quantitatively assess variation in the organic composition of the different settling particle classes. PCA indicates that the two velocity groups (slowly and fast sinking particles) differ in organic matter composition, giving evidence against this hypothesis (See Appendix 2.5).

Other studies [Goutx et al., 2007; Wakeham et al., 2009] reached the same conclusion after analyzing the composition of particles collected at 200 m in the Mediterranean Sea and separated by settling velocity. Samples from the Pacific Ocean also showed that material collected by in situ filtration, assumed to be suspended or with low settling rates, contained a remarkable abundance of labile organic compounds [Lee et al., 2000; Sheridan et al., 2002]. Therefore, the high bioavailability of slowly settling particles seems likely to be a general feature rather than an isolated case.

Small "suspended" particles may result from sinking particles disaggregated by physical forces [Burd and Jackson, 2009] or the activity of microbes and zooplankton [Sheridan et al., 2002], but also by self-assembly of dissolved organic material yielding porous microgels [Chin et al., 1998]. In all cases these small particles seem to be a suitable nutrient-rich habitat to be colonized by microorganisms. Indeed, recent studies have demonstrated a strong association between suspended particles and dark-ocean prokaryotic metabolism, supporting the view that microbial life is mainly dependent on small buoyant particles [e.g., Baltar et al., 2009]. The high microbial activity reported during summer and autumn in the mesopelagic zone of the Canary region [Arístegui et al., 2005], would support our observations of a greater contribution of slowly sinking particles during these periods.

In terms of carbon sequestration, the depth of organic matter decomposition determines whether respired CO_2 may be exchanged quickly with the atmosphere or rather be sequestered over long periods of time [Armstrong et al., 2001]. Thus, if slowly settling particles dominate the exportable carbon pool, most organic matter would be respired in the epipelagic and upper mesopelagic zones, acting as a biological source of CO_2 susceptible to exchange with the atmosphere. On the contrary, if fast-sinking particles contribute largely to the carbon flux, the carbon transfer efficiency to the mesopelagic waters increases, resulting in an enhanced carbon sequestration in the deep ocean.

The implications of this work for understanding regional and global ocean carbon balances are profound if slowly settling particles are a significant portion of the exportable carbon pool. This phenomenon may explain several unresolved issues of the ocean carbon cycle. In the context of climate change, if the predicted changes in phytoplankton community structure occur, slowly settling particles would be favored, modifying the strength of the biological pump in the ocean. Our results also highlight the urgent need to extend our regional database of the sinking particle velocity spectrum, as well as to develop new technologies to measure and collect the total spectrum of sinking particles in the ocean.

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Appendix I

2.6 Appendix I

2.6.1 Chlorophyll concentration and mixed layer depth seasonality

Methods and Interpretation

Figure 2.3 shows the time evolution of Chl-a concentration, and the depths of the mixed layer and the euphotic zone, as well as the depth of deployment of the sediment trap. Chl-a concentrations were obtained from SeaWifs images (http://oceancolor.gsfc.nasa.gov/) in a 8-day time resolution. All Chl-a images available every 8 days were averaged, and a new image created with a 9 km spatial resolution over the position of the sediment trap.

Seasonal variability of the mixed layer depth (MLD) was examined using the eddy resolving Mercator Océan global model at 1/12° resolution without data assimilation (Hurlburt et al. 2009). The vertical discretization of this system is based on 50 geopotential levels with high resolution at the surface, where the mixing is achieved through a 1.5-order turbulent closure scheme. The MLD was estimated as the depth at which the temperature has decreased by 0.2°C from the surface value. The MLD time series was then obtained by averaging over a three by three-gridpoint box centered on the sediment trap position and smoothing with a 15-day moving average.

The depth of the euphotic zone (Ze, 1% PAR) was assumed to be 100 m, as described by Neuer et al. (2007) from a 7-year cycle. This constant depth coincides with reported values obtained in previous works from the region of the trap deployment (Basterretxea and Arístegui 2000; Basterretxea et al. 2002).

The Chl-a seasonal evolution mirrored the seasonality of the MLD, with the highest values (>1.4 mg Chl-a m^{-3}) coinciding with the deepest MLD (107 m; end of February). This period of time also coincided with the highest fluxes and fastest settling velocities recorded (period II).

The depth interval between the bottom of the MLD and the depth of the sediment trap deployment is higher during the summer-autumn months (periods I and III). These results contradict the hypothesis that slowly settling particles resulted from deeply mixed surface waters and suggest that the slowly settling particles were passively collected.

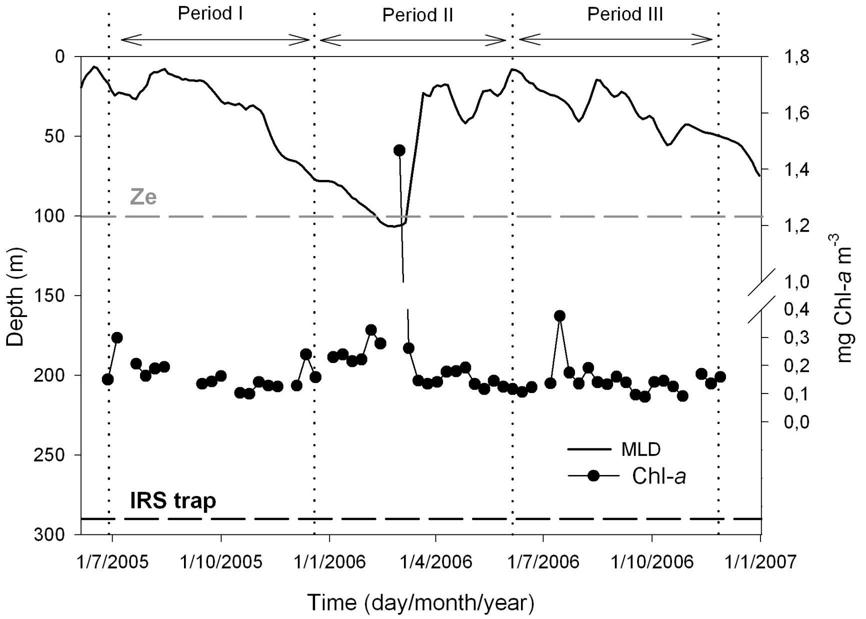

Figure 2.3: Seasonal variability of surface Chl-a concentration, mixed layer and euphotic zone depth (MLD and Ze, respectively). Empty spaces in the Chl-a time evolution are due to the presence of clouds.

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2.6.2 Principal components analysis

This section summarizes how principal components analysis (PCA) was performed on the original dataset and how the PCA was interpreted. This technique has been used extensively to analyze organic geochemical data (e.g. Goñi et al. 2000; Sheridan et al. 2002; Abramson et al. 2010).

PCA is a multivariate regression analysis that reduces a large number of variables to a few principal components. PCA was used here to quantitatively assess variation in the organic composition of fast vs. slowly sinking particles that were collected at 260 m depth in the Canary Current region. PCA was applied to a combined pigment and total hydrolyzed amino acids (THAA) composition data set. Prior to performing PCA, THAA and pigment mole% from each sample were standardized by subtracting the mean of all values and dividing by the standard deviation of all values (Dauwe and Middelburg, 1998; Sheridan et al. 2002). 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 for this study were carried out on Sirius for Windows ^{TM} Pattern Recognition System (version 7.0).

Interpretation of PCA
Figure 2.4 shows PCA performed on the amino acid and pigment dataset.

PC1 (which explained 44% of the variation) split samples in two major groups: 1) slowly settling particles, with fresh algal indicators ASP, GLU and Chl-a located at the right of PCA and 2) fast sinking particles, indicated by alteration products such as BALA, GABA and pyro, which are plotted towards the left on the PCA. This compositional difference between particles of different settling velocity has been observed before (Goutx et al. 2007). As the composition of the different particle velocity classes is dissimilar, we also infer that the faster settling particles (presumably larger) did not disagregate to form the more slowly settling particles (presumable smaller). Indeed, Abramson et al. (2010) investigated the exchange between suspended or slow-settling particles and sinking particles in the northwest Mediterranean and concluded that mixing between these two pools was limited. These results also contradict the hypothesis that slowly settling particles are formed artifactually during rotation of the IRS ball.

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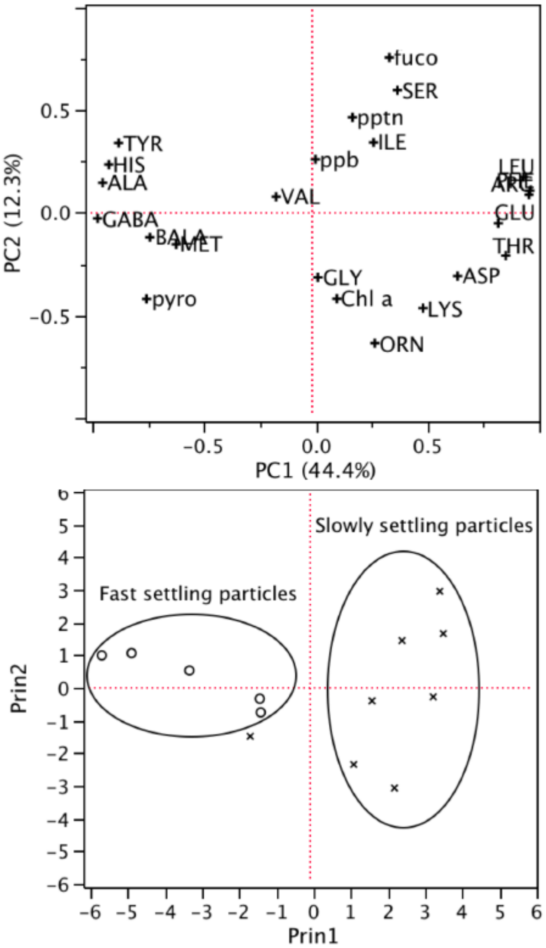

FIGURE 2.4: Principal component analysis (PCA) of the different particle velocity groups. PCA was conducted on amino acid and pigment composition data in material collected using IRSC sediment traps. Samples are divided into two categories: slowly settling particles (crosses) and fast settling particles (circles). This separation highlights the different compositions of these two classes of particles.

Part II

Suspended and slowly-sinking particulate organic carbon

Chapter 3

Lateral POC transport and consumption in surface and deep waters of the Canary Current region: a box model study

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Abstract

We have estimated the lateral transport and consumption, from surface to 3000 m, of suspended particulate organic carbon (POC), through a box model approach, in the Canary Current region (subtropical northeast Atlantic). Our results show that lateral POC fluxes are up to 3 orders of magnitude higher than vertical fluxes. In the mesopelagic ocean, the central waters (100-700 m) presented a net carbon consumption of 8.51 x 10^8 mol C d^{-1} with the highest POC entering through the more coastal section. This lateral flux accounted for 28-59% of the total mesopelagic respiration (R), on the basis of lower and upper case scenarios of vertical POC inputs and dissolved organic carbon contribution to R. We suggest that boundary currents may support higher lateral export of coastally produced POC than previously assumed. A large fraction of this POC would, however, be remineralized in the upper 1000 m instead of being transported to the ocean interior.

KEYWORDS: Lateral transport, suspended POC, remineralization

Contents

3.1 Introduction

One of the interests of boundary currents in the global ocean context is the role they may play in the transport and remineralization of organic matter produced in coastal waters of continental margins. Several studies have suggested that margins may export significant amounts of organic matter to the ocean interior, which are not considered in global ocean biogeochemical models [e.g., Walsh, 199; Falkowski et al., 1994; Santschi et al., 1999; Liu et al., 2000; Wollast and Chou, 2001; Arístegui et al., 2005a; Ducklow and McCallister, 2005; Inthorn et al., 2006]. However, the overall exchange rate of organic matter between the coast and the open ocean remains a matter of speculation since the lateral transport of organic matter, rather than being directly measured, has being estimated by mass balance approaches, frequently solely on the basis of sinking particles [Walsh, 1991; Liu et al., 2000; Wollast and Chou, 2001; Ducklow and McCallister, 2005]. Bauer and Druffel [1998], comparing the natural radiocarbon abundance in two coastal and open ocean profiles in the water column, found that continental slope and rise waters of the North American coasts contained both dissolved (DOC) and suspended particulate (POC_{susp}) organic carbon concurrently older and in higher concentrations that in the adjacent subtropical gyres of the Atlantic and Pacific Oceans. These results led the authors to conclude from their study that the POCsusp inputs from ocean margins to the ocean interior could be more than an order of magnitude greater than inputs of recently produced organic carbon derived from the surface ocean. In spite of their observations, and the general knowledge that the suspended POM pool is quantitatively far larger than the sinking pool [McCave, 1984; Kepkay, 2000; Verdugo et al., 2004], the construction of ocean carbon budgets is still largely based on vertical fluxes of sinking POM (POM_{sink}) collected with sediment traps. However, according to the abundance of suspended material, one would expect that a significant amount of excess suspended or low-sinking-rate particles, not remineralized on the continental margins, could be exported to the open ocean. Indeed, the analysis of POM_{sink} collected with sediment traps deployed across the path of the Canary Current, revealed that most of the particulate material collected in the deeper traps proceeded from the NW Africa coastal upwelling system

[Neuer et al., 2002a; Abrantes et al., 2002]. These particles traveled as far as 700 km off the coast, where the furthermost trap was deployed, suggesting a significant lateral transport of particles with low sinking rates from the continental margin to the open ocean.

The exchange of material between margins and the open ocean would presumably be particularly intense along eastern boundary currents, because of the high productivity of the upwelling regions and the high mesoscale variability of their coastal transition zones (CTZ), which help enhance the exchange of shelf waters with the open ocean. During the past two decades intense effort has been focused on complex multidisciplinary programs along the CTZ of eastern boundary regions, like the California Current [Brink and Cowles, 1991] and the Canary Current [Barton et al., 1998; Barton and Arístegui, 2004] in the northern hemisphere. However, most of this research was restricted to the near-surface waters, looking at fluxes [e.g., Álvarez-Salgado et al., 2007] and variability [e.g., Basterretxea and Arístegui, 2000; Arístegui et al., 2005a] at the mesoscale level, but ignoring the deep-water transport of organic matter to the ocean interior.

In this study we have estimated the horizontal transport and consumption, from surface to 3000 m depth, of particulate organic carbon (POC) collected with oceanographic bottles, assumed to be suspended in the water column or having very low sedimentation rates. We aimed to evaluate if the Canary Current and its underlying intermediate and deep waters act as links or sinks of organic matter transported from the NW African coast to the subtropical Gyre. The analysis was performed through a box model approach, with physical boundaries extending from 20° to 29° 10'N and 20° 35' to 26°W (1000 x 600 Km) in the Canary Current region (subtropical northeast Atlantic Ocean), during a low productivity period in the year. To our knowledge this is the first effort to directly estimate the lateral transport of POM_{susp} across an eastern boundary current toward the ocean interior.

3.2 Data and Methods

In September 2003, the R/V Thalassa carried out a high-density hydrographic survey along the path of the Canary Current (CORICA cruise). It consisted of four sections shaping a box with a total of 51 hydrographic (30 of them biogeochemical) stations (Figure 3.1). Conductivity, temperature and depth were recorded with a SeaBird 911 + CTD. The temperature and pressure sensors were calibrated at the SeaBird factory before the cruise. Salinity calibrations were carried out on board with a Guildline AUTOSAL model 8400 B salinometer (see Hernández-Guerra et al. [2005] for further details).

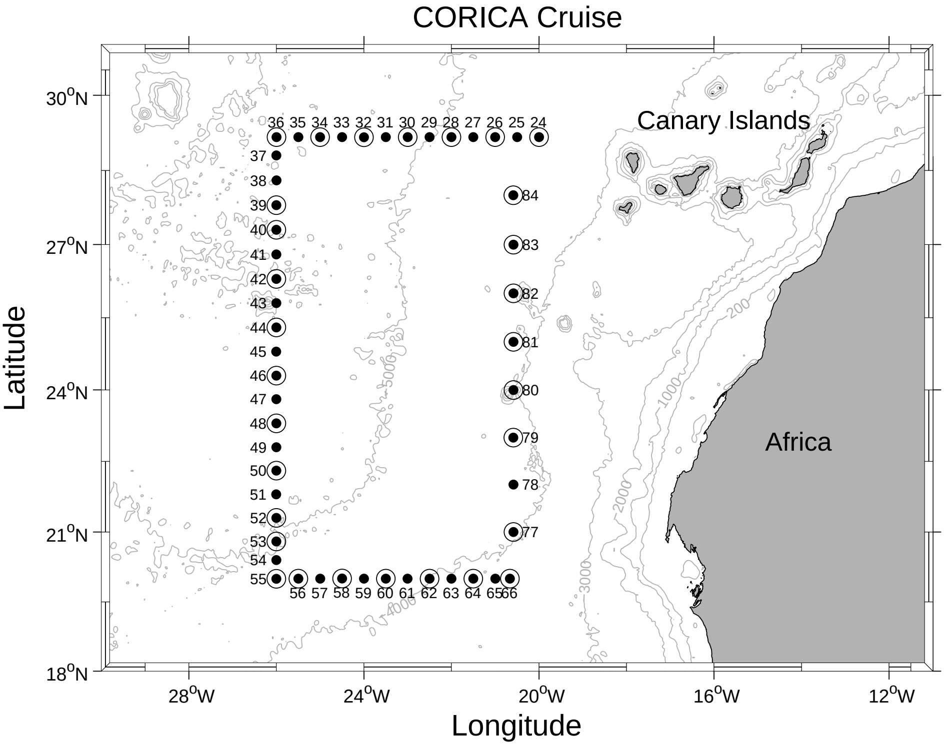


FIGURE 3.1: Hydrographic box: black dots indicate the position of CTD stations. Locations of biogeochemical stations are circled. The full box was sampled between 7 and 29 September 2003.

At the biogeochemical stations (Figure 3.1), discrete samples for particulate organic matter (POM) were obtained at selected depths from surface to 3000 m (5, 150, 300, 500, 700, 1000, 1200, 1500, 2000, 2500 and 3000 m), by means of a rosette sampler equipped with 24 10 L Niskin bottles. Water samples (2-6 L) for particulate organic carbon and nitrogen (POC and PON, respectively) were collected and filtered onto precombusted (450 °C, 12 h) 25 mm Whatman GF/F filters. The filters were wrapped in precombusted aluminum foil and frozen at - 20 °C until processed. In the laboratory, the filters were thawed and dried overnight at 55 °C, then placed overnight in a desiccator saturated with HCl fumes, dried again with silica gel and packed in nickel sleeves. The carbon analyses were performed with a Perkin- Elmer 2400 CHN elemental analyzer [UNESCO, 1994]. The DOC adsorption onto GF/F filters was subtracted from samples to avoid the overestimation of POC [Turnewitsch et al., 2007]. DOC adsorption onto the filters ranged from 0.6 to 2 mmol C per 25 mm diameter GF/F filter (about 3.2 cm^2 of exposed filter), being similar to the blanks reported by Moran et al. [1999] and Turnewitsch et al. [2007].

In order to quantify the transport of organic matter to the open ocean, and to investigate the relative importance of the remineralization processes versus the overall transport in the Canary Current, we used a box model approach. For this purpose we selected a grid box across the path of the Canary Current, which was spaced from the continental shelf about 250-450 miles at its eastern section. The reason for this distancing was to avoid the large mesoscale variability, in the form of eddies and filaments close to the upwelling jet, which would impede to estimate with accuracy the mass transport fluxes. Hence we assume that a large fraction of organic matter exported from the coast could be already remineralized before entering in our box.

The geostrophic velocities were obtained integrating the thermal wind equations, considering the neutral density level $\gamma_n = 28.072$ kg m^{-3} as the reference level of no motion. This level generally occurs at the 3000 m isobath, along the interface separating Middle North Atlantic Deep Water (MNADW) and Lower North Atlantic Deep Water (LNADW). The choice of the reference level of no motion at $\gamma_n = 28.072$ kg m^{-3} follows the study of

Ganachaud [2003] for the North Atlantic. The water column was divided into a number of layers on the basis of the neutral density that roughly separates different water masses. The upper four layers coincide with the thermocline waters, the next ones with intermediate waters, and the lowest layers with the NADW (MNADW and LNADW). The Ekman transport was added to the shallowest layer (see Hernández-Guerra et al. [2005] for further details). Lateral transports were calculated as $\mathrm{T}_{ij} = \rho_{ij}\ \mathrm{A}_{ij}\mathrm{V}_{ij}$, where i, j stand for each pair station and layer, respectively, ρ_{ij} is the density, A_{ij} is the area and V_{ij} is the geostrophic velocity. Since $\sum T_i = 0$, for each layer, it was not necessary to apply an inverse box model to estimate the geostrophic flow.

POC concentrations were linearly interpolated in neutral density layers and used along with the mass transport to obtain the perpendicular POC flux.

3.3 Results

3.3.1 POM Concentrations

In the north transect (29° 10'N) particulate organic carbon (POC) concentrations at stations to the west of 22°W decreased from about 4 mmol L^{-1} at surface to 1 mmol L^{-1} below 1000 m, whereas the eastern stations presented relatively higher and more constant concentrations (3 mmol mol L^{-1}) throughout the water column (Figure 3.2a). This resulted in a marked east-west zonal distribution, particularly noticeably below 500 m depth. At 25° W an extremely high POC concentration (15.1 mmol L^{-1}) was found in the interface layer between the North Atlantic Central Water (NACW) and the Antarctic Intermediate Waters (AAIW) and Mediterranean Intermediate Waters (MW). This value coincided with a sharp change in the density gradient at about 700 m (data not shown), suggesting passive accumulation of refractory material (C/N = 25). The C/N molar ratios show an opposite zonal trend than the POC, with lower average ratio (10.5 ± 2.3; n = 55) between 20°W and 22°W and higher (13.5 ± 3.5; n = 56) west of this longitude. It is noteworthy to observe that both the C/N and POC frontal gradients extended across different water masses in depth, down to at least 3000 m.

The south transect (20°N) showed variable but lower POC concentrations in comparison with the north transect, except in the upper 150 m where they reached 6 mmol L^{-1} west of 22°W (Figure 3.2b). The variability in the surface POC distribution and C/N ratios reflects the intersection of the south transect across the irregular meandering of the frontal system, caused by the confluence of the NACW and South Atlantic Central Water (SACW) and their interaction with the giant upwelling filament of Cape Blanc [Hernández-Guerra et al., 2005]. The zonal POC gradient at deep layers seen in the north transect is however not observed in this section. Below 500 m, POM concentrations were very low (<1 mmol L^{-1} POC), presenting high average (13.8 ± 2.2, $n = 35$) C/N ratios.

Along the west transect (26°W), POC concentrations were in general >4 mmol L^{-1} in the upper 200 m of the section, decreasing sharply with depth (<1.5 mmol L^{-1} below 1000 m) (Figure 3.2c). At 21°-23°N POC concentrations were, however, higher in the upper 1000 m than in the rest of the section, showing also lower C/N ratios. This region coincided with the area where the Canary Current turned to the southwest before flowing equatorward to feed the North Equatorial Current [Hernández-Guerra et al., 2005].

The east transect (20° 35'W) intersected two areas where high POC concentrations were measured throughout the whole water column (Figure 3.2d): one at 21°N, coinciding with the presence of the Cape Blanc giant filament, and the second north of 28°N, close to the Canary Islands, where the presence of a Mediterranean eddy (meddy) was reported [Hernández-Guerra et al., 2005]. At 21°N, C/N ratios were the lowest values measured along the section (<10), suggesting a more labile origin of the organic matter, because of the higher productivity of the Cape Blanc waters.

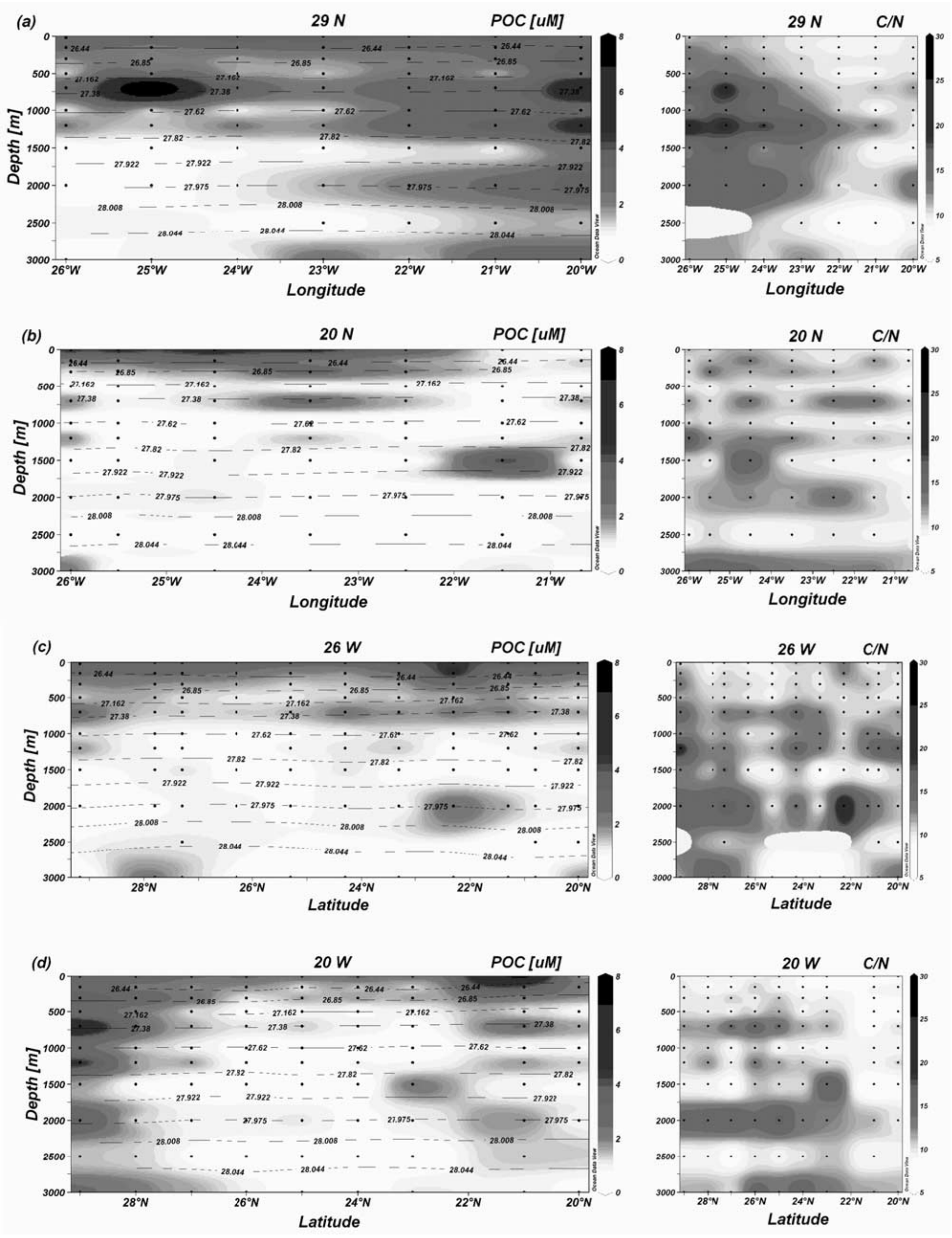


Figure 3.2: POC concentrations and C/N ratios along each section according to neutral density layers: (a) north, (b) south, (c) west, and (d) east transects. Locations and depths of sampling for POC are shown with black dots.

3.3.2 POC Transport

3.3.2.1 Mass Transport

Figure 3.3 illustrates the integrated mass transport for each section using the initial reference level of no motion at $\gamma_n = 28.072$ kg m^{-3} for geostrophy, and adding the Ekman transport in the first layer. As observed in Figure 3.3, the patterns of circulation for these layers are different depending on the section. The north and south transects present a similar pattern, with a northward and southward flow, respectively, at all layers, reaching a maximum transport value (1 x 10^9 kg s^{-1}) at intermediate waters (27.38-27.922 neutral density layers). Both the east and west transects show, however a considerable westward flow (11 x 10^9 kg s^{-1}) at the thermocline waters (Surface-27.38), whereas the east transect shows also a significant westward flow (4 x 10^9 kg s^{-1}) at intermediate waters. Remarkably, the most important water input within the box took place along the east transect, being a coastal to open ocean flow. Considering all layers together, the net integrated transport was almost zero, indicating that the mass transport was in balance inside the box.

3.3.2.2 Lateral POC Flux

POC fluxes were calculated excluding stations 24 (the easternmost station of the north transect), and the extremely high value observed at 700 m at station 34, since it would overestimate the average flux. Station 24 intersected part of a meddy and hence the fluxes were biased, since the flux at that station was northward albeit the eddy was drifting southwestward [Hernández-Guerra et al., 2005]. The resulting average transports of suspended POC for each section and water density layer are depicted in Figure 3.4 and Table 3.1. In the north transect the integrated POC transport through the surface layers was of 2.15 x 10^8 mol C d^{-1} southward, at a rate of 2.86 mol C m^{-2} d^{-1}. In the NACW a total of 5.37 x 10^8 mol d^{-1} of POC was also transported southward at a rate of 1.49 mol C m^{-2} d^{-1}. However, at intermediate (MW and AAIW) and deep (NADW) waters 4.11and 1.77 x 10^8 mol d^{-1} of POC was transported northward at rates of 0.76 and 0.23 mol C m^{-2} d^{-1}, respectively. The south

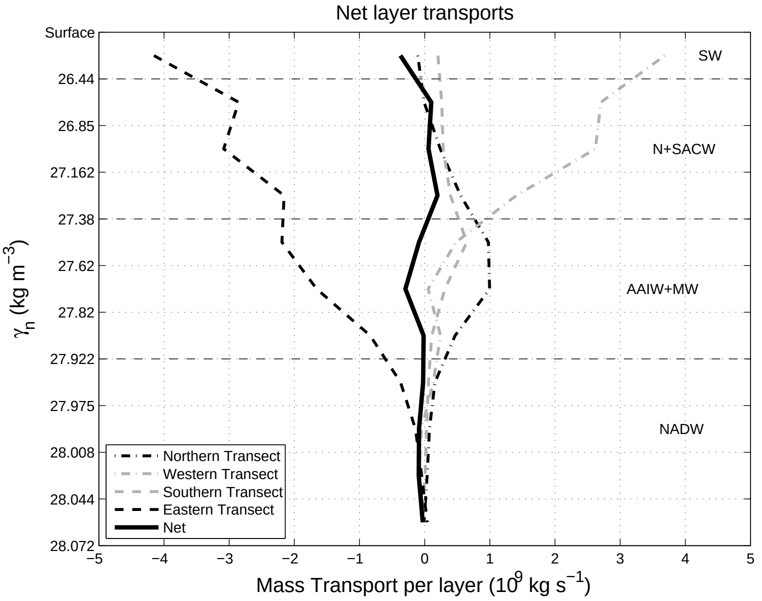


Figure 3.3: Integrated mass as a function of density layer for the north (black dash-dotted line), south (gray dashed line), west (gray dash-dotted line), and east (black dashed line) transects with their net transport (black solid line). For each transect, positive and negative values mean outputs and inputs, respectively. The sign of the net transport is positive (negative) for divergence (convergence) flow out of (into) the box.

transect followed the same pattern of circulation as the north one. Surface and central waters transported southward 0.77 and 1.97 x 10^8 mol d^{-1} of POC at rates of 1.14 and 1.55 mol C m^{-2} d^{-1}, while intermediate and deep waters transported 0.34 and 0.10 x 10^8 mol d^{-1} of POC at rates of 0.062 and 0.01 mol C m^{-2} d^{-1}, to the north. The surface waters along the west and east transects showed a westward transport of 11.62 and 15.33 x 10^8 mol C d^{-1}, at rates of 7.1 and 11.39 mol C m^{-2} d^{-1}, respectively. These estimates are much higher both in absolute terms and rates than in the north and south transects. The central waters also transported POC to the west (7.91 x 10^8 mol C d^{-1} and 13.02 x 10^8 mol C d^{-1} across 26°W and 20°W), although the average rate transport was considerably higher at 20°W (2.2 mol C m^{-2} d^{-1}) than at 26°W (1.5 mol C m^{-2} d^{-1}). The intermediate waters also displayed a westward component, transporting 3.24 and 2.85x10^8 mol d^{-1} of POC at rates of 0.32 and 0.3 mol

C m^{-2} d^{-1} in the east and west sections, respectively. These transports were less intense than the southward component observed at intermediate waters in the north and south transects. At the NADW layers, the transports (0.46 x 10^8 mol C d^{-1} for the east and 1.54 x 10^8 mol C d^{-1} for the west) and rates (0.05 mol C m^{-2} d^{-1} for the east and 0.12 mol C m^{-2} d^{-1} for the west) were low, like in the other sections, but in this case the flows were always toward the interior of the box. In summary, the meridional POC circulation in this area may be divided into a southward transport between surface and the bottom of the central waters and a northward transport below the central waters. The zonal POC circulation was dominated however by a significant coastal-open ocean transport affecting both the surface and central waters.

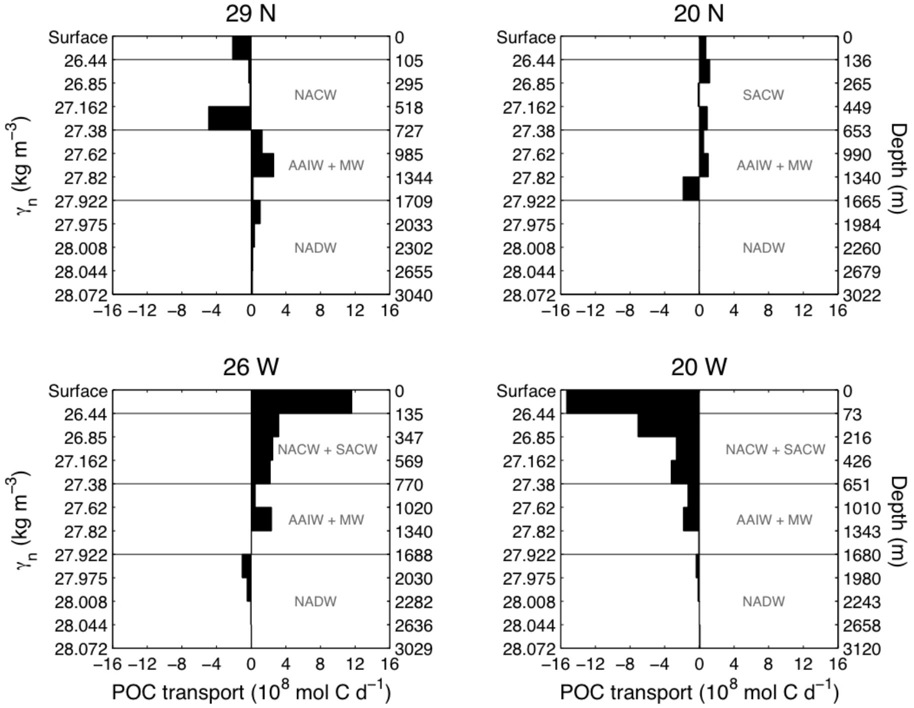
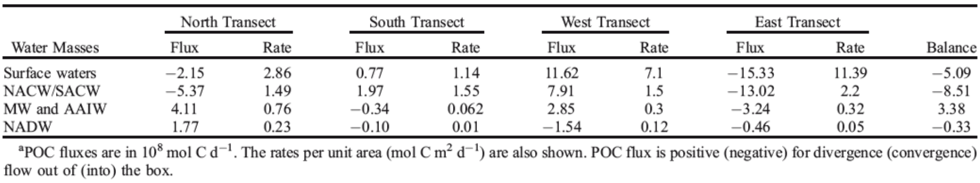


FIGURE 3.4: POC fluxes (10^8 mol C d^{-1}) as a function of neutral density layers at each transect. Negative values for POC transport indicate inputs, and positive values indicate outputs. The y axes are labeled on the left by the neutral density and on the right by the average depth of the interfaces of each layer.

Mass balance calculations in the upper surface water layer (above the neutral surface of 26.44) and the central waters (26.44-27.38) resulted in negative balances of 5.09x10^8 mol C d^{-1} and 8.51x10^8 mol C d^{-1}, respectively (Table 3.1), with the maximum transport concentrated through the more coastal section (20°W). Intermediate waters (27.38-27.922) presented lower transports, except in the north transect. The overall balance at this depth layer yielded a positive carbon export of 3.38 x 10^8 mol C d^{-1}, with most of the transport channeled through the north section. Interestingly, the exported carbon is not transported from the south, where POC values at intermediate layers are low. Rather it seems to be transported from the east, and particularly from the Cape Blanc and Canary Islands regions, as suggested by the high POC values observed at these latitudes along the eastern transect. Finally, in the deep waters (27.922-28.072), the suspended POC transport was almost negligible.

Table 3.1: POC Fluxes in the Different Water Masses for the North, South, West, and East Transects[a]



	North Transect		South Transect		West Transect		East Transect		
Water Masses	Flux	Rate	Flux	Rate	Flux	Rate	Flux	Rate	Balance
Surface waters	−2.15	2.86	0.77	1.14	11.62	7.1	−15.33	11.39	−5.09
NACW/SACW	−5.37	1.49	1.97	1.55	7.91	1.5	−13.02	2.2	−8.51
MW and AAIW	4.11	0.76	−0.34	0.062	2.85	0.3	−3.24	0.32	3.38
NADW	1.77	0.23	−0.10	0.01	−1.54	0.12	−0.46	0.05	−0.33

[a] POC fluxes are in 10^8 mol C d^{-1}. The rates per unit area (mol C m^2 d^{-1}) are also shown. POC flux is positive (negative) for divergence (convergence) flow out of (into) the box.

3.4 Discussion

3.4.1 Coastal Ocean Gradients in Suspended POM

Particles in the ocean exist in a continuum of sizes, but two classes are frequently recognized: suspended and sinking matter. They are distinguished operationally by the sampling method used to collect them: suspended matter with oceanographic bottles or large-volume in situ pumps [e.g., Turnewitsch et al., 2007], and sinking matter with sediment traps. Nevertheless, bottles may also trap particles with moderate to fast sedimentation rates [Gardner, 1977], whose contribution to the overall POM will depend on the relative importance of the sinking pool versus the suspended pool. The majority of POM in the water column is thought, however, to be formed by fine suspended material or particles with almost negligible sedimentation rates compared with horizontal fluxes [McCave, 1984; Kepkay, 2000; Verdugo et al., 2004]. These particles, referred to here as POC_{susp}, would be characterized by a conservative behavior in the water column undergoing lateral transport [Brun-Cottan, 1976].

In this study we have assumed that all POM collected with bottles represents suspended material or particles with very low sedimentation rates, susceptible of being transported horizontally. Strong evidence supports this hypothesis. Recent studies south of the Canary Islands, based on particle settling velocities using IRSC (Indented Rotating Sphere Carousel) traps [Peterson et al., 1993] during a 6 month period (summer to autumn 2005), indicate that about 60% of the POM collected in the traps have low sinking rates (<5 m d^{-1}), allowing particles to be laterally transported [Alonso-González et al., 2010]. Comparatively, the average POC sinking velocity recorded using the same sediment traps at the DYFAMED station in the Mediterranean Sea, is of 350 m d^{-1} [Peterson et al., 2005; Armstrong et al., 2009]. The reason for the low sedimentation rates in the Canary region is still a matter of debate [e.g., Arístegui et al., 2003], but would explain the low export ratio with respect to the f ratio, reported by Neuer et al. [2002b] at the ESTOC station, north of the Canary Islands, compared to the Bermuda Time Series Station (BATS). Paradoxically, the POM concentrations collected with bottles in the water column are much higher in the Canary region. Indeed, POC at the BATS [Steinberg et al., 2001], like in other open ocean regions [e.g., Menzel and Goering, 1966], decrease exponentially with depth, reaching values typically <1 mmol L^{-1} at depths >200 m. In our study, POC concentrations in the deep ocean (down to 3000 m) were >2 mmol L^{-1} in the eastern sector of the box, decreasing toward the open ocean. An intermediate situation (range 1-3 mmol L^{-1} POC at depths >200 m) is found in the Azores region [Vezzulli et al., 2002], a transition zone between the Canary Current and the central waters of the North Atlantic subtropical Gyre (NASG).

Our results agree with the autumn values reported by Neuer et al. [2007] for the 200-1000 m layer at the ESTOC, which were the lowest recorded during the annual cycle. The highest average POM values in the upper 1000 m (as high as 8 mmol L^{-1}) were reported for the spring months. No measurements were, however, carried out during summer [Neuer et al., 2007], when the upwelling activity, and hence the potential offshore export, is higher. Indeed, POC concentrations measured between the Canary Islands (28°N) and Cape Blanc (21°N), along four cruises carried out during spring (2003) and summer (2002), reached typical average concentrations of about 6 mmol L^{-1} down to at least 2000 m (J. C. Vilas, personal communication, 2007), without any indication of an exponential decrease with depth. Thus, lateral transport of organic matter generated over the NW-Africa continental shelf may largely contribute to the POM_{susp} observed in the Canary Current region. The transport would be more pronounced during the periods of higher upwelling intensity, decreasing the concentrations toward the open ocean because of remineralization processes. Vilas et al. [2009] reached the same conclusion after studying the distribution of POM around Seine, a seamount placed east of Madeira Island, in the Canary Current. These authors observed peaks of POC in the 200-1000 m layer at the stations closer to the continental shelf and coinciding with the highest activity of the upwelling system.

3.4.2 Offshore Suspended Organic Carbon Pumping to the Interior of the North Atlantic Ocean

To estimate the net lateral flux of POC_{susp} in the mesopelagic and bathypelagic waters, we first subtracted the open ocean 'baseline' POC concentration, obtained from averaging the monthly POC profiles in each depth layer at the Bermuda Atlantic Time-series (BATS) station, from the POC concentrations at the east and west transects. The BATS station, placed at the center of the NASG, presented a typical exponential decrease of POC with depth, reaching values $<1\mu M$ below 200 m. In a comparative study of three subtropical time series stations (BATS, HOT and ESTOC), Neuer et al. [2002b] concluded that the annually integrated net primary production was similar at all three sites, with slightly lower values at ESTOC. However, the POC sinking flux (measured with drifting traps at about 150-200 m) was approximately 2-3 mmol C m^{-2} d^{-1} at BATS (Bermuda) and HOT (north of Hawaii), while at ESTOC (north of the Canary Islands) was only about 20% of these values (0.55 mmol C m^{-2} d^{-1}). Recent results (J. Arístegui, unpublished data, 2007; Alonso-González, unpublished data, 2007) of sinking POC, collected with similar traps at 150-200 m, from 30°N to 21°N, outside the influence of the intense eddy field, indicate that the POC flux varies on average from 0.7 to 2 mmol C m^{-2} d^{-1} from spring to autumn, increasing to 3-4 mmol Cm^{-2} d^{-1} during the late winter bloom. Since sinking fluxes in our region of study are not higher than in BATS, we consider that the BATS POC would characterize the typical POC profile in the western Canary region, assuming only vertical flux of POC.

Lateral fluxes were particularly intense along the east and west transects. Thus, we focused our analysis on the net balance considering the fluxes through these two transects. We calculated a lateral flux of suspended POC at the central and intermediate waters (100-1700 m depth layer) of 8.77 x 10^8 mol C d^{-1} and 4.8 x 10^8 mol C d^{-1} for the east and west transects respectively, extending along 1.01 x 10^6 m in length (Figure 3.5).

In any case, a simple sensitivity analysis was added to assess the effect of baseline subtraction to the magnitude of the lateral POC fluxes. First, the BATS POC data were fitted to a power law function, and then a "fake baseline" was generated by applying the same equation observed at BATS to higher surface POC values (Figure 3.6). Subtracting the fake baseline from the POC concentrations at the east and west transects, the lateral fluxes of suspended POC at Central and intermediate waters were 5.78 and 4.26 x 10^8 mol C d^{-1} for the east and west transects respectively. The POC increase over the BATS baseline (1.5 times higher) results in a decrease in the lateral POC fluxes of 34% for the east transect and 11% for the west transect.

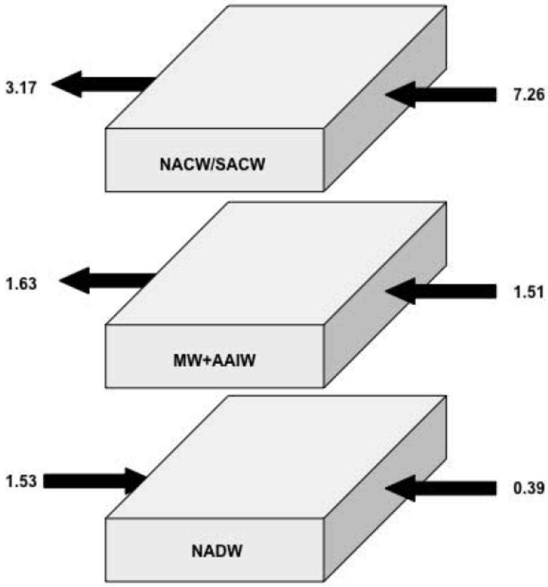


Figure 3.5: Offshore suspended organic carbon fluxes (10^8 mol C d^{-1}) in the different water masses. The values were obtained by subtracting the open ocean baseline POC concentration calculated from the Bermuda Atlantic Time series Study (BATS). Note that the highest POC fluxes are in central waters of the more coastal section.

Table 3.2 compares the vertical and lateral POC transport in the Canary region. The lateral fluxes correspond to this study, whereas the vertical fluxes were obtained from surface-tethered and deep-moored traps [Neuer et al., 1997, 2002b, 2007; Arístegui et al., unpublished data, 2003]. As observed, the lateral POC fluxes are 2 or 3 orders of magnitude higher than vertical fluxes depending on water masses, confirming our hypothesis of a more relevant horizontal versus vertical flux of POM per unit area. This conclusion is partly in agreement with the work of Bauer and Druffel [1998] who suggested that suspended POC inputs from ocean margins to the open ocean interior might be more than an order of magnitude greater than inputs of recently produced organic carbon derived from the surface ocean. However, we should keep in mind that the overall differential effect of the POC transport will depend on the aerial extension of the vertical versus lateral fluxes under consideration.

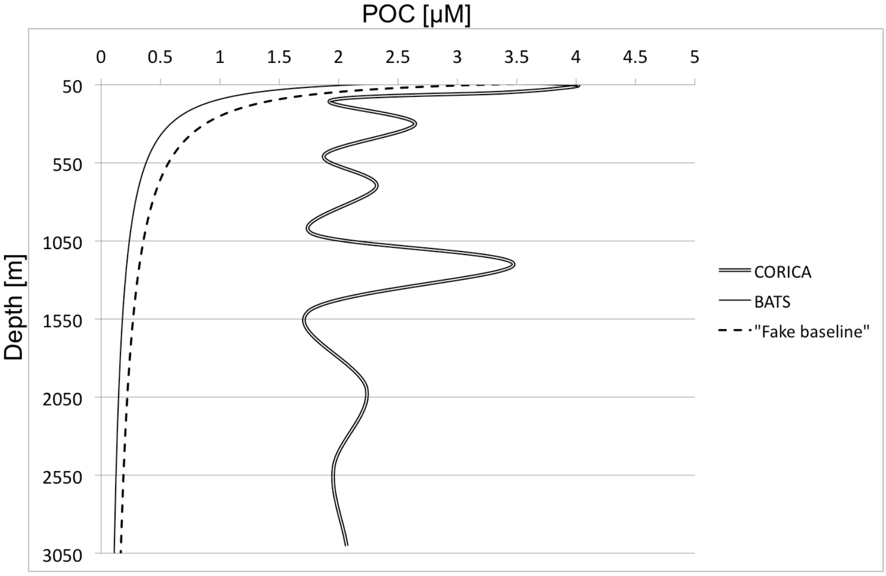
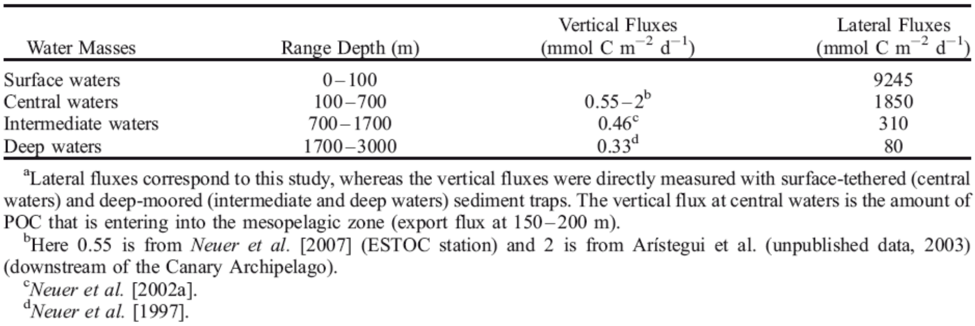


Figure 3.6: Comparison of the average POC profile measured during this study (CORICA) with the baselines used in the sensitive analysis to compute lateral POC fluxes. The BATS baseline was generated by fitting a power law equation to the average BATS POC profiles (black line). A fake baseline (dashed line) was derived by applying the same equation observed at BATS to higher surface POC values (see text for details).

Table 3.2: Estimates of Vertical and Lateral POC Fluxes in the Different Water Masses^a



Water Masses	Range Depth (m)	Vertical Fluxes (mmol C m^{-2} d^{-1})	Lateral Fluxes (mmol C m^{-2} d^{-1})
Surface waters	0–100		9245
Central waters	100–700	0.55–2^b	1850
Intermediate waters	700–1700	0.46^c	310
Deep waters	1700–3000	0.33^d	80

[a] Lateral fluxes correspond to this study, whereas the vertical fluxes were directly measured with surface-tethered (central waters) and deep-moored (intermediate and deep waters) sediment traps. The vertical flux at central waters is the amount of POC that is entering into the mesopelagic zone (export flux at 150–200 m).

[b] Here 0.55 is from *Neuer et al.* [2007] (ESTOC station) and 2 is from Arístegui et al. (unpublished data, 2003) (downstream of the Canary Archipelago).

[c] *Neuer et al.* [2002a].

[d] *Neuer et al.* [1997].

3.4.3 Carbon Budget and Mesopelagic Respiration

The surface waters (0-100 m) inside the box received an overall higher external input (17.48 x 10^8 mol C d^{-1}; sum of north and east transects) of POC_{susp} than exported (12.39 x 10^8 mol C d^{-1}; sum of south and west transects) outside the box (Table 3.1). The resultant balance is 5.09 x 10^8 mol C d^{-1} (0.85 mmol C m^{-2} d^{-1}). This value is in the range of the sinking POC flux reported above for the region of study, but somewhat higher than that estimated by Neuer et al. [2007] for the ESTOC (European Station for Time series in the Ocean, Canary Islands) north of the Canaries (Table 3.2). Sedimentation rates measured downstream the Canary Islands are however 2-4 times higher [Arístegui et al., 2004], because of the enhanced production and eddy filament exchange processes along the intense mesoscale field [Arístegui et al., 1994, 1997; Barton et al., 1998, 2004]. Island eddies are known to increase productivity leading to positive net community production [e.g., Arístegui and Montero, 2005]. A fraction of this excess production not sunk down may be laterally advected to the open ocean, contributing to the surface carbon budget inside our box. Assuming nonsignificant atmospheric inputs, the amount of carbon sedimented into the dark ocean (see above) would match the external inputs into the box, leading to a carbon balance in the surface waters. Nevertheless, Dachs et al. [2005] have reported high average net gaseous diffusive air water fluxes of organic carbon (25-30 mmol C m^{-2} d^{-1}) in the subtropical northeast Atlantic, which in case they occur during our study, would shift the balance toward a strong heterotrophy. Independently of whether the surface waters were or not in metabolic balance (see discussions by Duarte et al. [2001], Dachs et al. [2005], and Neuer et al. [2007]), the vertical export flux of POC to the dark ocean, which is the flux in which we are interested in our study, seems to be quite constant from spring to autumn, as derived from the sediment traps records.

In order to calculate the respiration rate that could support the total carbon supply below the surface waters, we considered all the carbon fluxes inside the box. Sinking POC collected with surface-tethered traps range from 0.55 to 2 mmol C m^{-2} d^{-1} (see the above section). Drifting sediment traps have been frequently reported to underestimate the export flux [Michaels et al., 1994; Buesseler, 1998; Buesseler et al., 2000; Neuer et al., 2007]. However, results comparing POC flux in BATS, both derived from surface-tethered traps and ^{234}Th [Buesseler, 1998], show that during low productivity (PP) periods (average PP from March to October: 36 mmol C m^{-2} d^{-1}) the traps and ^{234}Th estimates reasonably agree, yielding average POC sedimentation rates of 2.6 mmol C m^{-2} d^{-1}, which corresponded to an export/ production ratio (e ratio) of 5-10%. At the ESTOC station (which is closer to the upwelling region than our sampling area), the average annual PP is about 30 mmol Cm^{-2} d^{-1}, with the lowest values ($<$10 mmol C m^{-2} d^{-1}) recorded during autumn [Neuer et al., 2007]. Similarly, low PP was measured by Basterretxea and Arístegui [2000] in an offshore station west of the Canary Islands, during summer. An e ratio of 5-10% would therefore lead to a POC flux of 0.5-1 mmol Cm^{-2} d^{-1} at PP = 10 mmol C m^{-2} d^{-1}, and 1.5-3 mmol C m^{-2} d^{-1} at PP = 30 mmol C m^{-2} d^{-1}. These calculations provide confidence to the measured range in sedimentation rates with drifting traps (0.55-2 mmol C m^{-2} d^{-1}), which would represent a reasonable lower/upper scenario for passive sinking of POC in our region of study.

Diel migrating zooplankton contributes also to the vertical flux of POC (the so-called ‘active flux’) by feeding in surface during the night and defecating unassimilated POC at depth during the day. Hernández-León et al. [2001] estimated an active flux of 0.22 mmol C m^{-2} d^{-1} in the eddy field downstream the Canaries, similar to the average value (0.17 mmol C m^{-2} d^{-1}) reported by Steinberg et al. [2000] for BATS. These fluxes represented 25% and 8% of the passive POC fluxes in their respective regions. If we assume that the active flux represents at best a 20% of the passive flux, the vertical POC flux (passive + active) in our box would range from 0.7 to 2.4 mmol C m^{-2} d^{-1}. Multiplying these values by the box area (6 x 10^{11} m^2) yield a total POC supply of 4.2-14.4 x 10^8 mol C d^{-1}.

The central waters (approximately 100-700 m; hereafter named mesopelagic zone) inside our box received a net lateral POC supply of 8.5 x 10^8 mol C d^{-1}

(Table 3.1). If we assume that about 90% of the vertical POC flux is respired in the mesopelagic zone [Arístegui et al., 2005b], and adding the net lateral carbon supply we obtained a total mesopelagic POC reservoir (POC_{meso}) of 12.3-21.5 x 10^8 mol C d^{-1}.

How this POC flux compares with the DOC flux? The relative contribution of dissolved organic carbon (DOC) to total mesopelagic respiration (R) was estimated by Arístegui et al. [2003], in a section spanning the coastal transition zone (CTZ) in the Canary Current. In their study, DOC contributed 30% to the total mesopelagic oxygen consumption, a value 2 times higher than the average (15%) calculated by Arístegui et al. [2002] for the global ocean. Unlike the eastern Canaries-CTZ our region of study was characterized by a stable surface thermocline, and was outside the influence of the eddy field region, which might enhance vertical mixing. Thus, we would expect to have a lower contribution of DOC to total mesopelagic R. In a best case scenario of a 30% contribution of DOC, the total carbon fluxes (lateral and vertical fluxes of DOC and POC) would support an integrated (100-700 m) mesopelagic respiration rate of 2.9-5.1 mmol C m^{-2} d^{-1} (computed by dividing POC_{meso} by both the box area and 0.7). If DOC contributed 15% (a more reasonable contribution) the total R would be 2.4-4.2 mmol C m^{-2} d^{-1} (POC_{meso}/box areax0.85). From these calculations we can infer that the lateral POC would account for 28-49% of total mesopelagic R in the 30% DOC scenario, and 34-59% in the 15% DOC scenario.

Total R is about an order of magnitude lower than that estimated by Arístegui et al. [2005a] for the Canary Current region, during summer time, combining actual oxygen consumption measurements and enzymatic activities (ETS activity). The discrepancy in the magnitude of the rates may be explained by the fact that, during the summer sampling, the POC_{susp} concentrations were about 4-6 times higher in the water column than during this study (not shown) and that the summer rates were averaged including near coastal stations downward the Canary Islands region, where vertical POC flux is several times higher.

Our calculated R estimates are also about half of the mesopelagic oxygen consumption rates (9 mmol C m^{-2} d^{-1}) reported by Jenkins and Goldman [1985] for the NASG, inferred from changes in the apparent oxygen utilization (AOU) and the use of tracers to calculate the apparent age of the water mass. A similar twofold imbalance was observed in BATS between the AOU/tracers approach when compared with estimations of POC and DOC 1-D fluxes in the mesopelagic zone [Carlson et al., 1994; Michaels et al., 1994]. Although there are known pitfalls in the accurate determination of carbon fluxes [e.g., Buesseler, 1998; Hansell, 2002; Arístegui et al., 2005b], we must not exclude the uncertainty associated with the inference of mesopelagic respiration from changes in the oxygen field, because of eddy diffusivity [Jenkins and Wallace, 1992].

The sources of the lateral mesopelagic carbon fluxes to our region of study may be variable. Upwelling filaments have been identified as playing a key role in coastal ocean export of organic matter [Álvarez-Salgado et al., 2001]. According to Barth et al. [2002], the exported organic matter from filaments may be forced downward along sloping density surface through conservation of potential vorticity along the meandering jet path. These authors found a mesopelagic chlorophyll maximum in the California Current System over 300 Km offshore and between 150 and 250 m, reporting a carbon injection into the adjacent deep ocean of 2.4 x 10^6 Kg C per event. They suggested that the entire benthic mineralization rate could be supplied by five of these events per year. Eddies downstream the islands [Arístegui et al., 1997; Barton et al., 1998, 2004] are another potential source for deep-water transport of organic matter. Barton et al. [1998] estimated that island eddies may contribute to the nitrogen flux to the Canary region as much as coastal upwelling. McGillicuddy et al. [2007] calculated that carbon export inferred from oxygen anomalies in eddies in the Sargasso Sea accounted for one to three times as much as annual new production in the region. On the other hand, Arístegui et al. [1997] and Arístegui and Montero [2005] showed that anticyclonic eddies may entrain highchlorophyll water from upwelling filaments with which they interact.

Recent unpublished studies (e.g., Arístegui and Alonso-González, 2007) show that eddy entrainment is particularly strong in the frontal regions between eddy pairs and filaments, enhancing sinking of organic matter to depths >800 m. This organic matter could be laterally transported, accounting for some of the deep-water maxima observed in POM_{susp}. Additionally, meddies, frequently reported for the Canary Basin [Richardson et al., 1991; Shapiro and Meschanov, 1996; Richardson et al., 2000], may largely contribute to the deep-water transport of organic matter. During this study the core of a meddy was sampled (29°N, 20°W; 700-1500 m) yielding an average POC concentration of 7 μM. If we consider a southwestward flow of 1.2 Sv (as calculated by Hernández-Guerra et al. [2005]), the POC flux transported by the meddy would be 6.58 x 10^8 mol C d^{-1}. This value is only slightly lower than the net POC consumption in the Central waters. All these features (filaments, eddies and meddies) are limited in spatial extent and occur episodically, hence the difficulty in observing such events in hydrographic surveys or sediment traps. Therefore, the mesopelagic carbon deficit could be supplied by a few of these mesoscale events per year.

In conclusion, our results suggest that a significant fraction of the mesopelagic carbon budget in the western Canary Current may be fuelled by lateral suspended carbon advection from continental margins or mesoscale activity in the eastern boundary region. A large part of this mesopelagic carbon would be consumed in the boundary current, instead being transported to the open ocean. Our observations indicate that the influence of the lateral advected particulate carbon from the NW African coast on the oligotrophic subtropical gyre region can reach more than 1000 km offshore. If the lateral suspended POC fluxes estimated in this study are confirmed for other boundary regions, the coastal-open ocean POC transport would play a key, but unaccounted, role in the global carbon cycle of the oceans.

Acknowledgments

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CHAPTER 4

Spatio-temporal variability of water column respiration in the Canary Basin: the role of suspended particulate organic carbon

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Abstract

Here, we have studied the spatio-temporal variability in the epipelagic (0-200 m) and mesopelagic (200-1000 m) respiration through the enzymatic activity of the electron transport system (ETS) in microplankton. The study was conducted along two zonal sections (21°N and 26°N) extending from the northwest African costal upwelling to the open ocean waters of the North Atlantic subtropical gyre at 26°W, during autumn (September 2002) and late spring (June 2003).

The EST activity in the epipelagic waters exhibited contrasting zonal patterns of distribution. At 21°N, ETS was higher at the coastal stations associated with the Cape Blanc filament, decreasing towards the open ocean, while at 26°N the open-ocean waters presented higher ETS than near the African shelf.When averaging the values from each section, the highest ETS activities were found along 21°N, yielding to an important meridional variability. No significant temporal variability in the epepelagic ETS activity was observed. The ETS activity in the mesopelagic waters did not display clear patterns of either zonal or meridional distributions, except at 26°N, where ETS activity was clearly lower at the most coastal stations. The mesopelagic waters showed however a significant temporal variability, being the ETS activity 30% higher in autumn (202±19.3 mmol O_2 $m^{-2}d^{-1}$) than in late spring (150±13.9 mmol O_2 $m^{-2}d^{-1}$). The average integrated ETS activity in the mesopelagic zone (176±10.1 mmol O_2 $m^{-2}d^{-1}$) was high with respect to other oceanic regions, and comparable in magnitude to the epipelagic ETS (189±40.8 mmol O_2 $m^{-2}d^{-1}$). Based on significant correlations between average POC_{susp} concentrations and ETS activities from surface to 1000 m and previous results, we conclude that plankton respiration was mainly (65-74%) supported by seasonal fluctuations in the laterally advected suspended organic matter, highlighting a low contribution of sinking POC (<20%) to the water column respiration. This finding could help to explain the apparent imbalance between the carbon sources and the oxygen utilization rates in the mesopelagic waters when accounting only for the vertical sinking POC collected with sediment traps.

KEYWORDS: ETS activity; suspended organic carbon; ocean respiration; carbon imbalance; Canary Basin

Contents

4.1 Introduction

Primary production, respiration and the organic matter transport mechanisms are the main factors controlling the ocean carbon cycle. The classical view of the biological pump consider that the organic matter synthesized in the ocean is mostly respired within surface waters, being the non-oxidized matter transported vertically into the dark ocean. However, some studies have shown that lateral particulate organic carbon (POC) inputs from ocean margins to the ocean interior could be more than an order of magnitude greater than inputs of vertically transported organic carbon derived from the surface (Bauer and Druffel, 1998; Alonso-González et al. 2009). Supporting this idea, Barth et al. 2002, concluded that the off-shelf flux of carbon from coastal margins to the ocean interior must be considered when computing oceanic carbon budgets. These lateral inputs of organic matter would be particularly intense along eastern boundary currents, because of the high productivity of the nearby upwelling regions.

Recent studies in the coastal transition zone of the Canary Current region indicates that upwelling filaments may transport offshore up to 50% of coastal upwelling primary production, accounting for 2.5 to 4.5 times the offshore carbon export driven by Ekman transport. Nevertheless, most of this surface-export carbon takes place in dissolved form (see review in Álvarez-Salgado et al., 2007). A more plausible mechanism of shelf-offshore carbon transport is through suspended particles along density gradients in the dark ocean (e.g. Vilas et al., 2009). Indeed, Alonso-González et al. 2009 estimated, through a box-model approach, that suspended POC in the mesopelagic zone of the Canary Current could account for up to 60% of the total mesopelagic respiration. They suggested that a large fraction of this POC could be originated in the nearby coastal upwelling region, being respired in the upper 1000 m of the Canary basin, instead of being transported to the ocean interior. To test the hypothesis of the correlation between suspended POC and respiration we have looked at regional gradients and temporal variability in water column respiration and suspended particulate organic material.

Here, we report results from two cruises that took place in the Canary Current region in September 2002 (COCA I) and June 2003 (COCA II). We measured suspended particulate organic matter and the microbial respiratory activity at 10 stations placed along two sections expanding from the African coast to the open ocean. The aim of the work was to characterize and quantify the spatio-temporal variability of surface and mesopelagic respiration in the Canary region, and to show whether this variability responds to fluctuations in suspended organic matter supply, which presumably could be largely originated in the continental margin.

4.2 Data and Methods

4.2.1 Data sources

The study was conducted along two zonal sections (21°N and 26°N) extending from the costal upwelling to the open ocean at 26°W (Figure 4.1). The cruises consisted of a total of 31 hydrological stations and 10 biogeochemical stations, half of them along each section, which were roughly equidistant. At each station, conductivity, temperature and depth were determined by means of a 911+ CTD and fluorescence with a Seapoint sensor. Bottle casts were made down to 1000 m and seawater samples were collected at fixed depths every 50 m from surface to 1000 m for respiratory electron transport system (ETS) activity and suspended particulate organic carbon (POC_{susp}) analyses.

As a control system, we used measurements of ETS and POC_{susp} at the European Station for Time Series in the Oceans, Canary Islands, (ESTOC), located 100 Km north of the Canary Islands. The ESTOC is not under the influence of the high mesoscale activity generated south of the Canary Islands. ETS measurements at ESTOC were carried out during 2002, while POC_{susp} data was obtained from Neuer et al. 2007.

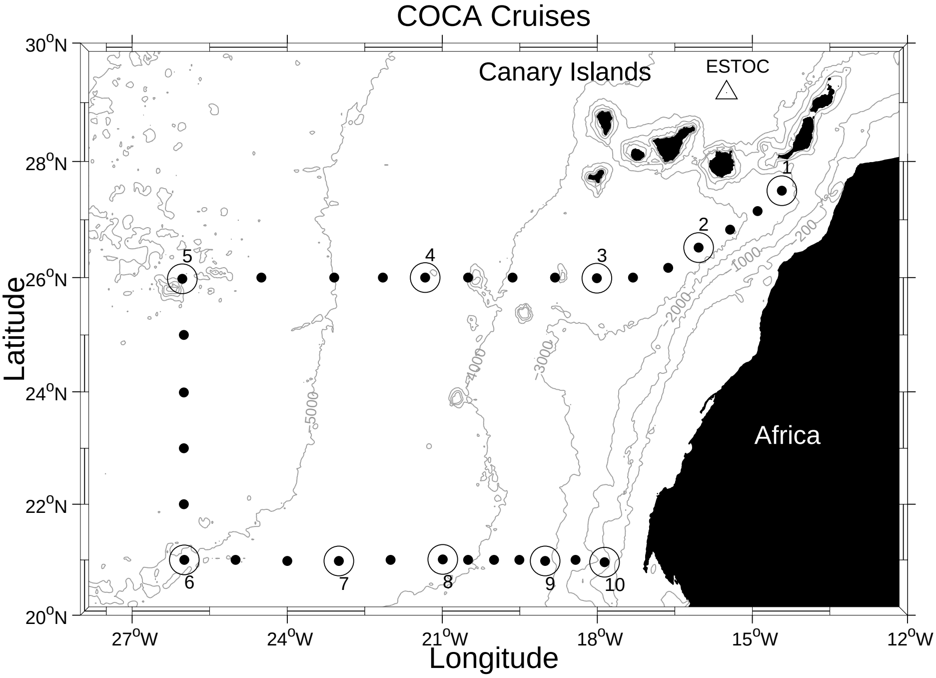


Figure 4.1: Map indicating the stations location along two sections extending from the NW African coast to the open ocean. Black dots indicate the position of CTD stations. Locations of biogeochemical stations are circled. Position of the European Station for Time Series in the Oceans, Canary Islands, (ESTOC) is also showed.

4.2.2 Respiratory Electron Transport System (ETS) activity

Seawater samples (10-20 L) were filtered through 47 mm Whatman GF/F glass-fiber filters at a low vacuum pressure (<0.3 atm). The filters were immediately stored in liquid nitrogen until being assayed in the laboratory within a few weeks. ETS determinations were carried out according to the Kenner and Ahmed (1975) modification of the tetrazolium reduction technique proposed by Packard (1971) as described in Arístegui and Montero (1995). The frozen filters were mechanically ground for 2 min by means of a drill equipped with a teflon bit in 5 ml of cold homogenization buffer. The obtained homogenate was centrifuged at 14,000 r.p.m. for 15 min at 0-3 °C. An incubation time of 20 min at 18 °C was selected from a previous time and temperature kinetic study. ETS activities measured at 18 °C were converted to activities at in situ temperatures by using the Arrhenius equation. A calculated mean activation energy of 16 kcal mol^{-1} was used. This activation energy value is similar to the activation energy values obtained from other studies in oceanic regions (Arístegui and Montero, 1995).

4.2.3 POM analysis

Water samples (2-4 L) for particulate organic carbon and nitrogen (POC and PON, respectively) were filtered onto precombusted (450 °C, 12 h) 25 mm Whatman GF/F filters. The filters were wrapped in pre-combusted aluminum foil and frozen at - 20 °C until processed. In the laboratory the filters were thawed and dried overnight at 60 °C, then placed overnight in a desiccator saturated with HCl fumes, dried again in a new desiccator with silica gel and packed in pre-combusted nickel sleeves. The carbon analyses were carried out on a Perkin-Elmer 2400 CHN elemental analyzer (UNESCO, 1994). The DOC adsorption onto GF/F filters ($<$12% of the POC signal) was subtracted from samples to avoid the overestimation of POC (Turnewitsch et al., 2007).

4.3 Results

4.3.1 Hydrographic structure

4.3.1.1 Water masses

The water masses distribution along the two sections is shown by a θ-S diagram in Figure 4.2. Above the seasonal thermocline, important differences between the two periods were found. During June, the surface waters were saltier and colder than in September, where a clear signal of upwelling activity was found. When comparing the two sections, 26°N presented saltier and colder surface waters than 21°N. Below the seasonal thermocline, no significant differences between the two periods were found, while a clear meridional variability was observed. The main thermocline (100-600 m) in the northern section (26°N) consists of North Atlantic Central Water (NACW) and in the southern section (21°N) mainly of South Atlantic Central Water (SACW). Below 600 m, corresponding to intermediate layers, two well-differentiated water masses are reported for this area: Antarctic Intermediate Water (AAIW) identified by a relative salinity minimum, and Mediterranean Water (MW) clearly distinguished by its salinity maximum. Spatial distribution of AAIW and MW is well defined: MW signature is stronger in the northern section and the AAIW in the southern section (Hernández-Guerra et al. 2005). However, since our stations were made down only to 1000 m, MW was not detected.

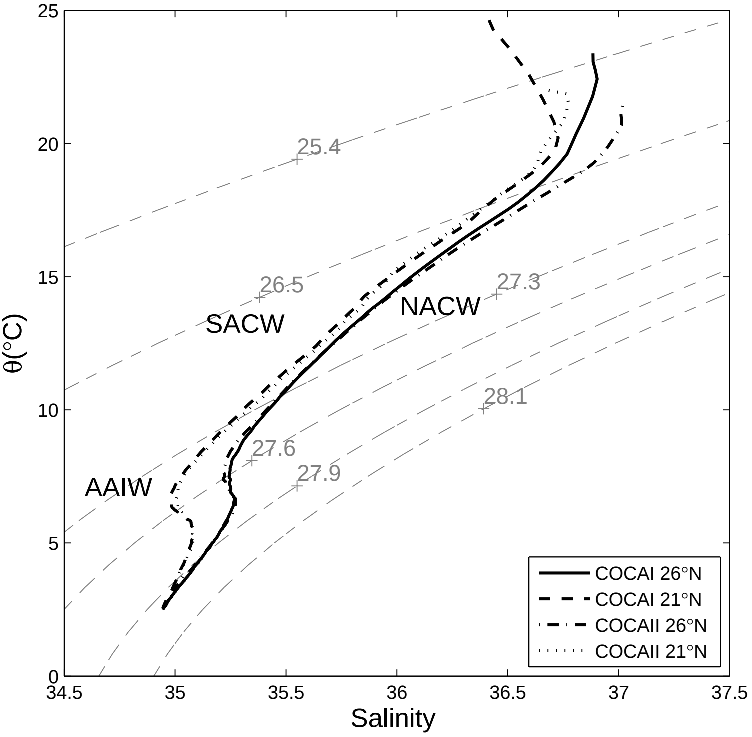


Figure 4.2: Mean θ/S curves for 21°N September 2002 (COCA I) and June 2003 (COCA II) and for 26°N September 2002 (COCA I) and June 2003 (COCA II). σ_θ isolines are also indicated.

4.3.1.2 Vertical sections

Figures 4.3 and 4.4 display vertical sections of temperature and salinity during COCA I and COCA II cruises, respectively. Figure 4.3 shows that temperature during September 2002 was generally higher than 21 °C decreasing to 18 °C toward the African coast in the northern section (26°N). At 21°N a weaker temperature gradient between open-ocean and coastal stations was observed. During September 2002, low-salinity surface waters invaded the easternmost part of the 26°N section, probably advected by upwelling filaments generated in the upwelling area off northwest Africa. Figure 4.4 shows that temperature during June 2003 follows a similar pattern than during September 2002, except in the 21°N section where colder surface waters were present. Subtropical high salinity water characterized by high salinity values (>37.1) due to excessive evaporation was observed in the northwestern corner of the northern section. Figures 4.3 and 4.4 show the isotherms and isohalines outcropping toward the African coast.

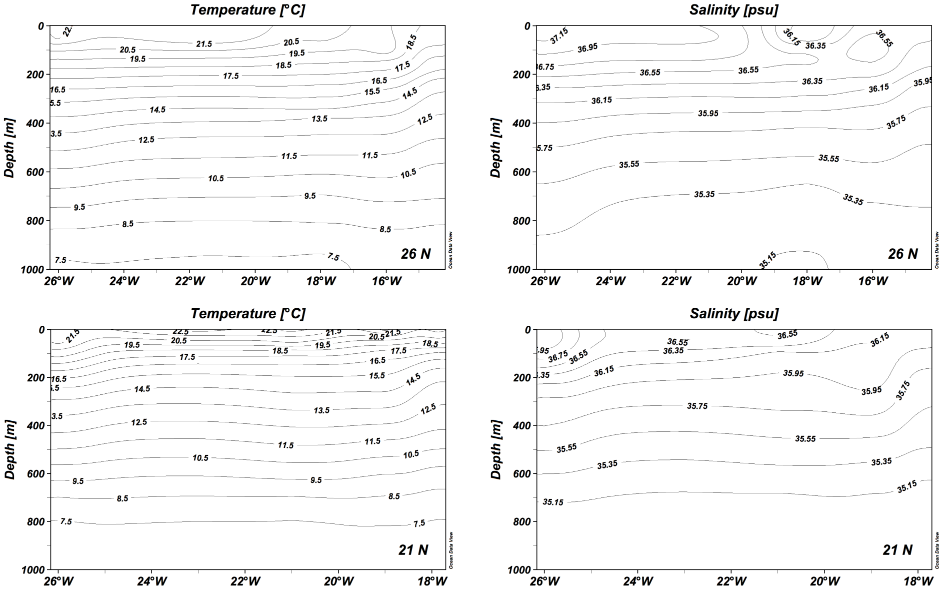


Figure 4.3: Vertical distribution (0-1000 m) of temperature (°C) and salinity (psu) during COCA I cruise (September 2002).

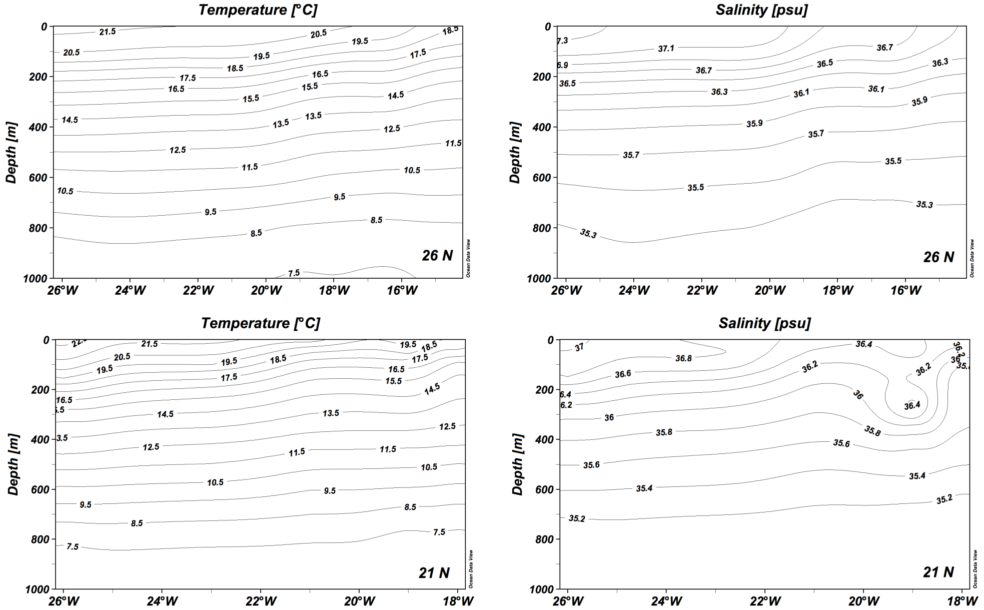


Figure 4.4: Vertical distribution (0-1000 m) of temperature (°C) and salinity (psu) during COCA II cruise (June 2003).

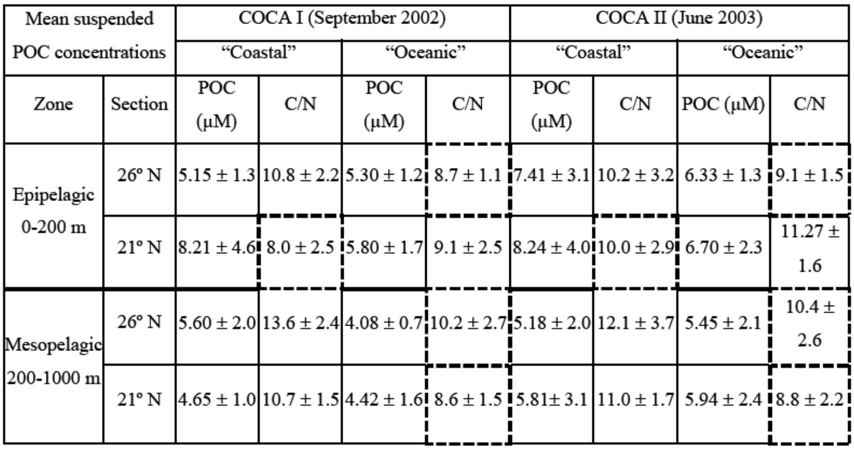
4.3.2 Suspended particulate organic matter distribution

Table 4.1 displays the mean suspended particulate organic carbon (POC_{susp}) concentrations and their C/N ratios. In the epipelagic zone (0-200 m), at 21°N POC_{susp} concentrations decreased from coastal to oceanic stations, with a parallel increase in the carbon to nitrogen ratios (C/N). At 26°N, POC_{susp} concentrations did not reflect a clear decrease toward offshore stations, whereas C/N ratios were higher (10.8 and 10.2) at the most coastal than in the oceanic stations (8.7 and 9.1 for COCA I and II, respectively). Since C/N ratios are proxies of lability, their highest values near the coast indicate either that "coastal" organic matter was less biodegradable or just more "carbon-enriched" than open ocean samples.

In the mesopelagic zone (200-1000 m), there were not significant differences in average POC_{susp} concentrations between coastal and oceanic stations or the two sections. C/N ratios showed however a characteristic trend with significant

($p<0.05$) higher values at the coastal stations (Table 4.1).

Table 4.1: Mean suspended POC concentrations and C/N ratios (±standard deviation) in the epipelagic and mesopelagic waters during the two periods of study (September 2002 and June 2003). "Coastal": average value of coastal stations (stations 1 and 2 at 26°N, stations 9 and 10 at 21°N); "Oceanic": average value of oceanic stations (stations 3, 4 and 5 at 26°N, stations 6, 7 and 8 at 21°N).



Mean suspended POC concentrations		COCA I (September 2002)				COCA II (June 2003)			
		"Coastal"		"Oceanic"		"Coastal"		"Oceanic"	
Zone	Section	POC (μM)	C/N	POC (μM)	C/N	POC (μM)	C/N	POC (μM)	C/N
Epipelagic 0-200 m	26° N	5.15 ± 1.3	10.8 ± 2.2	5.30 ± 1.2	8.7 ± 1.1	7.41 ± 3.1	10.2 ± 3.2	6.33 ± 1.3	9.1 ± 1.5
	21° N	8.21 ± 4.6	8.0 ± 2.5	5.80 ± 1.7	9.1 ± 2.5	8.24 ± 4.0	10.0 ± 2.9	6.70 ± 2.3	11.27 ± 1.6
Mesopelagic 200-1000 m	26° N	5.60 ± 2.0	13.6 ± 2.4	4.08 ± 0.7	10.2 ± 2.7	5.18 ± 2.0	12.1 ± 3.7	5.45 ± 2.1	10.4 ± 2.6
	21° N	4.65 ± 1.0	10.7 ± 1.5	4.42 ± 1.6	8.6 ± 1.5	5.81± 3.1	11.0 ± 1.7	5.94 ± 2.4	8.8 ± 2.2

4.3.3 Spatial variability in respiratory activity

Respiratory Electron Transport System (ETS) activity for all stations is shown in Figure 4.5. The results obtained from both cruises revealed a strong spatial variability across the two studied sections. The epipelagic (0-200 m) waters exhibited contrasting zonal patterns of distribution. At 21°N, the epipelagic ETS was higher ($p<0.05$) on the coastal stations (44.34 ± 20.6 and 43.54 ± 8.4 μmol O_2 m^{-3} h^{-1} for COCA I and COCA II, respectively), associated with the Cape Blanc filament, decreasing toward the open ocean (36.48 ± 9.4 and 32.86 ± 10.2 μmol O_2 m^{-3} h^{-1} for COCA I and COCA II, respectively). On the contrary, at 26°N the surface open-ocean waters presented a 2 to 5-fold higher ETS activity (COCA II and COCA I, respectively) than near the African shelf (Table 4.2). When comparing the two sections (21°N and 26°N), a significant ($p<0.05$) meridional variability in the epipelagic ETS was observed in both cruises (Table 4.2). The highest ETS activities were found along the 21°N section (39.3 ± 5.3 μmol O_2 m^{-3} h^{-1}, average value of both cruises), coinciding with the Cape Blanc region, while much lower values were observed at 26°N (22.9 ± 14.5 μmol O_2 m^{-3} h^{-1}). The epipelagic integrated ETS activities also show this contrasting zonal pattern between sections (Table 4.3). At 21°N, the integrated epipelagic ETS was higher on the coastal stations (10.34 mmol O_2 m^{-2} h^{-1}), decreasing toward the open ocean, while at 26°N the surface open-ocean waters presented higher integrated ETS than near the African shelf (8.31 and 1.93 mmol O_2 m^{-2} h^{-1}, respectively).

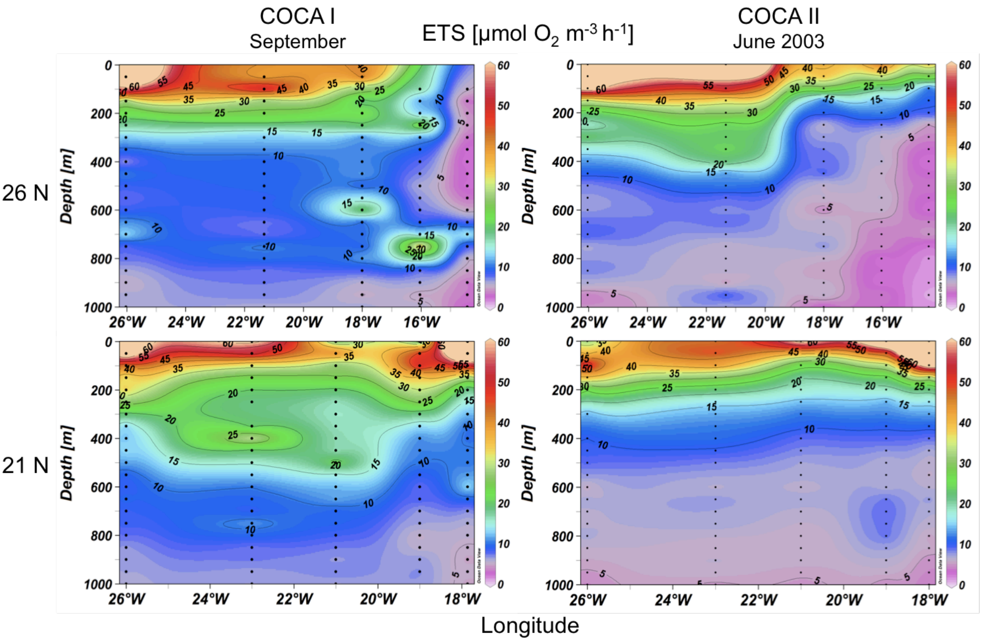
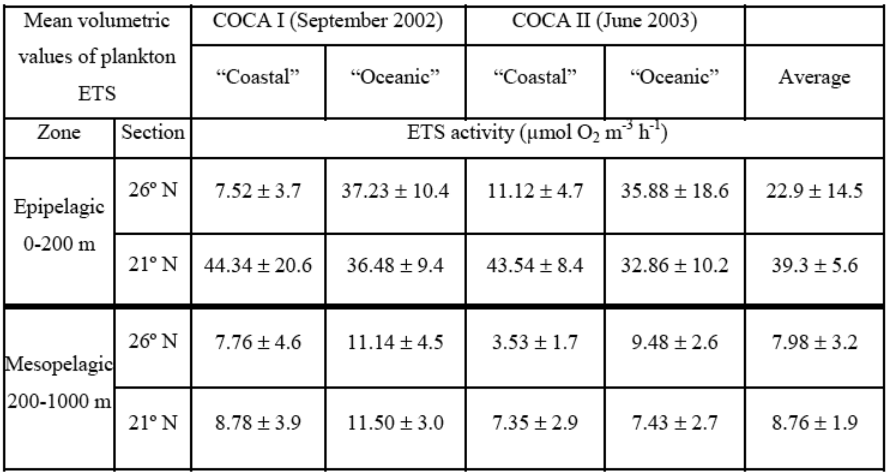


FIGURE 4.5: Vertical distribution (0-1000 m) of respiratory electron transport system (ETS) activity (μmol O_2 m^{-3} h^{-1}) for each cruise and section. Dots represent depths sampled at each station.

The ETS activity in the mesopelagic zone (200-1000 m) did not display a clear meridional trend, like in the epipelagic, except at coastal stations during June 2003 (Table 4.2). However, a significant zonal gradient with higher ($p<0.05$) ETS at the open ocean was clearly apparent at 26°N (Table 4.2, Figure 4.5). Integrated ETS rates for the mesopelagic waters also showed important zonal variations, with a minimum at the coastal stations (mean 7.21 and 6.25 mmol O_2 m^{-2} h^{-1} for 21° and 26°N, respectively) and a maximum at open ocean stations (mean 9.72 and 9.36 mmol O_2 m^{-2} h^{-1}) during September, following the same pattern during June (Table 4.3).

Table 4.2: Mean volumetric values (±standard deviation) of plankton ETS activities in the epipelagic and mesopelagic waters during the two periods of study (September 2002 and June 2003). For "coastal", "oceanic" criteria see Table 4.1 caption.



Mean volumetric values of plankton ETS		COCA I (September 2002)		COCA II (June 2003)		
		"Coastal"	"Oceanic"	"Coastal"	"Oceanic"	Average
Zone	Section	ETS activity (µmol O_2 m^{-3} h^{-1})				
Epipelagic 0-200 m	26° N	7.52 ± 3.7	37.23 ± 10.4	11.12 ± 4.7	35.88 ± 18.6	22.9 ± 14.5
	21° N	44.34 ± 20.6	36.48 ± 9.4	43.54 ± 8.4	32.86 ± 10.2	39.3 ± 5.6
Mesopelagic 200-1000 m	26° N	7.76 ± 4.6	11.14 ± 4.5	3.53 ± 1.7	9.48 ± 2.6	7.98 ± 3.2
	21° N	8.78 ± 3.9	11.50 ± 3.0	7.35 ± 2.9	7.43 ± 2.7	8.76 ± 1.9

4.3.4 Temporal and depth variability in respiratory activity

The epipelagic ETS activity did not show a significant temporal variability ($p>0.05$), being the mean values, 40.41±5.5 and 38.2±7.5 μmol O_2 m^{-3} h^{-1} for 21°N and 22.4±21.0 and 23.5±17.5 μmol O_2 m^{-3} h^{-1} for 26°N, during COCA I and II, respectively. However, there was an important difference in the mesopelagic ETS activity between the two periods. On average, the ETS activity in the mesopelagic waters was 9.8±1.8 μmol O_2 m^{-3} h^{-1} (202 mmol O_2 m^{-2} d^{-1}) during September while in June the mean ETS activity in the mesopelagic zone was a ~30% lower (6.9±2.5 μmol O_2 m^{-3} h^{-1}; 150 mmol O_2 m^{-2} d^{-1}).

Table 4.3: Integrated (epipelagic 0-200 m; mesopelagic 200-1000 m) values of plankton ETS activity from stations in the two sections during September 2002 and June 2003. For "coastal", "oceanic" criteria see Table 4.1 caption.

Integrated values of plankton ETS			COCA I (September 2002)				COCA II (June 2003)			
			0-200 m		200-1000 m		0-200 m		200-1000 m	
Section	"Status"	Station	ETS activity (mmol O_2 m^{-2} h^{-1})				ETS activity (mmol O_2 m^{-2} h^{-1})			
26° N	coastal	1	0.80	1.93	3.04	6.25	3.64	4.30	2.22	3.80
		2	3.05		9.45		4.95		5.37	
	oceanic	3	6.19	8.31	8.95	9.36	5.28	8.97	5.22	7.83
		4	7.35		11.79		11.24		10.04	
		5	11.40		7.34		10.38		8.24	
21° N	oceanic	6	10.78	8.12	9.03	9.72	8.43	7.88	6.45	6.34
		7	8.12		10.50		8.85		6.91	
		8	5.45		9.62		6.36		5.66	
	coastal	9	8.18	10.34	7.76	7.21	6.90	12.21	6.71	6.26
		10	12.50		6.65		17.52		5.80	

The depth distribution of the average ETS activity and suspended organic carbon concentrations for each cruise, and the average of both cruises are shown in Figure 4.6. Average ETS activity shows high values in the epipelagic waters (33.47 and 31.19 μmol O_2 m^{-3} h^{-1} for COCA I and COCA II, respectively), but also large deep maximums (values exceeding 10 μmol O_2 m^{-3} h^{-1}) between 200 and 400 m and between 700 and 800 m. Remarkably, the depth distribution of average POC_{susp} follow exactly the same pattern as the ETS activity independently of the season, suggesting that this pool of organic matter is the main substrate supporting ETS activity (Figures 4.6a and 4.6b). Figure 4.6c displays the depth distribution of the average (COCA I and II) ETS activity and POC_{susp} concentrations and compare it with the control station ESTOC. ETS activity within the epipelagic waters at ESTOC station showed similar ETS values than COCA cruises. However, mesopelagic waters presented a clear lower ETS activity, with little variation between depth levels. POC concentrations at ESTOC station were apparently constant and lower than 4 μM, although the sampling depths resolution is much lower than in our study (Neuer et al. 2007).

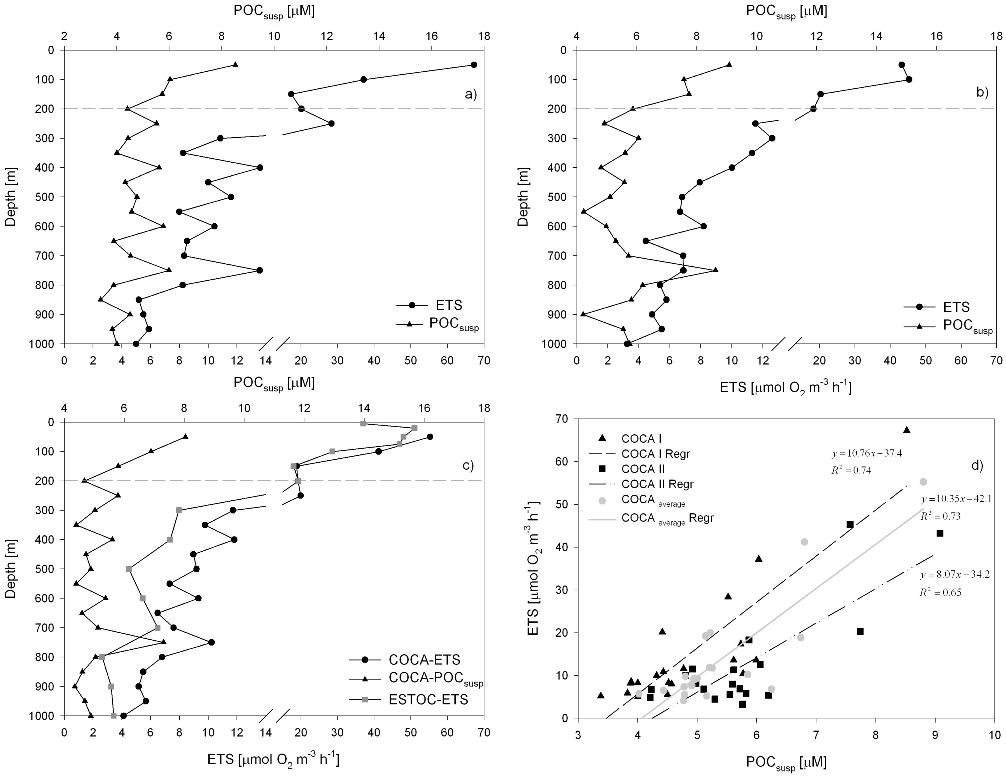


Figure 4.6: Vertical distribution of average (both sections) ETS and POC$_{susp}$: (a) COCA I cruise (September 2002). (b) COCA II cruise (June 2003). (c) COCA I-COCA II average of POC$_{susp}$ and ETS activity and ETS activity from the ESTOC station. (d) Regression lines for the relationship between ETS activity and POC$_{susp}$ concentration during COCA I, COCA II and the COCA average cruises. Notice the deep peaks in POC$_{susp}$ coinciding with the mesopelagic ETS maximums. The dashed lines stand for the interface between epipelagic and mesopelagic waters.

Regression lines were calculated to describe the dependence of respiratory ETS activity on suspended POC concentration. Figure 4.6d shows the relationship between the average POC$_{susp}$ concentrations and ETS activity from surface to 1000 m. We found that respiratory ETS activity was correlated with POC_{susp} in both seasons (September and June). The correlation was stronger in September ($R^2 = 0.74$) than in June ($R^2 = 0.65$). Again, this strong correlation suggests that respiration was directly or indirectly based on suspended particulate organic carbon.

4.4 Discussion

4.4.1 Epipelagic respiration

Respiratory ETS activity was in general high (> 0.7 mmol O_2 m^{-3} d^{-1}) in the whole epipelagic waters. Overall, the ETS values reported here are higher than those previously reported from open ocean waters of the north Atlantic (Arístegui and Harrison, 2002) and the Canary region (Arístegui et al., 2003). The high epipelagic ETS activities coincide also with high POC concentrations. Indeed, the mean values of POC_{susp} along the study sections (Table 4.1) were significantly higher than values observed in previous studies in this area (Arístegui et al., 2003; Alonso-González et al., 2009). POC_{susp} inputs to the epipelagic zone can be due to local primary production, lateral advection from the coast or atmospheric carbon inputs. Unfortunately, we do not have enough data to discriminate the contribution of these different inputs to the POC_{susp} pool in the epipelagic zone. Nevertheless, since a large metabolic deficit in the balance between plankton primary production and respiration has been routinely observed in this area (Duarte et al. 2001; Robinson et al. 2002), it seems reasonable to think that the high respiratory activity is fuelled by external organic matter inputs.

The meridional variability in ETS activity in the epipelagic waters is related to differences in the POC_{susp} concentrations (Table 4.1). The presence of the giant filament off Cape Blanc seems to cause the high POC concentrations values and hence the increase in ETS near the coast. Several studies have reported the influence of NW African filaments on biogeochemical properties, metabolism and plankton community structure (Gabric et al., 1993; Head et al., 1996; Olli et al., 2001, Arístegui et al., 2004). However, the observed zonal variability at the 26°N section cannot be explained only by the distribution of the suspended organic matter. As observed in Table 4.1, the highest ETS activity at 26°N values are closely related to the lower C/N ratios of the suspended organic matter (dashed lines), suggesting that the total amount of POC is not the only factor controlling the magnitude of the ETS activity. Another factor affecting the ETS activity may be the temperature of the water. Temperatures during September 2002 were generally higher than 21 °C at open ocean stations, decreasing to 18 °C toward the African coast. Temperature-dependence studies have shown that ETS activity increase with temperature (Ramírez et al. 2006). Therefore, the high ETS activity reported for the surface waters of open ocean stations could be associated both with less refractory material (lower C/N ratios) and higher temperatures.

4.4.2 Mesopelagic respiration

The mesopelagic waters are thought to be a zone of intense organic matter remineralization. Indeed, the major decrease in molecular-characterized material occurs in the mesopelagic zone, even though the larger relative decrease in flux is in the euphotic zone (Lee et al. 2004). The substantial decrease in the amount of organic matter that may be easily identified at the molecular level is indicative of a high bacterial and zooplankton activity. In spite of the key role of the mesopelagic waters as the site where the bulk of the exported matter from the epipelagic zone is remineralizated, to our knowledge there are no studies that tackle both the spatial and temporal respiration variability in the mesopelagic zone. In this work, we first provide a regional description of the mesopelagic respiratory variability, and then correlate it with the organic matter supply, its labiliy and the hydrological conditions.

The mesopelagic waters did not present a clear meridional ETS variability. As can be observed in Table 4.1, there are no large mesopelagic differences in POC_{susp} concentrations between the two sections, like in the epipelagic zone. This opposite trend with respect to the epipelagic waters could be a consequence of the different organic matter sources between both depth levels. The major source of POC_{susp} in the epipelagic waters is via primary production, which is highly variable with latitude and affected by mesoscale features. However, the potential sources of POC_{susp} to the mesopelagic waters are disaggregation of particles sinking from the epipelagic zone and lateral advection of suspended material at density gradients. Contrary to the epipelagic zone, the mesopelagic waters presented a marked zonal variability in ETS with the highest values in the open-ocean rather than near the coast. Surprisingly, POC_{susp} concentrations in the mesopelagic zone did not show important differences between coastal and oceanic stations. However, the C/N ratios in the mesopelagic waters were lower at open-ocean than coastal stations (Table 4.1). These results suggest that the source of the POC_{susp} at open ocean stations is not mainly related to the continental margin. Suspended particles at open ocean stations may result from sinking particles disaggregated by physical forces (Burd and Jackson, 2009) or by lateral transport of organic matter biosynthesized within the eddy-field generated upstream (south of the Canaries). According to this, a recent study focused on the organic matter composition indicated that the open ocean stations (approximately same stations) were more associated with chlorophyll-a and fresh cytoplasm components, while coastal station presented an strong heterotrophic signature (Alonso-González et al. 2010). Alternatively, the "freshness" of the POC_{susp} at open ocean stations may be related to the self-assembly of dissolved organic material yielding porous microgels (Chin et al. 1998), although we do not have any data supporting this hypothesis. In all cases these suspended particles seem to be a suitable nutrient-rich habitat to be colonized by microorganisms. Thus, the zonal variability in the mesopelagic ETS activity is found to be controlled by the degradation state of the suspended organic matter.

On the other hand, the mesopelagic waters showed an important temporal variability, being the ETS 30% higher in autumn than in late spring. Since mesoscale activity is higher during autumn than spring (Pacheco and Hernández-Guerra, 1999), we hypothesize that the temporal variability in the mesopelagic respiration was mainly controlled by fluctuations in the suspended organic matter supply from mesoscale activity, rather than from vertical sinking of particles from the euphotic zone after the late-winter/spring bloom. Several evidences supported this hypothesis: (i) the lack of a clear depth gradient in ETS activity suggest that its substrate is not related to the sinking particles, (ii) deep peaks in ETS activity were observed through the mesopelagic zone associated to POC_{susp} peaks, (iii) low export fluxes recorded with drifting sediment traps during the same study (unpublished), and (iv) a control station (ESTOC station, north of the Canary Islands), not affected by mesoscale activity, showed a clear lower ETS activity in the mesopelagic zone.

4.4.3 Contribution of POC_{susp} to water column respiration

The correlation between the particulate fraction of the organic matter pool and the ETS activity of planktonic communities could be expected a priori taking into account that the ETS activity represent also a living biomass (enzyme) measurement . However, total prokaryote abundances in the sampled mesopelagic waters represented only a small fraction of total POC. Prokaryote abundances ranged from 1 to 3 x 10^5 cells ml^{-1} (Gasol et al. 2009). Assuming an average (coastal and open ocean stations) carbon conversion factor of 20 fg $cell^{-1}$ (Fukuda et al. 1998) the maximum prokaryote abundance (3 x 10^5 cells ml^{-1}) yields a prokaryotic carbon content of 0.5 μmol C L^{-1}. This value represents less than 12% of total POC_{susp} and suggests that the correlation between ETS activity and POC_{susp} is not biomass dependent.

The regression between ETS and POC_{susp} in the whole water column (0-1000 m) suggests that respiratory activity is mainly supported by suspended particulate organic carbon. The correlation analysis reveals that POC_{susp} supports between 65% and 74% of the respiration in the water column. These results are in agreement with a recent box-model study in the Canary Current region, which provides evidence that POC_{susp} may account up to 60% of the total mesopelagic oxygen consumption (Alonso-González et al. 2009). Assuming that dissolved organic carbon contributes only 10% to 25% to total respiration in the mesopelagic zone (Arístegui et al. 2002; Arístegui et al. 2003), the contribution of the sinking POC would be lower than 25%. These estimations would explain the metabolic imbalance observed between sources and sinks in the dark waters of the North Atlantic when accounting only for the vertical sinking POC, collected with sediment traps (Reinthaler et al. 2006; Baltar et al. 2009; 2010).

In order to calculate the total sinking POC flux necessary to support the "oceanic" ETS activity found in this study, we transformed the average integrated (200-1000 m) ETS respiratory activity to actual respiration rates (R) in carbon units. R was calculated using a respiratory quotient of 1 and a R:ETS conversion factor ranging from 0.2 to 0.6 (see Baltar et al. 2010 for discussion). The average integrated "oceanic" ETS activity during this study was 8.3 mmol O_2 m^{-2} h^{-1} (Table 4.3). Applying the above conversion factors yield an average mesopelagic respiration rate of 40 to 120 mmol C m^{-2} d^{-1}. The measured sinking POC rates, which would represent a reasonable lower/upper scenario for passive sinking of POC in our oceanic stations range from 1 to 8 mmol C m^{-2} d^{-1} (Neuer et al. 2007; Alonso-González et al. 2010), which would account for 1 to 20% of R.

On the other hand, another simple evidence that supports the idea that the suspended POC is the principal substrate for respiration is the presence of intermediate depth peaks (400 to 800 m) of POC associated with ETS peaks, suggesting hot-spots of POC remineralization which might be laterally transported. Some of these deep POC maximums coincide with the depth of the Deep Scattering Layer (DSL), probably due to the disaggregation of fresh daily fecal pellets onto suspended particulate matter because of zooplankton swimming activity. In a previous work, Arístegui et al. 2003 reported the presence of mesopelagic ETS peaks associated with the relative maxima of DOC at the DSL. Recently, Baltar et al. 2009, also found significant correlations between POM and ETS in the bathypelagic waters (1000 m to 3000 m) of the subtropical North Atlantic. These findings, together with our results, indicate that microbial metabolism in the mesopelagic waters is mainly fuelled by suspended POC.

Why suspended particles show enhanced microbial activity vs. sinking particles? A possible explanation for the greater contribution of suspended matter to respiration is that these particles have longer residence times in the water column compared with the faster sinking particles. Therefore, they would be relatively more "accessible" than the faster particles, and hence more efficiently colonized by heterotrophic organism. Supporting this idea, Goutx et al. (2007) concluded that the faster settling particles (with indicators of ‘fresh material’) contain less bioavailable organic matter, whereas slower settling particles (with "reworked material" indicators) were more bioavailable. Biomarker compositions of samples from the Pacific Ocean also showed that material collected by in situ filtration, assumed to be suspended or with low settling rates, presents a remarkable abundance of labile organic compounds (Wakeham et al. 1988; Lee et al. 2000).

4.5 Conclusions

Epipelagic waters showed a clear meridional variability with highest ETS activities along the 21°N section, while no temporal variability was observed. On the contrary, mesopelagic waters, mainly at 26°N, presented an opposite zonal variability with higher ETS activities in open-ocean stations, coinciding with lower C/N ratios in the organic material. Temporal variability was also observed in the mesopelagic, being the ETS activity 30% higher in autumn than in late spring. The spatio-temporal variability in the mesopelagic waters was found to be related to the availability of suspended POC from mesoscale activity and its degradation state. The estimated integrated mesopelagic respiratory activities are comparable in magnitude to the epipelagic zone. This gives evidence of the importance of the dark waters of this coastal transition zone (CTZ) as a sink of carbon in the northeast Atlantic Ocean. Our results also indicate that R in this area is likely controlled by seasonal fluctuations in the lateral advection of suspended particulate organic carbon rather than by sinking particles from the euphotic zone. This finding could explain the apparent imbalance between the carbon sources and sinks in the mesopelagic waters when accounting only for the vertical sinking POC collected with sediment traps. This study underlines the fact that respiration changes in the deep ocean do not occur uniformly over time and space. Hence, the urgent need to expand our database on regional and large scales to gain a better understanding of the global carbon cycle in the ocean.

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Part III

Sinking particulate organic carbon: role of mesoscale eddies

CHAPTER 5

Regional and temporal variability of sinking organic matter in the subtropical northeast Atlantic Ocean: a biomarker diagnosis

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Abstract

Sinking particles through the pelagic ocean have been traditionally considered the most important vehicle by which the biological pump sequesters carbon in the ocean interior. Nevertheless, regional scale variability in particle flux is a major outstanding issue in oceanography. Here, we have studied the regional and temporal variability of total particulate organic matter fluxes, as well as chloropigment and total hydrolyzed amino acid (THAA) compositions and fluxes in the Canary Current region, between 20-30°N, during two contrasting periods: August 2006, characterized by warm and stratified waters, but also intense winds which enhanced eddy development south of the Canary Islands, and February 2007, characterized by colder waters, less stratification and higher productivity. We found that the eddy-field generated south of the Canary Islands enhanced by >2 times particulate organic carbon (POC) export with respect to stations (FF; far-field) outside the eddy-field influence. We also observed flux increases of one order of magnitude in chloropigment and 2 times in THAA in the eddy-field relative to FF stations. Principal Components Analysis (PCA) was performed to assess changes in particulate organic matter composition between stations. At eddy-field stations, higher chlorophyll enrichment reflected "fresher" material, while at FF stations a higher proportion of pheophytin indicated greater degradation due to microbes and microzooplankton. PCA also suggests that phytoplankton community structure, particularly the dominance of diatoms versus carbonate-rich plankton, is the major factor influencing the POC export within the eddy field. In February, POC export fluxes were the highest ever reported for this area, reaching values of $\sim$15 mmol C m^{-2} d^{-1} at 200 m depth. Compositional changes in pigments and THAA indicate that the source of sinking particles varies zonally and meridionally and suggest that sinking particles were more degraded at near-coastal stations relative to open ocean stations.

KEYWORDS: sinking organic matter, eddies, biomarkers

Contents

5.1 Introduction

Export of organic matter via particles settling out of the euphotic zone is one of the main mechanisms by which atmospheric CO_2 can be transported to the deep ocean. Organic matter production and its subsequent cycling by zooplankton and microbes are key processes in carbon export. Several studies suggest that mesoscale features may have a major impact on upper ocean biogeochemistry by enhancing biological activity (Falkowski et al., 1991; Sweeney, 2001; Bidigare et al., 2003; Benitez-Nelson et al., 2007; McGillicuddy et al., 2007). Recently, intense effort has been focused on complex multidisciplinary mesoscale programs, like E-Flux (North Pacific) and EDDIES (EDdy Dynamics, mixing, Export, and Species composition, North Atlantic) to address the role of mesoscale eddies in downward export flux. Surprisingly, both programs concluded that eddies did not enhance carbon flux, although they might increase the flux of biogenic silica (Benitez-Nelson and McGillicuddy, 2008). Moreover, these programs revealed our lack of knowledge about the complex mechanisms that control organic matter export from the euphotic zone within eddies.

Most sediment trap studies have measured bulk properties of the fluxes, such as total carbon and nitrogen, while individual organic compounds have received much less attention. Although total carbon and nitrogen values are useful, knowledge of the specific compounds provides more precise information on lability, interaction with other elements, and mechanisms of degradation (Lee et al., 2000; Sheridan et al., 2002; Ingalls et al., 2006). Unfortunately, there are only a limited number of studies, mainly focused on pigment composition determined in suspended material, that have documented changes in the organic matter composition within mesoscale features (Jeffrey and Hallegraeff, 1980; Olaizola et al., 1993; Rodríguez et al., 2003). More recently, some studies have highlighted the important role of frontal structures on organic matter fluxes by using sediment trap biomarkers in the Alborán Sea (Sánchez-Vidal et al., 2004; Tolosa et al., 2004, 2005) and in the northeast Atlantic Ocean (Goutx et al., 2005).

In this work we report, together with total POC/PON fluxes, mesoscale and regional trends in amino acid (THAA) and chloropigment compositions and fluxes obtained from free floating sediment trap deployments in the northeast Atlantic Ocean. Both THAA and chloropigments are useful indicators of decomposition, source and transport in the water column (e.g., Wakeham et al., 1997; Dauwe and Middelburg, 1998; Lee et al., 2000). Amino acids are structural components of proteins, making up a major fraction of characterized carbon in marine particulate matter (Lee et al., 2004). Since inorganic nitrogen can control the biological pump through its role as a limiting nutrient, the decomposition and remineralization of organic nitrogen as amino acids are of particular importance. Chloropigments are key indicators of organic matter diagenesis, since their origin stems from surface water communities. By following chlorophyll degradation as particles fall from the surface through the water column we can determine the ‘freshness’ of organic matter during its transport to deeper layers.

Our study was conducted during two different periods of the year: (i) August 2006 (cruise RODA I), characterized by warm and stratified waters, but also intense winds which enhanced eddy development south of the islands, and (ii) February 2007 (cruise RODA II), characterized by colder waters and less stratification. RODA I was planned to evaluate the role of the Canary eddy field in the enhancement of organic matter fluxes. RODA II was designed to look at the spatial variability in the Canary Current region, between 20-30°N, during the time of the year when primary production is highest (Arístegui et al., 2001; Hernández-León et al., 2007). We hypothesized (1) that organic matter fluxes would be more intense during the most productive season (February), increasing towards the upwelling region, and (2) that eddies south of the Canary Islands would induce changes in organic matter composition, as well as the enhancement of fluxes, compared with waters outside the eddy field.

5.2 Methods

5.2.1 Locating mesoscale eddies

Before the sediment traps were deployed, eddy features in the Canary Current region were identified by satellite sea-surface temperature (AVHRR) images. Once the approximate location was obtained, high-resolution expendable bathythermograph (XBT) transects were carried out to determine the thermal gradients of the mesoscale eddy field. Four eddies were selected for this study: two anticyclonic (AE1 and AE2) and one cyclonic, (CE1) during RODA I and one cyclonic (CE2) during RODA II (Figure 5.1, Table 5.1). Hydrographic sections across the selected eddies were performed to determine the exact location of the eddy core. Conductivity, temperature and depth were recorded with a SeaBird 911+CTD; temperature and pressure sensors were calibrated by the manufacturer just before the cruise. The fluorescence signal of in vivo chlorophyll a (chl-a) was measured with a Seapoint sensor.

5.2.2 Sample collection

Sinking particles were collected from 150 m depth at three eddy and two far-field (FF; outside eddy-field influence) stations during RODA I and from 200 m depth at CE2 and 8 non-eddy stations (S1-S8) southwestward of the eddy field, during RODA II (Table 5.1, Figure 5.1). We used a free-drifting multi-trap array holding 8 cylinders (9 cm diameter: 50 cm length and 0.005 m^2 collection area), similar to the model described by Knauer et al. (1979). NaCl ($\sim$45 g L^{-1}; analytical reagent-grade) was added to increase the salinity inside the traps. No poisons were used to retard bacterial decomposition during the deployment. Upon recovery (24 h after deployment), samples were visually checked and all fluid from each cylinder filtered onto pre-combusted (450 °C, 12 h) 25 mm Whatman GF/F filters. Swimmers were rarely present, but if so were processed in the laboratory according to the procedure described by Heussner et al. (1990). Large swimming organisms were removed by wet sieving through a 1 mm nylon mesh, while organisms <1 mm were handpicked under a microscope with fine-tweezers. The filters were wrapped

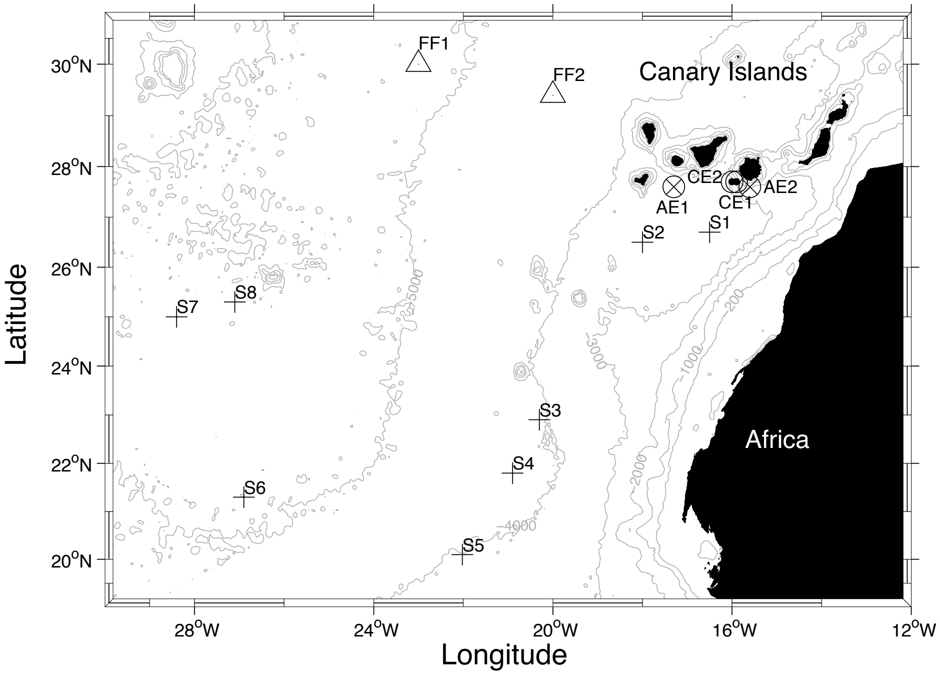


Figure 5.1: Map showing the location of the free-drifting sediment trap deployments carried out during August 2006 and February 2007. △ far-field, ⊗ anticyclonic eddy, ⊙ cyclonic eddy and + S stations.

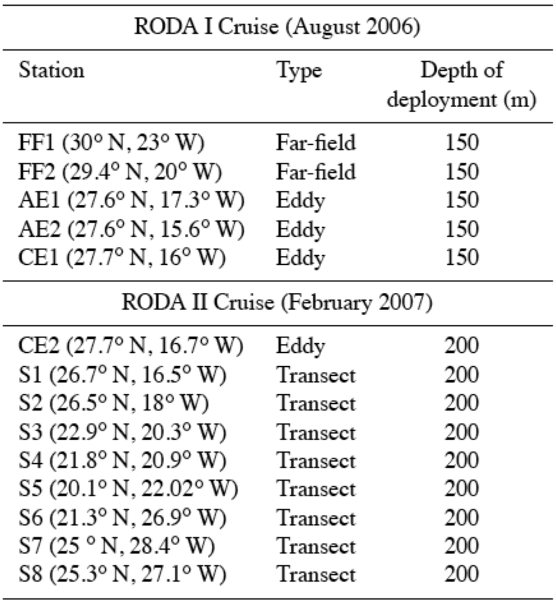
in pre-combusted aluminum foil and frozen at -20 °C until processing. One filter (corresponding to the filtration of 1 or 2 cylinders) was analyzed for POC/PON and one for chloropigments and amino acids in all samples except for CE2.

5.2.3 POM analysis

In the laboratory, filters for particulate organic carbon (POC) and nitrogen (PON) analysis were thawed and dried overnight at 60 °C, then placed overnight in a desiccator saturated with HCl fumes, dried again for 24 h in a second desiccator with silica gel and packed in ultra clean nickel sleeves.

The carbon analyses were carried out on a Perkin-Elmer 2400 CHN elemental analyzer (UNESCO, 1994). The DOC adsorption onto GF/F filters

Table 5.1: RODA drifting traps characteristics: type and station locations and depths of deployment. Time of sediment trap deployment was 24 h for both cruises. AE: anticyclonic eddy; CE: cyclonic eddy; FF: Far-field station.



RODA I Cruise (August 2006)		
Station	Type	Depth of deployment (m)
FF1 (30° N, 23° W)	Far-field	150
FF2 (29.4° N, 20° W)	Far-field	150
AE1 (27.6° N, 17.3° W)	Eddy	150
AE2 (27.6° N, 15.6° W)	Eddy	150
CE1 (27.7° N, 16° W)	Eddy	150
RODA II Cruise (February 2007)		
CE2 (27.7° N, 16.7° W)	Eddy	200
S1 (26.7° N, 16.5° W)	Transect	200
S2 (26.5° N, 18° W)	Transect	200
S3 (22.9° N, 20.3° W)	Transect	200
S4 (21.8° N, 20.9° W)	Transect	200
S5 (20.1° N, 22.02° W)	Transect	200
S6 (21.3° N, 26.9° W)	Transect	200
S7 (25 ° N, 28.4° W)	Transect	200
S8 (25.3° N, 27.1° W)	Transect	200

was subtracted from samples to avoid the overestimation of POC (Turnewitsch et al., 2007). DOC adsorption onto the filters ranged from 0.3-1.6 μmol C per 25 mm diameter GF/F filter (less than 3.5% of the POC signal), similar to the blanks reported by Moran et al. (1999) and Turnewitsch et al. (2007).

5.2.4 Pigment analysis

Chloropigments (chlorophyll-a, pheophytin-a, pheophorbide-a and pyropheophorbide-a) and fucoxanthin were determined using reverse-phase High Performance Liquid Chromatography (HPLC) as described in Lee et al. (2000). Pigments were extracted with 100% acetone and sonicated for 10 min. The tube containing the filter was centrifuged for 7 min at 3000 r.p.m., and the supernatant collected. Each sample was extracted twice because a third extract contains less than 1% of the total pigment content (Sun et al., 1991). Combined extracts were filtered through 0.2 μm Phenomenex nylon membrane filters and stored at -20 °C prior to pigment analysis. The filtered extract was diluted 20% with MilliQ water and injected onto a 5-μm Alltima C-18 column (250 mm x 4.6 mm i.d.). Detection was accomplished with a Shimadzu RF-551 fluorescence detector using an excitation wavelength of 440 nm and an emission wavelength of 660 nm and with a Shimadzu SPD-6AV UV absorbance detector using a wavelength of 446 nm. Retention times and chloropigment and fucoxanthin concentrations were determined by comparison of sample peaks with authentic pigment standards (chl-a: Turner Design; fucoxanthin: DHI Water and Environment; pheophorbide-a: Porphyrin Products; pheophytin-a and pyropheophorbide-a: synthesized from purified chl-a and analyzed spectrophotometrically after King, 1993). Duplicate analyses of the same extract agreed within 10%.

5.2.5 Amino acid analysis

Amino acids were measured on the same filters analyzed for pigments; this was accomplished by HPLC using precolumn *o*-pthaldialdehyde (OPA) derivatization after hydrolysis (Lindroth and Mopper, 1979; Lee and Cronin, 1982; Lee et al., 2000). Acetone-extracted filters were sealed in glass tubes under N_2 with 6N HCl plus 0.25% phenol and hydrolyzed for 20 h at 110 °C. Acid hydrolyzates were filtered through 0.2 μm membrane filters and stored at -20 °C prior to amino acid analysis. An acid extract aliquot was transferred to a combusted glass vial, evaporated under N_2, and dissolved in 60% MilliQ water: 40% methanol. A Waters 4 μm Nova Pack C-18 150 mm x 3.9 mm i.d. column equipped with a guard column was eluted at a flow rate of 1 ml/min. Mobile phases used in the gradient elution consisted of solvent A: 0.05M sodium acetate (pH 5.7) and 5% THF and solvent B: 80% methanol and 20% acetone. The program used was 44% B to 53% B in 30min, then to 100% B in 38 min. OPA-derivatized amino acids were detected by fluorescence (excitation λ=330 nm; emission λ=418 nm) and identified by retention time. Peak areas were converted to concentrations using response factors calculated using authentic standards. Standards used included a commercial amino acid standard mixture (Pierce Chemical, Standard H) with ornithine, β-alanine and γ-aminobutyric acid (Sigma Chemical) added. Duplicate analyses of the same hydrolyzate agreed within 10-15%.

5.2.6 Statistical analyses (PCA)

Principal Components Analysis (PCA) is commonly used in the analysis of complex organic datasets (Goñi et al., 2000; Ingalls et al., 2006; Goutx et al., 2007). It is a multivariate regression analysis that reduces a large number of variables to a few principal components. PCA was used here to quantitatively assess variation in the organic composition of sinking particles that were collected at eddy stations and over a range of latitudes. PCA was applied to pigment and THAA composition data. Prior to performing PCA, abundance data in mole% from each sample were standardized by subtracting the mean of all values and dividing by the standard deviation of all values (Dauwe and Middelburg, 1998; Dauwe et al., 1999; Sheridan et al., 2002). 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 were carried out on Sirius for Windows^{TM} Pattern Recognition System (version 7.0).

5.3 Results

5.3.1 Oceanographic settings

The vertical thermal structure across selected eddies revealed a clear upward (cyclonic) and downward (anticyclonic) perturbation of both the seasonal and main thermoclines (Figure 5.2). The 18 °C isotherm shoaled 65 m at CE1 and 70m at CE2 over horizontal scales of 70 and 20 km, respectively. On the contrary, AE1 and AE2 indicated depression of the 18 °C isotherm of 70 and 30 m, respectively. Figure 5.3 displays the vertical profiles of potential temperature and fluorescence at all stations sampled. Deeper mixed layers (125-165 m) were found in February as a result of winter cooling, while shallower mixed layers (<50 m) were observed in August, a period of warmer surface temperature (Figure 5.3a and 5.3 b). In August, the CE1 station, a cold-core cyclonic eddy, exhibited the lowest temperature values ranging from 22.8 °C at surface to 15.5 °C at 200 m, whereas the warmest temperatures were observed at the warm-core of the anticyclonic eddy AE1 ranging from 24 °C at surface to 18 °C at 200 m (Figure 5.3a). A counterintuitive cold signature in surface waters at AE2 was due to cold water encroachment from a nearby filament. In February, water temperatures were lower at coastal stations (S1, S2, S3, S4 and S5) than at the open-ocean stations (S6, S7 and S8), indicative of the influence of the nearby coastal upwelling (Figure 5.3b). The lowest temperature in the upper 75 m was found at CE2. Below the mixed layer, all stations were strongly stratified.

The deep fluorescence maximum (DFM) in August was located between 100-125 m in the far-field (FF) stations, shoaling to 50 m at AE2 and CE1 stations, where fluorescence was >0.8 volts (Figure 5.3c). AE1 exhibited an intermediated situation with a DFM at 75 m reaching 0.6. In February, the highest surface fluorescence values along the S stations were found at the coastal stations S3, S4 and S5, and were 2 to 3 times higher than at open ocean stations (Figure 5.3d). The only eddy station sampled during February (CE2) showed an extremely high fluorescence signal (>2 volts) between surface and 150 m.

5.3.2 Sinking POM fluxes

At all three eddy stations sampled during August 2006, the POC and PON fluxes at 150 m were higher than at FF stations (Figure 5.4a). POC fluxes ranged from an average value of 5.8±0.3 mmol C m^{-2} d^{-1} at FF stations to 9.7±2.0 mmol C m^{-2} d^{-1} at eddy stations (67% higher). PON fluxes were calculated to be 0.8±0.05 mmol N m^{-2} d^{-1} within the eddy cores relative to 0.4±0.007 mmol N m^{-2} d^{-1} at the FF stations (two times higher at eddy-field

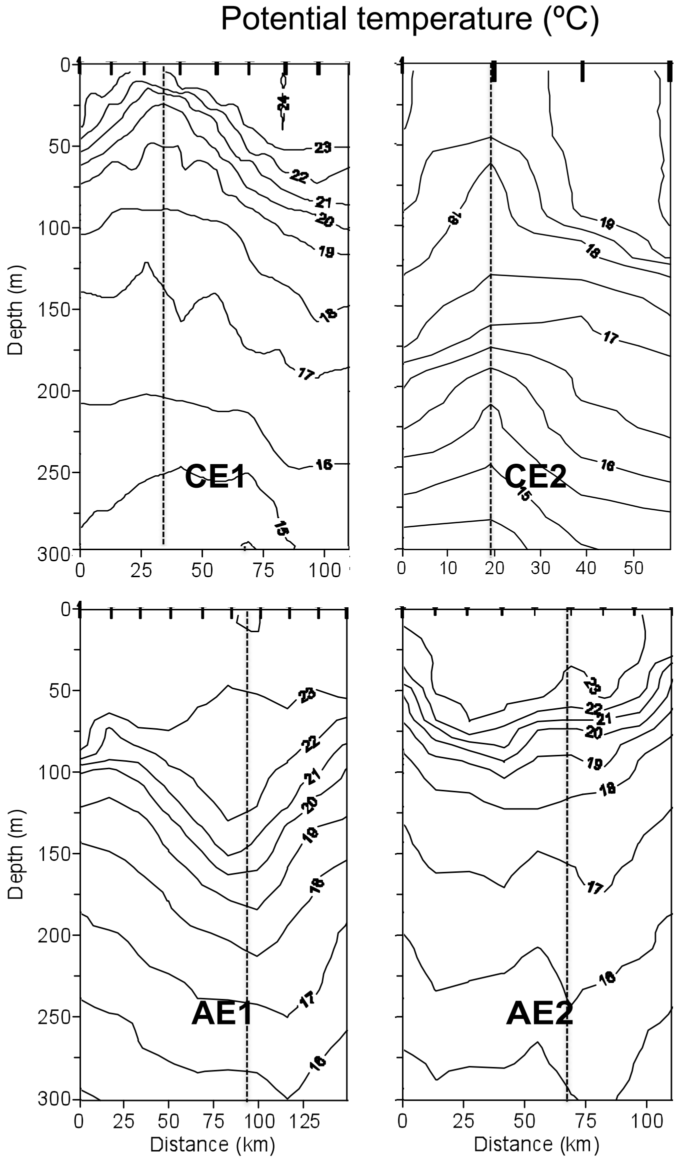


Figure 5.2: Vertical distribution of potential temperature across eddies CE1, CE2, AE1 and AE2. Ticks on the top axis represent XBT stations. Dashed lines indicated stations where sediment traps were deployed, coinciding with the location of the eddy core.

versus FF stations). POC flux within the CE2 eddy core (February 2007) was extremely high (28.5 mmol C m^{-2} d^{-1}): 2.3 fold higher than other stations,

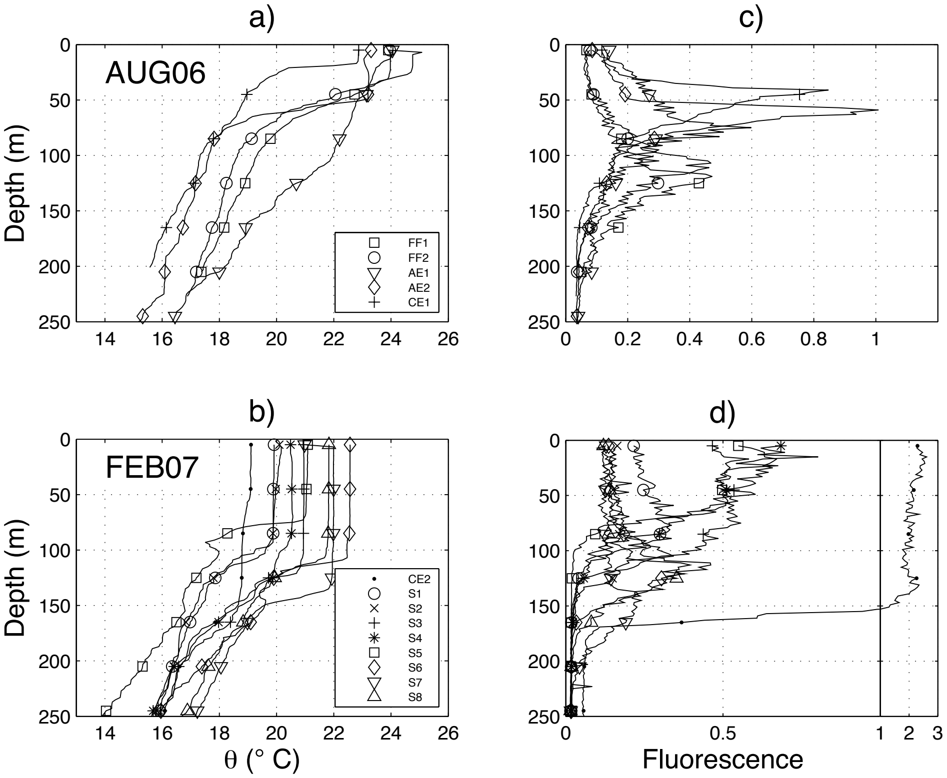


FIGURE 5.3: Depth profiles of potential temperature (a and b) and fluorescence (c and d) at eddy-field, far-field (FF) and S stations.

including S3, S4 and S5, which were close to the coastal upwelling. PON flux within the CE2 eddy was 1.1 mmol N m^{-2} d^{-1} at 200 m; approximately the same magnitude as stations south of the Canary Islands (S1 and S2), but lower than stations affected by the upwelling (S3-S5). Molar C/N ratios in August ranged from 8.2±2 at eddy-field stations to 14.1±0.7 at FF stations, always higher than the Redfield ratio (C/N = 6.6). The lowest value (C/N = 8.2) was observed at the CE1 eddy station. In February, C/N ratios were lower (5.5-10.3), except at eddy CE2, which exhibited an extremely high C/N ratio (C/N = 32).

Substantial temporal variability in POC and PON fluxes was found when comparing the two study periods (Figure 5.4a and 5.4b). POC and PON fluxes

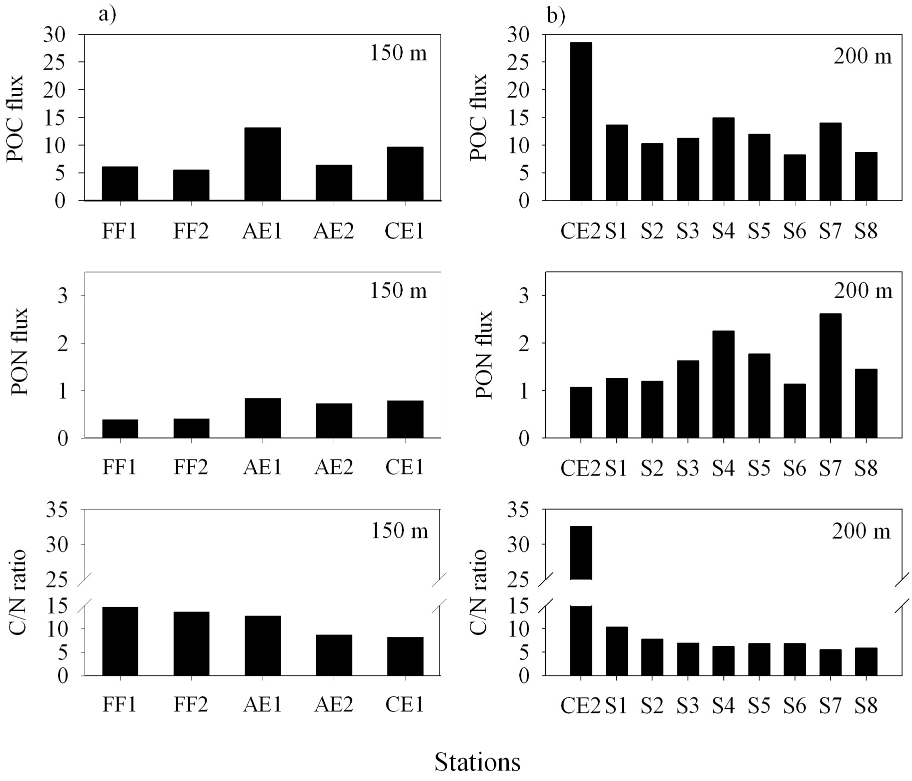


FIGURE 5.4: (a) POC and PON fluxes (mmol m^{-2} d^{-1}) and C/N ratios at eddy-field and far-field stations; (b) POC and PON fluxes (mmol m^{-2} d^{-1}) and C/N ratios at S stations.

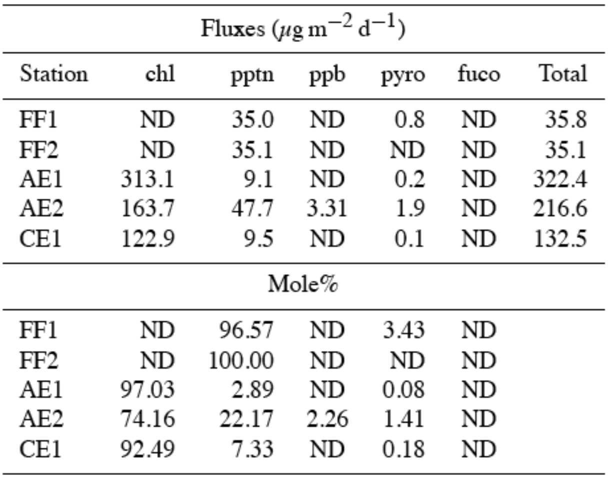
were about 2 times higher in February (8.3-28.5 mmol Cm^{-2} d^{-1}; 1.1-2.6 mmol N m^{-2} d^{-1}) than in August (5.5-13.1 mmol C m^{-2} d^{-1}; 0.4-0.8 mmol N m^{-2} d^{-1}). The mean C/N ratio in February samples was Redfieldian (6.6±1.9, excluding the CE2 station), while in August it was 11.6±2.9 (including eddy stations).

The regional variability in POC and PON fluxes was characterized by high fluxes and low C/N ratios (6.7±0.16) at stations affected by upwelling (S3-S5) and lower (30-35% less) POC and PON fluxes at stations S2, S6 and S8. Surprisingly, fluxes at the oceanic station S7 were comparable to the more coastal stations. S1, located south of the Canaries, exhibited a high POC and PON fluxes and also a high C/N ratio (Figure 5.4b).

5.3.3 Pigment fluxes and composition

Table 5.2 shows the variability in pigment fluxes and composition between eddy-field and FF stations. Pigment fluxes ranged over an order of magnitude from 35 to 322 μg m^{-2} d^{-1} (Table 5.2). They were 4 to 9-fold greater at the eddy-field stations, with an average value of 224 μg m^{-2} d^{-1}, compared to the FF stations (average value 35.3 μg m^{-2} d^{-1}). Among eddy-field stations, pigment fluxes in anticyclonic AE1 and AE2 eddies were higher than in the cyclonic eddy CE1.

Table 5.2: Chloropigment fluxes and compositions at 150 m in sediment trap samples from far-field (FF) and eddy-field stations during August 2006. chl: chlorophyll-a; pptn: pheophytin-a; ppb: pheophorbide-a; pyro: Pyropheophorbide-a: fuco: fucoxanthin. ND- not detected.

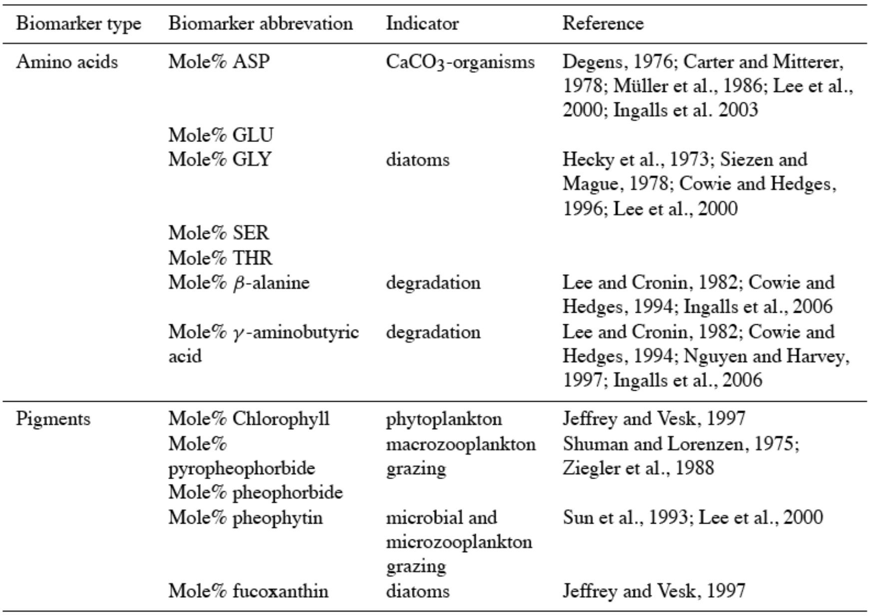


Fluxes (μg m^{-2} d^{-1})						
Station	chl	pptn	ppb	pyro	fuco	Total
FF1	ND	35.0	ND	0.8	ND	35.8
FF2	ND	35.1	ND	ND	ND	35.1
AE1	313.1	9.1	ND	0.2	ND	322.4
AE2	163.7	47.7	3.31	1.9	ND	216.6
CE1	122.9	9.5	ND	0.1	ND	132.5
Mole%						
FF1	ND	96.57	ND	3.43	ND	
FF2	ND	100.00	ND	ND	ND	
AE1	97.03	2.89	ND	0.08	ND	
AE2	74.16	22.17	2.26	1.41	ND	
CE1	92.49	7.33	ND	0.18	ND	

Differences in chloropigment composition were also found between eddy-field and FF stations (Table 5.2). The mole% of chl a, fucoxanthin, and chlorophyll degradation products (pheophytin-a, pheophorbide-a and pyropheophorbide-a), were calculated to examine the role of eddy-field stations in phytoplankton generation and degradation (see Table 5.3 for references).

Chl a was the major chloropigment present at all eddy-field stations making up an average of 88±12 mole% of pigments measured, while pheophytin-a dominated FF stations. Pheophorbide-a was present in small amounts at anticyclonic eddy AE2, suggesting a low zooplankton grazing activity (Shuman and Lorenzen, 1975; Ziegler et al., 1988). Pyropheophorbide-a ranged from 0.08 to 3.43 mole% at AE1 and FF1, respectively. Fucoxanthin was not detectable in these samples probably it could have been a detection problem due to sample size. Extensive degradation of pigments may also have been responsible for the near absence of fucoxanthin in these samples (Ingalls et al., 2006).

Table 5.3: Diagnostic table of amino acid and pigment biomarkers used to examine variation in organic composition of sinking particles collected during the RODA project.



Biomarker type	Biomarker abbrevation	Indicator	Reference
Amino acids	Mole% ASP	$CaCO_3$-organisms	Degens, 1976; Carter and Mitterer, 1978; Müller et al., 1986; Lee et al., 2000; Ingalls et al. 2003
	Mole% GLU		
	Mole% GLY	diatoms	Hecky et al., 1973; Siezen and Mague, 1978; Cowie and Hedges, 1996; Lee et al., 2000
	Mole% SER		
	Mole% THR		
	Mole% β-alanine	degradation	Lee and Cronin, 1982; Cowie and Hedges, 1994; Ingalls et al., 2006
	Mole% γ-aminobutyric acid	degradation	Lee and Cronin, 1982; Cowie and Hedges, 1994; Nguyen and Harvey, 1997; Ingalls et al., 2006
Pigments	Mole% Chlorophyll	phytoplankton	Jeffrey and Vesk, 1997
	Mole% pyropheophorbide	macrozooplankton grazing	Shuman and Lorenzen, 1975; Ziegler et al., 1988
	Mole% pheophorbide		
	Mole% pheophytin	microbial and microzooplankton grazing	Sun et al., 1993; Lee et al., 2000
	Mole% fucoxanthin	diatoms	Jeffrey and Vesk, 1997

Considerable variability in pigment fluxes was found when comparing the two periods of study. Average total pigment fluxes were 6-fold higher in February (838±502 μg m^{-2} d^{-1}), when primary production is known to peak

(Arístegui et al., 2001; Hernández-León et al., 2007), compared to August (Table 5.4). Important variability in chloropigment composition between August and February was also found. Chl a was highest at all stations during the February cruise and at the eddy-field stations in August, while pheophytin-a dominated FF stations during the August cruise. Chloropigment compositions in February samples and August eddy-field samples were similar.
Chloropigment fluxes vary spatially within this region, ranging from 376 (S7) to 1803 μg m^{-2} d^{-1} (S4), with enhanced export occurring over the Cape Blanc upwelling area (S4 and S5 stations). Lower fluxes were found at the most oceanic stations (S7-S8; Table 5.4). Differences in the chloropigment composition were also observed in February samples (Table 5.4). Mole% chl a was highest at all stations exceeding 80% (except S3); mole% pheophytin-a ranged from 2.4 to 96.8%; pheophorbide-a was present in a considerable proportion at S2 and S4, indicative of zooplankton grazing. Mole% pyropheophorbide-a follows the same trend as pheophorbide-a ranging from 0.08 to 7.16 mole%. Fucoxanthin was only detected at coastal stations S2 and S4.

Table 5.4: Chloropigment fluxes and compositions at 200 m depth obtained from sediment trap samples during February 2007. chl: chlorophyll-a; pptn: pheophytin-a; ppb: pheophorbide-a; pyro: Pyropheophorbide-a: fuco: fucoxanthin. ND Ð not detected.

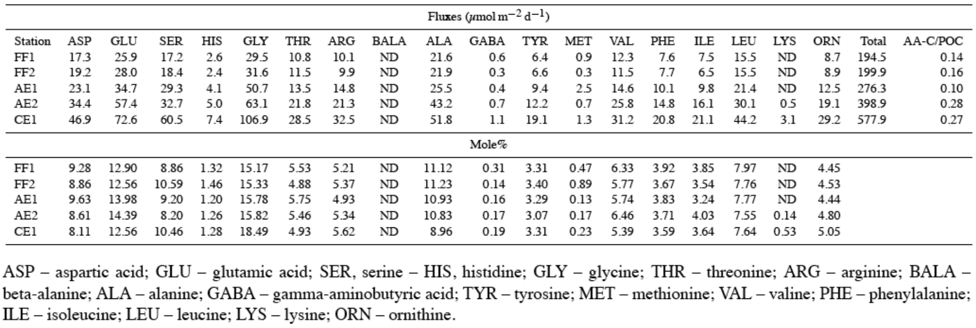
	Fluxes (μg m^{-2} d^{-1})					
Station	chl	pptn	ppb	pyro	fuco	Total
S2	673.2	31.5	15.8	11.6	1.18	733.2
S3	ND	465.3	6.3	3.7	ND	475.2
S4	1542.8	84.5	82.7	81.5	11.04	1802.6
S5	1046.8	91.4	4.0	2.2	ND	1144.4
S6	832.8	20.5	5.3	6.0	ND	864.5
S7	349.8	26.2	ND	ND	ND	375.9
S8	471.0	ND	ND	0.2	ND	471.2
	Mole%					
S2	89.73	4.30	3.17	2.58	0.22	
S3	ND	96.85	1.92	1.24	ND	
S4	80.94	4.55	6.53	7.16	0.81	
S5	91.00	8.16	0.53	0.31	ND	
S6	95.53	2.41	0.91	1.14	ND	
S7	92.87	7.13	ND	ND	ND	
S8	99.92	ND	ND	0.08	ND	

5.3.4 Total hydrolyzable amino acid (THAA) fluxes and composition

Amino acid export was in general higher (2 times) at eddy-field stations than at FF stations during August (Table 5.5). Furthermore, individual and total amino acids fluxes also revealed considerable differences between eddy types. Cyclonic eddy CE1 had a 2-fold higher amino acid flux compared to anticyclonic eddies AE1 and AE2 (Table 5.5).

Sinking particles had gross amino acid compositions similar to those reported by Lee and Cronin (1984) and Lee et al. (2000) for sinking particles in the Pacific Ocean. Aspartic acid, glutamic acid, serine, glycine and alanine were the most abundant amino acids, although there were differences in amino acid compositions between eddy-field and FF stations, as well as among the different eddies (Table 5.5). Mole% of glycine and glutamic acid (except CE1) were enriched at eddy-field stations relative to FF stations. On the other hand, mole% γ-aminobutyric acid (only at FF1), histidine and methionine were enriched at FF relative to eddy-field stations. Mole% aspartic acid, glutamic acid, threonine and alanine were enriched in anticyclonic eddies AE1 and AE2 relative to cyclonic eddy CE1, whereas mole% of serine and glycine were enriched at cyclonic eddy CE1.

Table 5.5: Amino acid fluxes and compositions at 150 m in sediment trap samples from far-field and eddy-field stations during August 2006. AA-C/POC is the contribution of amino acids to the total POC flux. ND -not detected.



Station	ASP	GLU	SER	HIS	GLY	THR	ARG	BALA	ALA	GABA	TYR	MET	VAL	PHE	ILE	LEU	LYS	ORN	Total	AA-C/POC
Fluxes (μmol m^{-2} d^{-1})																				
FF1	17.3	25.9	17.2	2.6	29.5	10.8	10.1	ND	21.6	0.6	6.4	0.9	12.3	7.6	7.5	15.5	ND	8.7	194.5	0.14
FF2	19.2	28.0	18.4	2.4	31.6	11.5	9.9	ND	21.9	0.3	6.6	0.3	11.5	7.7	6.5	15.5	ND	8.9	199.9	0.16
AE1	23.1	34.7	29.3	4.1	50.7	13.5	14.8	ND	25.5	0.4	9.4	2.5	14.6	10.1	9.8	21.4	ND	12.5	276.3	0.10
AE2	34.4	57.4	32.7	5.0	63.1	21.8	21.3	ND	43.2	0.7	12.2	0.7	25.8	14.8	16.1	30.1	0.5	19.1	398.9	0.28
CE1	46.9	72.6	60.5	7.4	106.9	28.5	32.5	ND	51.8	1.1	19.1	1.3	31.2	20.8	21.1	44.2	3.1	29.2	577.9	0.27
Mole%																				
FF1	9.28	12.90	8.86	1.32	15.17	5.53	5.21	ND	11.12	0.31	3.31	0.47	6.33	3.92	3.85	7.97	ND	4.45		
FF2	8.86	12.56	10.59	1.46	15.33	4.88	5.37	ND	11.23	0.14	3.40	0.89	5.77	3.67	3.54	7.76	ND	4.53		
AE1	9.63	13.98	9.20	1.20	15.78	5.75	4.93	ND	10.93	0.16	3.29	0.13	5.74	3.83	3.24	7.77	ND	4.44		
AE2	8.61	14.39	8.20	1.26	15.82	5.46	5.34	ND	10.83	0.17	3.07	0.17	6.46	3.71	4.03	7.55	0.14	4.80		
CE1	8.11	12.56	10.46	1.28	18.49	4.93	5.62	ND	8.96	0.19	3.31	0.23	5.39	3.59	3.64	7.64	0.53	5.05		

ASP – aspartic acid; GLU – glutamic acid; SER, serine – HIS, histidine; GLY – glycine; THR – threonine; ARG – arginine; BALA – beta-alanine; ALA – alanine; GABA – gamma-aminobutyric acid; TYR – tyrosine; MET – methionine; VAL – valine; PHE – phenylalanine; ILE – isoleucine; LEU – leucine; LYS – lysine; ORN – ornithine.

Maximum fluxes of amino acids occurred at the 200 m traps during February. Total mean fluxes of amino acids ranged from 197±3.8 (FF stations in August) to 838±502 μmol m^{-2} d^{-1} (February) (Tables 5.5 and 5.6). Fluxes also showed marked latitudinal differences, with highest fluxes (1447 and 1657 μmol m^{-2} d^{-1} at S3 and S4, respectively) in the Cape Blanc upwelling region. The mean amino acid flux at open ocean stations (S6 and S7) was 976±167 μmol m^{-2} d^{-1}, 40% less than the upwelling stations, but 30% higher than the more coastal stations S2 and S5 (Table 5.6).
Small but important spatial and temporal variations in THAA composition were evident (Table 5.6). S2, S3 and S4 were enriched in aspartic acid relative to S5, S6, S7 and S8. Serine was considerably higher (9.46±1.03 mole%) in the August samples at all stations than in February where a mean mole% serine of 6.97±0.6 was found. Glycine (15.52±1.3 mole%) was the most abundant amino acid in all August samples (FF and eddies) and was highest at cyclonic CE1 station (18.49 mole%). Mole% glutamic acid and glycine were the most abundant amino acids in all February samples. Non-protein amino acids, β-alanine and γ-aminobutyric acid, were present at stations S2, S4, S5 and S7 and may have been present in other samples but in concentrations below our detection limit.

Table 5.6: Amino acid fluxes and compositions at 200 m depth obtained from sediment trap samples during February 2007. AA-C/POC is the contribution of amino acids to the total POC flux. S8 amino acid sample was lost during analysis. See names for amino acids in Table 5.5. ND - not detected.

										Fluxes (μmol m^{-2} d^{-1})										
Station	ASP	GLU	SER	HIS	GLY	THR	ARG	BALA	ALA	GABA	TYR	MET	VAL	PHE	ILE	LEU	LYS	ORN	Total	AA-C/POC
S2	72.7	102.7	55.8	9.5	106.6	48.0	35.0	1.4	95.4	1.9	22.6	3.8	48.2	27.0	27.9	55.4	ND	41.4	755.2	0.33
S3	166.3	197.2	96.0	21.1	177.8	88.4	73.6	ND	178.6	0.3	40.7	10.8	90.1	51.2	51.2	104.7	2.7	96.7	1447.9	0.58
S4	166.4	216.0	115.2	19.4	247.5	103.2	81.7	1.2	214.2	3.6	48.5	6.4	110.4	61.4	68.3	122.4	1.6	110.3	1697.7	0.51
S5	55.6	81.9	44.0	8.7	83.3	39.6	31.8	0.3	80.3	3.0	20.4	13.9	42.6	24.8	25.7	51.8	ND	35.1	642.9	0.24
S6	78.8	113.6	68.1	12.5	119.8	47.4	42.9	ND	95.3	1.3	26.7	15.5	50.6	31.8	32.3	66.5	1.1	53.3	857.4	0.47
S7	102.4	165.7	71.0	15.7	131.2	61.4	54.0	ND	132.9	0.5	30.9	20.7	70.2	40.1	43.4	83.1	1.8	69.5	1094.6	
										Mole%										
S2	9.62	13.60	7.38	1.25	14.12	6.35	4.64	0.19	12.63	0.26	3.00	0.50	6.38	3.57	3.69	7.33	ND	5.48		
S3	11.48	13.66	6.63	1.46	12.28	6.11	5.08	ND	12.33	0.02	2.81	0.74	6.22	3.53	3.54	7.23	0.19	6.68		
S4	9.80	12.72	6.78	1.14	14.58	6.08	4.81	0.07	12.61	0.21	2.86	0.38	6.50	3.61	4.02	7.21	0.09	6.50		
S5	8.65	12.74	6.85	1.35	12.96	6.16	4.94	0.05	12.49	0.47	3.18	2.16	6.62	3.86	3.99	8.06	ND	5.46		
S6	9.19	13.25	7.94	1.46	13.97	5.53	5.00	ND	11.11	0.15	3.12	1.81	5.90	3.71	3.76	7.76	0.12	6.22		
S7	8.77	14.06	6.23	1.37	12.24	5.51	5.25	0.03	12.81	0.06	2.76	2.18	6.35	3.63	4.15	7.91	0.09	6.58		

5.4 Discussion

5.4.1 Eddy-field influence on organic matter fluxes

Several previous studies have focused on the changes induced by eddies on nutrient distributions, primary production, phytoplankton composition and organic matter export (Jeffrey and Hallegraeff, 1980; Falkowski et al., 1991; McGillicuddy et al., 1998; Garçon et al., 2001; Bidigare et al., 2003; Rodríguez et al., 2003; Benitez-Nelson et al., 2007; Maiti et al., 2008). These studies show the sequence of processes induced by cyclonic eddies in the ocean: upward displacement of isopycnal surfaces, nutrient injection into the euphotic zone, enhancement of phytoplankton growth, changes in plankton community structure, and differential effect on total particle export. However, there is little discussion of the variability in the composition of the exported organic matter, which can be used as a tracer of export and remineralization processes.

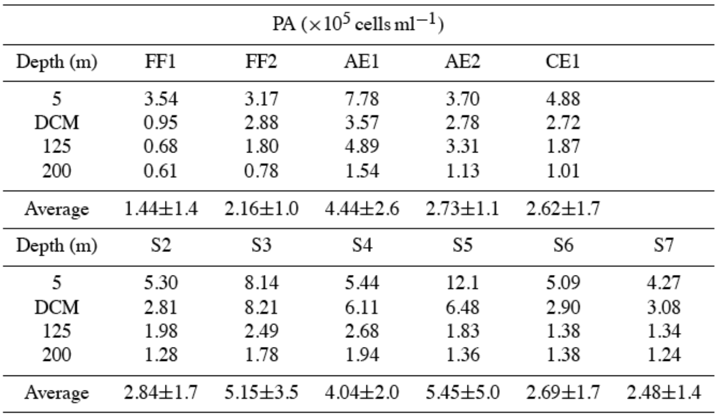
Our study reveals that bulk organic matter (POC and PON) fluxes were substantially influenced by the presence of the mesoscale eddy field south of the Canary Islands. In August, carbon and nitrogen exports within eddy-field stations were approximately 1.7 and 2 fold higher, respectively, than those measured at FF stations. During the bloom period (February), the only cyclonic eddy (CE2) sampled also had 2.3-fold higher POC export compared to ambient waters not affected by mesoscale eddies (including upwelling stations). These results indicate that the eddy field generated south of the Canary Islands may increase carbon export with respect to surrounding waters by >2 times. Our observations are different from results obtained in cyclonic eddies at the lee of Hawaii, which showed strong silica export (Benitez-Nelson et al., 2007) but no evidence of enhanced particulate carbon export (Benitez-Nelson and McGillicuddy, 2008; Buesseler et al., 2008; Verdeny et al., 2008). The difference in the biogenic silica export could be explained by the silicate distribution. On average, the nutrient source waters in the Pacific have higher ratios of silicic acid to nitrate and phosphate than those in the Atlantic (Ragueneau et al., 2000). Thus, diatoms would be favored in the opal-dominated Pacific Ocean relative to the carbonate-dominated Atlantic Ocean.

Why then does the Canary Island eddy field show enhanced POC export? To try to answer this question we first analyzed the fluxes and composition of chloropigments and amino acids within eddy-field and FF stations.

Total chloropigment fluxes within eddy-field stations were up to an order of magnitude higher than in FF stations. Since pigments are originally derived from surface phytoplankton, we may hypothesize that eddies enhance both primary production and sinking fluxes in this region. Alternatively, the higher pigment fluxes within eddy-field stations could originate from a lower pigment degradation rate relative to surrounding waters, although in this case, a lower prokaryotic abundance (PA) would be expected. However, the August eddies had 2 times higher PA compared to station FF stations (Table 5.7). Looking at the differences in chloropigment compositions between eddy-field and FF stations, we found that chl a is the dominant pigment within eddies, while at FF stations, pheophytin-a was dominant. Higher chlorophyll enrichment reflects ‘fresher’ material within eddies, while at FF stations a higher proportion of pheophytin-a illustrated the more important role of microbes and microzooplankton in organic matter degradation (Shuman and Lorenzen, 1975; Sun et al., 1993; Strom, 1993). The absence or very low fluxes of pheophorbide-a and pyropheophorbide-a at both FF and eddy-field stations indicate a minimum impact of grazing by mesozooplankton (Shuman and Lorenzen, 1975; Ziegler et al., 1988). Low pheopigment fluxes have been previously reported in the NE subarctic Pacific where the impact of mesozooplankton herbivory was negligible during summer (Thibault et al., 1999).

Total average amino acid fluxes within cyclonic and anticyclonic eddy-field stations were 2-fold higher than in FF stations, similar to POC flux, which is in agreement with the fact that a significant fraction of POC in surface waters consists of amino acids (Lee et al., 2004). Additionally, the comparison of the amino acids carbon content with respect to the total POC (AA-C/POC) give direct information on the contribution of THAA to the total POC flux. Table 5.5 shows an enhanced AA-C/POC within eddies, except at AE1, suggesting that the high POC flux observed in this station must come from other compounds. As is the case for chloropigments, the higher amino acid fluxes within eddy-field relative to FF stations are likely to be a result of enhanced primary production in the mesoscale structures caused by nutrient pumping. Although amino acid compositions are generally similar in both eddy-field and FF samples (Table 5.7), there are some marked differences.

Table 5.7: Prokaryotic abundance (PA) determined by flow cytometry in water samples from surface to 200 m during August 2006 and February 2007. S2, S3, S4 and S5 correspond with 'coastal' stations while S6 and S7 stand for oceanic stations.



PA ($\times 10^5$ cells ml^{-1})						
Depth (m)	FF1	FF2	AE1	AE2	CE1	
5	3.54	3.17	7.78	3.70	4.88	
DCM	0.95	2.88	3.57	2.78	2.72	
125	0.68	1.80	4.89	3.31	1.87	
200	0.61	0.78	1.54	1.13	1.01	
Average	1.44±1.4	2.16±1.0	4.44±2.6	2.73±1.1	2.62±1.7	
Depth (m)	S2	S3	S4	S5	S6	S7
5	5.30	8.14	5.44	12.1	5.09	4.27
DCM	2.81	8.21	6.11	6.48	2.90	3.08
125	1.98	2.49	2.68	1.83	1.38	1.34
200	1.28	1.78	1.94	1.36	1.38	1.24
Average	2.84±1.7	5.15±3.5	4.04±2.0	5.45±5.0	2.69±1.7	2.48±1.4

We used Principal Components Analysis (PCA) on a data set that included compositions (in mole%) of amino acids and chloropigments at FF and eddy-field stations with the aim of correlating differences in amino acid compositions with degradation state and source of organic matter (Fig 5.5a). Often, the first principal component (PC1) is associated with the degradation index of organic matter (Dauwe and Middelburg, 1998), but the source can be just as important as decomposition (Sheridan et al., 2002; Ingalls et al., 2006). In our case, the first principal component (PC1) indicates that the two FF stations differ in organic matter source. FF2 was enriched in glycine and serine, suggesting the presence of diatoms. FF1 was more enriched in aspartic and glutamic acids and γ-aminobutyric acid (GABA), suggesting a mixture of fresh calcium-carbonate associated organic matter and microbially degraded organic matter (Table 5.3). The second principal component (PC2) appeared to be related to organic matter degradation state, with pheophytin and GABA at the top and chl a towards the bottom of the PCA. There was a clear difference between eddy-field (negative site scores) and FF stations (positive site scores), consistent with the idea that there was more degraded organic matter at FF than at eddy-field stations (Figure 5.5a).

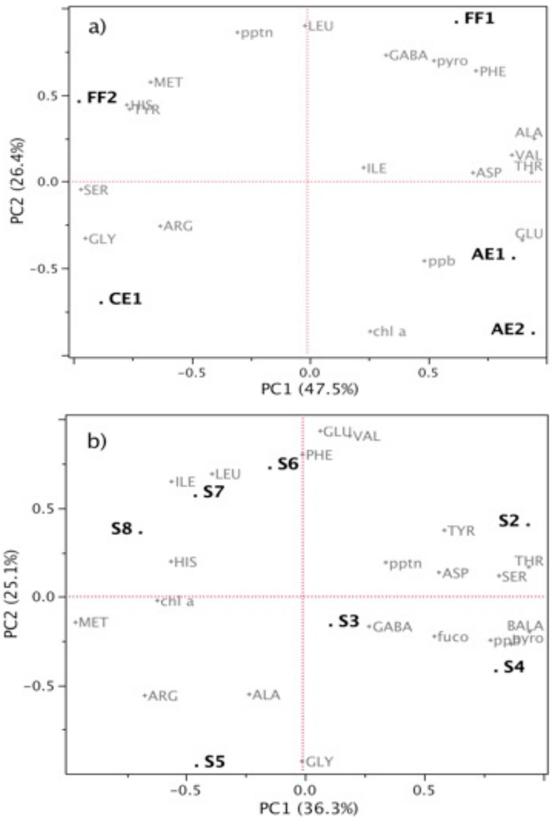


Figure 5.5: Principal components analysis (PCA) comparing: (a) eddyfield and far-field stations and (b) S station samples. The data set used included mole% of individual amino acids and chloropigments. The first two principal components (PC1 and PC2) explain most of the variance in the data set. See Tables 5.2 and 5.5 for pigments and amino acids names, respectively.

Our amino acid and chloropigment compositional data indicate low impact of grazing by micro and mesozooplankton within eddy-field stations (Tables 5.5 and 5.2). Therefore, the more likely fate of the organic matter produced by the eddy-field stations is downward export out of the euphotic zone as macroaggregates. This hypothesis is also corroborated by the current knowledge of the phytoplankton community structure of this area. The phytoplankton biomass of this region is dominated by small size cells such as picoplankton and flagellates (Head et al., 2002; Arístegui et al., 2004) and calcium-carbonate producing organisms (Fischer et al., 1996; Abrantes et al., 2002). These latter authors found that the composition of the sinking matter collected in deep sediment traps in the Canary region was dominated by coccolithophorids, which were found in both fecal pellets and aggregates all year round. Based on sediment trap data, Klaas and Archer (2002) suggest a more efficient transport of POC through the mesopelagic waters in 'calcifying' regions. Ingalls et al. (2006) also suggested that, in diatom-rich areas, the grazing pressure by mesozooplankton is higher than in $CaCO_3$-rich areas, and that the latter areas would have higher aggregate export instead of fecal pellet production. Indeed, Head et al. (2002) concluded that, with small size cells dominating phytoplankton biomass, only 15% of the carbon in phytoplankton standing stock could be directly used by mesozooplankton grazers.

Returning back to the question posed at the beginning of this discussion, we hypothesize that the impact of zooplankton grazing caused the difference in the relative export fluxes between eddies of Hawaii and Sargasso Sea (E-Flux and EDDIES programes) and the Canary Islands. In Hawaiian and Sargasso Sea eddies, zooplankton grazing was observed to be an important process controlling diatom blooms inside eddies (Benitez-Nelson and McGillicuddy, 2008; Goldthwait and Steinberg, 2008; Landry et al., 2008; Maiti et al., 2008). On the contrary, our results suggest that zooplankton grazing pressure had a minimum impact in the Canary Island eddy field. Indeed, Hernández-León et al. (2001) found a much lower zooplankton biomass in the core of a cyclonic eddy generated south of the Canary Islands compared to waters outside the eddy. Our findings are consistent with the hypothesis proposed by the above programs of zooplankton grazing as a mechanism to reduce POC export within eddies. However, based on our PCA analysis, we also suggest that phytoplankton community structure, particularly diatom-rich vs. $CaCO_3$-rich, is a major factor influencing the zooplankton grazing pressure and subsequent organic matter export within the eddy-field stations. Moreover, our amino acid compositional data are in agreement with a highly carbonate-ballasted organic matter. In the last decade, several works have indicated that a significant fraction of organic matter produced in surface waters is transported to depth associated with mineral ballast (Armstrong et al., 2002; Francois et al., 2002), and specially with carbonate (Klaas and Archer, 2002). Therefore, the enhanced POC flux observed in the eddies generated south of the Canary Islands could be due to the increased particle settling velocity in highly carbonate-ballasted systems in comparison to those in opal-ballasted system (like Hawaii) as also suggested by a recent study off Cape Blanc (Iversen et al., 2010).

5.4.2 Cyclonic vs. anticyclonic eddies

In order to determine biogeochemical differences between eddies, we compared bulk organic matter export in combination with pigment and amino acid compositions and fluxes. Since the anticyclonic eddy AE2 was sampled during its early formation state (close to the coast of Gran Canaria Island), we focused our comparative analysis on the anticyclonic AE1 and cyclonic CE1 eddies. POC fluxes were 1.3 fold higher within AE1 relative to CE1, while PON fluxes were similar. Thus C/N ratios were higher (12.8) at AE1 than at CE1 (8.2). Although these total organic carbon and nitrogen values are useful, knowledge of the specific compounds provides us with better information about the different types of eddies.

Comparing total amino acid fluxes between eddies, we found that CE1 had a 2-fold higher total amino acid flux than AE1. Within cyclonic eddies an upward displacement of nutrient-rich isopycnal surfaces occurs, presumably yielding an external source of nutrients from the thermocline to the euphotic zone (McGillicuddy and Robinson, 1997). On average, the supply of nitrate to the euphotic zone would be balanced by the export of organic nitrogen contained mainly in sinking particles exported to the mesopelagic zone. Therefore, the greater THAA flux at CE1 eddy station relative to AE1 eddy is consistent with a higher surface new primary production reaching the trap as a result of a nutrient enrichment of surface waters. The AE1 eddy station presented a higher prokaryotic abundance (PA) than that at CE1 (Table 5.7). Therefore, the greater THAA flux at CE1 relative to AE1 could be caused by a lower heterotrophic activity at CE1 resulting in a higher fraction of net primary production reaching the trap. This would also explain why C/N ratios were lower at CE1 than at AE1.

However, when comparing the total chloropigment fluxes between eddies an opposite pattern to the amino acids is observed. In this case, we found that within AE1 chl a fluxes were 2.4 fold higher than in CE1. Several other studies have found this pattern as well. Moore et al. (2007) found that, based on 6 years of satellite and in situ estimates of chl a, anticyclonic eddies in the Western Australian Coast showed higher phytoplankton biomass than cyclonic. Other studies found that anticyclonic eddies contain relatively elevated chl a concentrations that originated from entrainment (during eddy formation) of water enriched in chl a from the continental shelf or upwelling areas (Arístegui et al., 1997; Ginzburg et al., 2002; Waite et al., 2007). A possible explanation for this counterintuitive result could be associated with the eddy's intrinsic physical structure. Anticyclonic eddies have a deeper mixed layer than cyclonic eddies (Figure 5.3a), so vertical mixing is more pronounced (up to 20 times faster and deeper) than in cyclonic eddies, yielding a 'vertical' homogeneity (Thompson et al., 2007). Thus, cells are displaced vertically from surface to deeper layers within anticyclonic eddies (see deeper DFM at AE1 relative to CE1, Figure 5.3 c). Shade-adapted (deeper) cells have higher chl:carbon ratio than sun-adapted (shallower) cells (Falkowski, 1980; Laws and Bannister, 1980; Geider, 1987; Armstrong, 2006), suggesting that at equal carbon export, a higher chl a flux within anticyclonic eddies would occur. An alternative explanation to the observed difference in standing stocks between both eddy types could be related to the eddy/wind interactions. Based on an eddy/wind interaction model, McGillicuddy et al. (2007) predicted a downwelling in the interior of cyclonic eddies, and a divergence in the center of anticyclonic eddies. This situation could led to the enhanced chloropigment flux observed within AE1.

PCA analysis also reveals important differences in amino acid and chloropigment compositions between CE1 and AE1 eddies (Figure 5.5a). CE1 was enriched in mole% serine and glycine suggesting enrichment in diatom-derived organic matter. However, anticyclonic eddies were more enriched in mole% aspartic and glutamic acids. These two latter amino acids often indicate the presence of $CaCO_3$-forming organisms (Degens, 1976; Carter and Mitterer, 1978; Muller et al., 1986; Lee et al., 2000; Ingalls et al., 2003), suggesting that the dominant phytoplankton organisms within AE1 were coccolithophorids. These organisms tend to thrive in layers of reduced light intensity and low nutrient concentrations, which is in agreement with the deeper DFM of AE1 relative to CE1. Therefore, the greater presence of coccolithophorids in anticyclonic eddies would explain the higher fluxes of chl a and aspartic and glutamic acid. Regarding organic matter lability, both types of eddies showed similar negative site scores on PC2, suggesting that organic matter exported from CE1 and AE1 had similar degradation states.

5.4.3 Regional variability in organic matter composition and flux

Particulate organic carbon fluxes at 200 m ranged from ∼8.5 mmol C m^{-2} d^{-1} at open ocean stations S6 and S8, to ∼12 mmol C m^{-2} d^{-1} at S1 and S2 stations located south of the Canary Islands, to ∼13 mmol C m^{-2} d^{-1} at stations S3, S4 and S5 affected by upwelling. These POC export values are the highest ever reported for this area, probably because it is the first time that they were measured during the phytoplankton bloom period. In autumn, the POC sinking flux, measured with drifting traps at about 200 m, was approximately 0.3mmol C m^{-2} d^{-1} at the ESTOC time series station (North of the Canary Islands, Neuer et al., 2007). However, POC fluxes collected with similar traps at 150-200 m, along two coastal-ocean sections (26°N and 21°N), during summer and fall, outside the influence of the intense eddy field and the coastal upwelling, varied on average from 0.7 to 4.9 mmol C m^{-2} d^{-1} (J. Arístegui, unpublished). All these results reflect a strong spatio-temporal variability of POC fluxes within this region.

The elemental composition of sinking particulate organic matter was relatively uniform and close to the classical Redfield ratio (C/N = 6.4) at the upwelling and open ocean stations. However, south of the Canary Islands (S1 and S2 stations) C/N ratios were 9.1, which is consistent with the high remineralization rates reported for this area (Arístegui et al., 2005). Interestingly, contrary to what might be expected from the August eddy results, the C/N ratio in trap material collected at 200 m in the CE2 eddy was extremely high (C/N = 32), even higher than at the FF stations during August. Unfortunately, we do not have chloropigment and amino acid data within the CE2 eddy to try to explain this result. However, the CE2 eddy had an extremely strong fluorescence maximum (Figure 5.3d) and a high gross primary production rate (Arístegui and Alonso-González, unpublished), so we might expect sinking of fresh phytoplankton-derived material. Thus, assuming that this high C/N value is correct, it probably reflects a carbon excess more than the presence of highly refractory organic matter. The molar C/N ratios of transparent exopolymer particles (TEP) are generally above the Redfield ratio, with a mean value of 26 (Engel and Passow, 2001). Thus, production of TEP during a bloom condition is one mechanism that could yield such high C/N ratio within CE2. Alternatively, the high C/N ratios measured at FF stations during August and within CE2 during February may be related to terrestrial organic matter inputs, although we do not have any data supporting this hypothesis.

Chloropigment fluxes clearly showed a decrease with increasing distance from the coast, similar to the POC flux. A simple explanation for this decrease could be that gross primary production was 1.2 to 7 times lower at open ocean stations than at more coastal stations (Arístegui and Alonso-González, unpublished). On the contrary, THAA fluxes did not show as clear a pattern as chloropigments, with high amino acids fluxes at open ocean station S7.

The composition of sinking particulate organic matter showed several differences in the PCA analysis (Figure 5.5b). PC1, which explains 36% of the variance, appears to reflect the organic matter degradation state, with the chl a at the left and the pheophytin and Gaba towards the right of the PCA. PC2 appears to be related to the organic matter source, with glycine at the bottom and glutamic and aspartic acids towards the top of the PCA. Thus stations closer to the coast (S2, S3, S4 and S5) appear to be dominated by diatom, bacterial and zooplankton indicators, suggesting that the organic matter biosynthesized was actively remineralized by heterotrophic organisms. This is corroborated by the significant higher prokaryotic abundance (PA) found in these stations relative to open ocean stations ($p<0.05$, Table 5.7). However, the open ocean stations S6, S7 and S8 were more associated with chl a and fresh cytoplasm components, which is in agreement with the low PA observed in this stations (Table 5.7). Again, the relationship between the magnitude of the fluxes and quality of organic matter suggests that stations with high carbon fluxes present ÒreworkedÓ material, whereas stations with low carbon fluxes show more ‘fresh’ material. The capture of laterally advected particles from the upwelling margin could be one reason for the lower lability of the coastal samples. If a significant proportion of the particles collected at the coastal station were laterally advected, having a longer residence time in the water column, they might be relatively older compared to the particles traveling vertically. Indeed, recent studies have demonstrated that the lateral transport of particulate material from the African coast is a key process controlling the organic carbon dynamic in this area (Karakas et al., 2006; Alonso-González et al., 2009; Fischer et al., 2009). Another possible explanation for this counter-intuitive result could be that in coastal stations the heterotrophic community (particularly mesozooplankton) is more active than in open ocean stations. This hypothesis is supported by the relative enrichment of pheophorbide-a and pyropheophorbide-a in coastal stations, indicating zooplankton grazing activity.

5.5 Conclusions

In summary, we found that the eddy field generated south of the Canary Islands enhanced POC export with respect to open ocean waters by >2 times. Flux increases of one order of magnitude in chloropigment and 2 times in THAA are also observed in the eddy-field relative to FF stations. The enhancement of particulate organic matter fluxes by mesoscale eddies in The Canary Islands seems to be related to the low zooplankton grazing pressure. Our findings are consistent with the hypothesis proposed by the E-Flux and EDDIES programs of higher trophic levels reducing POC export within eddies. However, we suggest phytoplankton community structure, particularly diatom-rich vs. $CaCO_3$- rich organisms, ballasting, and subsequent zooplankton activity as major factors influencing organic matter export within eddies. Overall, eddies during the August period behaved partly like the ambient waters during the bloom period, enhancing POC, PON, amino acid and pigment fluxes. However, several differences were found between the different types of eddies. Cyclonic eddy CE1 had higher total amino acid flux than the anticyclonic eddies, while the contrary is true for pigments. The organic matter composition was different, with the cyclonic eddy more enriched in diatom-derived organic matter and the anticyclonic eddies more enriched in $CaCO_3$-forming organisms. At eddy stations, higher chlorophyll enrichment reflects ‘fresher’ material, while at FF stations a higher proportion of pheophytin illustrates the more important role of microbes and microzooplankton in degrading organic matter. These results suggest that the eddy field generated by the Canary Islands may simulate bloom conditions acting as ‘fresh’ organic matter pump to the mesopelagic waters.

Our February POC export values are the highest ever reported for this area, probably as result of measuring fluxes during the phytoplankton bloom period. This large variability must be taken into account in building annual carbon budgets for the region. Both, pigments and THAA compositional changes show that the source of sinking particles varies zonally and meridionally and suggests that sinking particles were more degraded at coastal relative to open ocean stations. The capture of laterally advected particles from the upwelling margin together with an active heterotrophic community at coastal station seem to be the reason for the greater degradation of organic matter in the coastal samples.

Acknowledgments

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5.6 References

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Chapter 6

Increased carbon sequestration by mesoscale eddies in the northeast Atlantic Ocean

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Abstract

It is generally assumed that episodic nutrient pulses by cyclonic eddies into surface waters support a significant fraction of the primary production in subtropical oceans. However, contradictory results related to the role of cyclonic eddies on particulate organic carbon (POC) export have been reported.

Here we present new results from a sediment trap mooring deployed within the path of cyclonic eddies generated from the Canary Islands over a 1.5-year period. We find that, during summer and autumn (when surface stratification is stronger and coccolithophorids dominate), POC export due to cyclonic eddies was 2-4 times higher than observed for non-eddy conditions. However, during late winter and spring (when mixing is strongest and the diatom-rich seasonal phytoplankton bloom occurs), no significant enhancement of POC export associated with eddies was observed. Our data thus illustrate how the balance between $CaCO_3$ and biogenic opal production influences POC export. The absence of an eddy effect on POC flux during the late-winter phytoplankton bloom most likely result from a bypassing of mesopelagic traps by vertically migrating zooplankton and a loss of material to dissolution and disaggregation in the deep scattering layer. We also show that material exported during the late-winter bloom is mainly recycled in the mesopelagic zone, whereas cyclonic eddies during the summer-autum stratification period enhance carbon sequestration below 1000 m depth, highlighting the important role of these features on the global carbon cycle.

KEYWORDS: cyclonic eddies, migrant zooplankton, carbon demand, carbon sequestration, biomarkers

Contents

6.1 Introduction

Which mechanisms controls carbon export to the deep ocean is a major outstanding question in oceanography. Sinking particulate organic carbon (POC) fluxes measured with current techniques (sediment traps and Thorium) do not account for the oxygen utilization rates in the deep ocean (e.g. Steinberg et al. 2008; Baltar et al 2009). This apparent imbalance indicates either the existence of unknown sources of organic carbon, an overestimation of the metabolic activity in the dark ocean, or the fact that the vertical particle flux is underestimated.

A possible mechanism to supply some of the "missing carbon" locally would be intermittent and undersampled carbon pulses by mesoscale eddies. Nevertheless, field studies regarding the effects of eddies on organic matter fluxes have shown conflicting results. A limited number of studies have shown direct evidence of enhanced carbon export mediated by mesoscale eddies (e.g. Sweeney, 2003; Bidigare et al. 2003; McGillicuddy et al. 2007). However, recent interdisciplinary programs that focused on the effects of eddies on carbon export (E-Flux in the North Pacific and EDDIES in the North Atlantic) have shown unexpected results. Surprisingly, both programs concluded that the studied eddies did not enhance carbon flux, although they increased the flux of biogenic silica (e.g. Benitez-Nelson and McGillicuddy, 2008; Maiti et al. 2008). More recently, a study conducted in the Canary Current region reported new results that fuel this controversy (Alonso-González et at. 2010a). These authors found that the eddy-field generated south of the Canary Islands enhanced by >2 times POC export with respect to stations outside the eddy-field influence.
One hypothesis proposed by the E-Flux and EDDIES programs was that intermittent carbon pulses might be undersampled during research cruises. Determining the influence of eddies on carbon export and organic matter composition using time series observations is needed to test this hypothesis.

Here, with the aim of addressing this challenge, we measured POC, amino acid and chloropigment fluxes and compositions in samples collected from a mooring deployed in the area of generation of cyclonic eddies south of Gran Canaria (Canary Islands). This island sheds oceanic eddies all year round (Sangrá et al. 2007; Jimenez et al. 2008; Piedeleu et al. 2009), making this region the perfect place to investigate the effect of eddies on the biogeochemistry of an oligotrophic subtropical system. This study reports results from the longest time series to date monitoring organic matter composition and export within cyclonic eddies to date and the unique that integrates its annual effect.

6.2 Methods

6.2.1 Studied area and sampling

A sediment trap mooring was deployed at 27° 29’ 57”N; 016° 15’ 19”W, 3600 m bottom depth, for three 6-month periods (from June 2005 to December 2006). Rough sea conditions forced the mooring location to be situated closer to the islands during Period III (27° 30’ 4”N; 15° 44’ 32”W, 2500 m bottom depth). The mooring accommodated 3 PPS3/3 sediment traps (TECHNICAP) at 290, 500 and 1000 m, programmed to collect particles (0.125 m^2 collection area) in a time-series mode, with a sampling interval of 15 days. All sediment trap cups were poisoned with mercuric chloride and samples processed according to the protocol described in detail in Heussner et al. (1990).

In order to monitor the presence of "eddy" and "non-eddy" conditions, Aanderaa RCM7/8 current-meters were placed on the mooring 2 m below the sediment trap depths. The presence of eddies was monitored by combining current-meter temperature anomalies with sea surface temperature (SST) and chlorophyll from satellite images. The negative temperature anomalies from the mooring, associated with cyclones, matched well with SST negative anomalies obtained from satellite images (see Piedeleu et al. 2009 for more details).

6.2.2 POC and biomarkers analysis

Particulate organic carbon (POC), amino acids and chloropigments were measured as described earlier (Alonso-González et al. 2010). Organic carbon analyses were performed with a Perkin-Elmer 2400 CHN elemental analyzer (UNESCO, 1994). DOC adsorption on GF/F filters ($< 4\%$ of the POC signal) was subtracted from samples to avoid overestimation of POC (Turnewitsch et al. 2007).

Chloropigments (chlorophyll a, pheophytin a, pheophorbide a, and pyropheophorbide a) were determined using reverse-phase High Performance Liquid Chromatography (HPLC) as described in detail by Lee et al. (2000) and Wakeham et al. (2009).

Amino acids were measured by HPLC on the same filters analyzed for pigments, using pre-column o-pthaldialdehyde (OPA) derivatization after hydrolysis (Lee et al. 2000; Wakeham et al. 2009). In addition, we calculated the degradation state of organic matter in each sample using an amino-acid-based Degradation Index (Dauwe and Middelburg, 1998; Ingalls et al. 2003).

6.2.3 Principal components analysis (PCA)

Principal components analysis (PCA) was used here to quantitatively assess variation in the organic composition of eddy vs. seasonal bloom sinking particles that were collected at 290, 500 and 1000 m depth in the Canary Current region. PCA is commonly used in the analysis of complex organic gechemical datasets (Goñi et al., 2000; Ingalls et al., 2006; Goutx et al., 2007). We applied PCA to a dataset that included both pigment and total hydrolyzed amino acid (THAA) composition. Prior to performing the analysis, the mole% values of individual THAA and pigment compounds in each sample were standardized by subtracting the mean of all values and dividing by the standard deviation of all values for each class separately (Dauwe and Middelburg, 1998; Sheridan et al. 2002). All PCA for this study were carried out on Sirius for Windows ^{TM} Pattern Recognition System (version 7.0).

6.3 Results and Discussion

6.3.1 Impact of cyclonic eddies and zooplankton activity on organic matter fluxes and composition

The Eulerian measurements recorded at this fixed position allow us to evaluate the impact of cyclonic eddies on the local biogeochemistry. An average of 10 cyclonic eddies per year, 5 during summer/autumn and 5 during winter/spring were registered (Piedeleu et al. 2009). To observe the effects of the passage of each cyclonic eddy, Figure 6.1 illustrates the temporal evolution of POC, chloropigments and amino acids fluxes as well as the "eddy" (grey bars) and "non-eddy" (white spaces) conditions. However, due to the difficulty in assessing the individual contribution of each eddy to the total flux, we summed fluxes during eddy and fluxes during non-eddy periods separately for each of the 3 periods. This averaging approach is feasible because of the short time separation ($<$10 days) between eddies, which results in an overlap of their effects.

Our results reveal a significant influence of cyclonic eddies on POC fluxes during summer and autumn (Periods I and III), when surface waters are stratified and eddies are more intense due to the combined effect of flow perturbation and wind forcing (Arístegui et al. 1997; Jiménez et al. 2008). In these periods, average carbon export during eddy conditions was approximately 2 to 4 fold higher than that measured during non-eddy conditions (Table 6.1). However, during Period II (winter and spring), cyclonic eddies seem to have little effect on POC export compared to non-eddy conditions (Table 6.1, Figure 6.1).

In periods I and III, total chloropigment fluxes during eddy conditions were also 2 to 4 times higher than during non-eddy conditions (Figure 6.1). Since pigments are originally derived from surface phytoplankton, we may hypothesize that cyclonic eddies enhanced both primary production and POC fluxes in this region. Total amino acid fluxes at 500 and 1000 m were up to an order of magnitude higher within cyclonic eddies relative to non-eddy conditions (Figure 6.1b,c). As for chloropigments, the higher amino acid fluxes within cyclonic eddies relative to non-eddy conditions are likely to be a result of enhanced primary production caused by nutrient pumping.

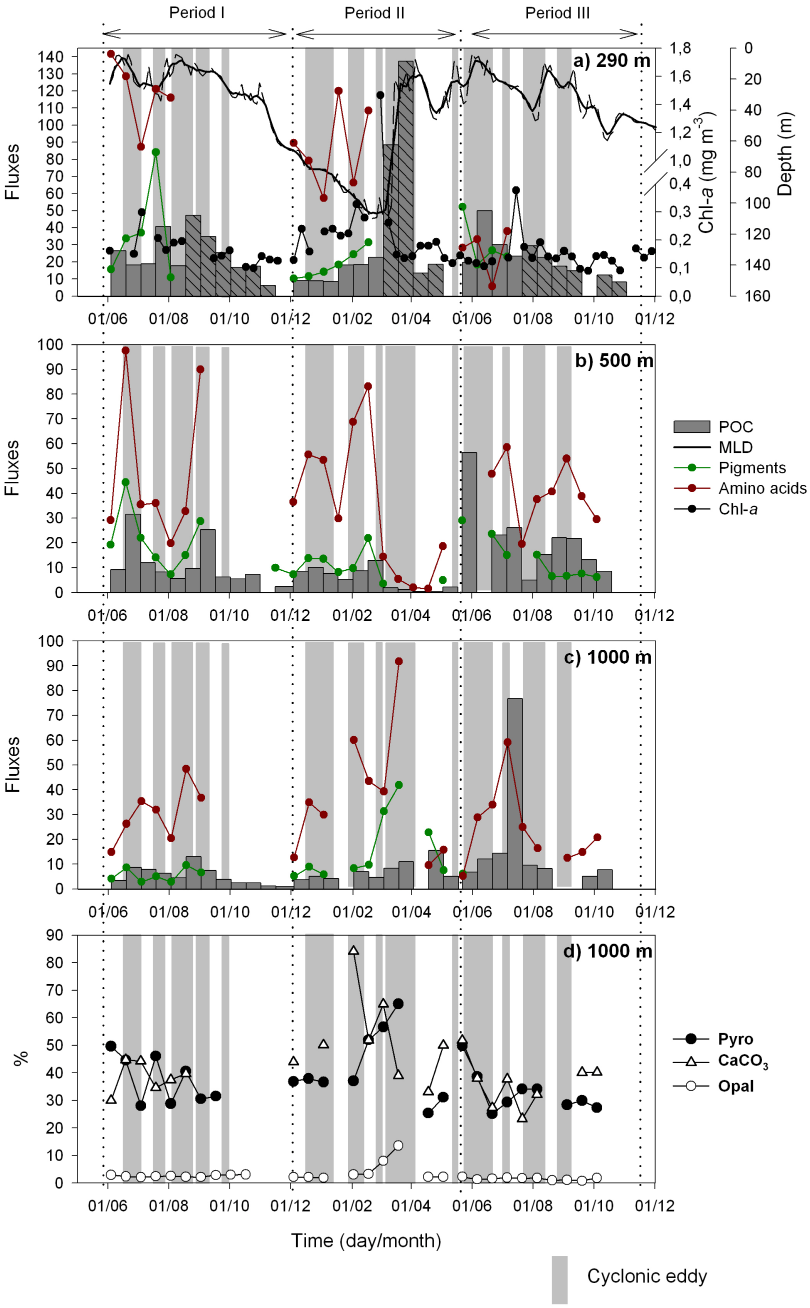

Figure 6.1 (see caption in next page).

Figure 6.1: POC (dark grey bars), amino acids (red dots) and chloropigments (green dots) fluxes collected at a) 290 m, b) 500 m and c) 1000 m. Dark grey shaded bars indicate POC fluxes derived from a IRSC sediment trap located 30 m above of the PPS3 (Alonso-González et al. 2010b). Grey bars indicate "eddy" while the white spaces indicate "non-eddy" conditions (see Piedeleu et al. 2009). Black line of the upper panel represents the depth of the mixed layer (MLD), while black dots stand for the surface chlorophyll derived from satellite images (Alonso-González et al. 2010b). d) Pyropheophorbide mole%, % of $CaCO_3$ and % of biogenic opal measured in 1000 m samples. Period I: from June 2005 to December 2005, Period II: from December 2005 to May 2006, and Period III: from May 2006 to December 2006.

We hypothesize that cyclonic eddies generated during winter/spring (Period II) did not have a significant effect on primary production and carbon export because the surface waters were already mixed down to 120 m and nutrient enriched (Figure 6.1a).

Table 6.1: Influence of eddies on POC fluxes. Average (±1 SD) fluxes (mg m^{-2} d^{-1}) of POC for eddy and non-eddy conditions. T_{eff} = mesopelagic transfer efficiency defined as 500/290m and 1000/500m POC flux. R eddy/non-eddy = POC flux ratio between eddy and non-eddy conditions. Average eddy-induced carbon flux increase at 1000 m calculated as POC fluxes during eddy conditions minus POC fluxes during non-eddy conditions (9.9+21.3)/2 - (2.1+4.1)/2) = 12.5 mg C m^{-2} d^{-1}. I: June 2005-December 2005; II: December 2005-June 2006; III: June 2006-December 2006. * Anomalous values mediated by vertically migrating zooplankton (see text and Figure 6.3 for explanation).

Period	I			II (bloom period)			III		
Depth (m)	eddy	non-eddy	$R_{eddy/non-eddy}$	eddy	non-eddy	$R_{eddy/non-eddy}$	Eddy	non-eddy	$R_{eddy/non-eddy}$
290	29.1 (9.1)	16.4 (7.8)	1.8 ($p<0.05$)	14.3 (6.2)	64.5 (59.4)	0.2 ($p>0.05$)	29.2 (10.9)	14.9 (2.6)	2.0 ($p<0.05$)
T_{eff} (500/290m)	49.9%	32.9%		48.9%	1.6%*		84.2%	66.4%	
500	14.5 (9.8)	5.4 (2.2)	2.7 ($p<0.05$)	7.0 (2.6)	1.0 (0.9)	7.0* ($p<0.05$)	24.6 (17.3)	9.9 (3.2)	2.5 ($p<0.05$)
T_{eff} (1000/500m)	54.4%	38.9%		90%	100%*		86.6%	61.6%	
1000	9.9 (2.9)	2.1 (1.1)	3.8 ($p<0.01$)	6.3 (2.7)	5.1 (1.2)	1.2 ($p>0.05$)	21.3 (27.2)	4.1 (1.9)	3.5 ($p<0.05$)

Alternatively, the higher POC, chloropigment and amino acid fluxes during eddy conditions could originate from a lower degradation rate of these components relative to non-eddy conditions. In this case, a lower degradation state of the collected organic matter would be expected. Figure 6.2 shows the degradation state of the organic matter collected at 500 and 1000 m using an amino-acid-based Degradation Index (DI) (Dauwe and Middelburg, 1998; Ingalls et al. 2003). Since the amino acid composition among organisms is so similar, the differences in amino acid composition arise primarily from degradation (Dauwe and Middelburg, 1998; Ingalls et al. 2003). The more negative the DI, the more degraded the organic matter in the sample, while positive DI values suggest fresher organic mater. Both 500 and 1000 m DI values show a lower degradation state for the organic matter collected during eddy relative to non-eddy conditions (Figure 6.2). This result is more consistent with a slower POC flux attenuation with depth within cyclonic eddies than that during non-eddy conditions. The degree of flux attenuation can be expressed as the ratio of POC flux between two depth levels (transfer efficiency, T_{eff}). During eddy conditions POC T_{eff} between 500/290 m and 1000/500 m ranged from 49 to 90%, whereas for non-eddy conditions POC T_{eff} ranged from 2 to 66% (Table 6.1). This pattern of more efficient POC transfer within eddies must be related to the biogeochemical perturbations generated by these mesoscale features.

Overall, these findings suggest that cyclonic eddies generated south of the Canary Islands act as physical-biological pumps of fresh organic matter to the deep ocean. Thus, our observations contrast with results obtained in cyclonic eddies in the lee of Hawaii, which showed strong silica export (Benitez-Nelson et al. 2007) but no evidence of enhanced particulate carbon export (e.g; Benitez-Nelson and McGillicuddy, 2008; Buesseler et al, 2008). In a recent study of organic matter composition within mesoscale eddies, Alonso-González et al. (2010a) describe the major factors influencing POC export within the Canary Islands eddy field. These authors suggest that phytoplankton community structure, particularly the dominance of $CaCO_3$ organisms over diatoms, efficient ballasting, and subsequent low zooplankton activity are the major factors influencing organic matter export within eddies. To evaluate these factors, we analyzed at 1000 m depth the variability in biogenic opal and

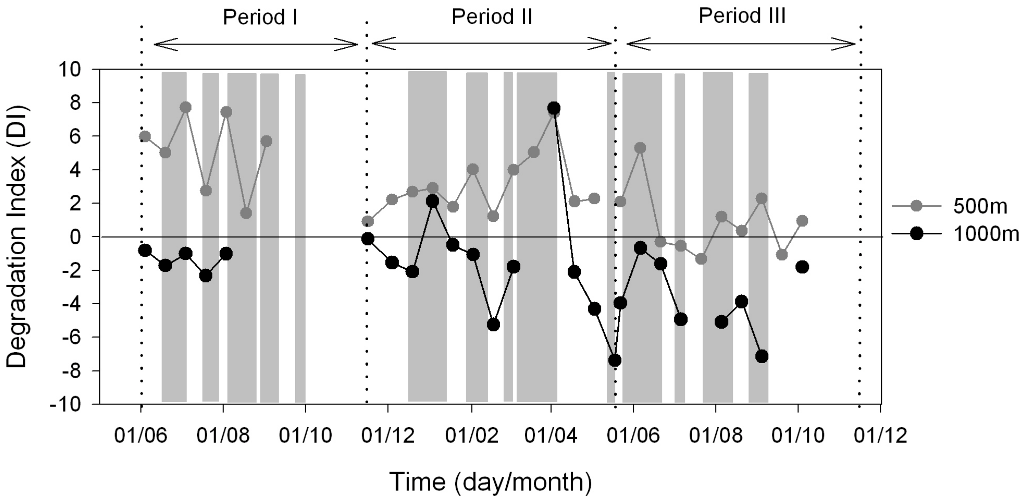

Figure 6.2: Organic matter degradation state. Time evolution of the amino acid Degradation Index (DI) of the organic matter collected at 500 m (grey circles) and 1000 m (black circles) depth. See Figure 6.1 for period dates.

calcium carbonate (Sanchez-Vidal et al., in prep.), as well as pyropheophorbide, an indicator of mesozooplankton grazing (Figure 6.1d). Our results show a carbonate-dominated region with a low percentage of opal, indicative of low silica supply from the nutrient source waters (NACW), as stated by Ragueneau et al. (2000). However, considering the low opal% in this area, its 6-fold increase during the late-winter bloom (Figure 6.1d) must induce important changes in the food web structure. Indeed, associated with this increase in opal there was a decrease in $CaCO_3$% and an increase in pyro mole% (Figure 6.1d). These data are suggestive of surface silica enrichment because of winter mixing (see deeper mixed layer depth, MLD; Figure 6.1a), relative enhancement of diatoms and subsequent increase in POC export at 290 m (Figure 6.1a).

Surprisingly, the signal of the POC peak generated during the seasonal bloom is missed at 500 m (Figure 6.1b). This raises the question, *what is the fate of the organic carbon exported during the late-winter bloom?* The pyro mole% increase at 1000 m suggests a high contribution of organic matter processed by mesozooplankton (fecal pellets). This hypothesis is supported by direct microscopic observations, which confirm a high proportion of fecal pellets at 1000 m during the seasonal bloom, and by a principal component analysis (PCA) based on pigment and amino acid compositions (Figure 6.3). PCA splits samples into three major groups and indicates that material collected at 1000 m during the late-winter bloom is enriched in markers typical of diatom-derived fecal pellets. These findings suggest a carbon flux mediated by vertically migrating zooplankton feeding in surface and upper mesopelagic waters, bypassing the depth of 500 m and defecating in the deep scattering layer (DSL; 600-800 m depth). Since the DSL is particularly well developed in Canary Island waters (Hernández-León et al. 2001), excretion by migrant organisms could potentially contribute significantly to the vertical carbon flux below the mesopelagic zone (Hernández-León et al. 2010). However, our results show that the POC Teff between 290 and 1000 m during the seasonal bloom was only 8%, but ranged from 27 to 73% in the presence of eddies during the stratified periods I and III (Table 6.1). Moreover, the PCA based on pigment and amino acid compositions indicates that samples collected during the seasonal bloom at 290 and 500 m presented a stronger microbial signature than other samples (Figure 6.3), suggesting that sinking POC at these depths is rapidly processed by the microbial community. Additionally, a fraction of the organic carbon biosynthesized during the seasonal bloom would be bypassed by migrants to the DSL and transformed to non-sinking POC, which is in agreement with the low sinking POC transfer efficiency at 1000 m. Arístegui et al. (2003), in a previous study in this area, reported the presence of peaks of dissolved organic carbon (DOC) at 600 m depth, coinciding with the depth of the DSL. Moreover, profiles of suspended POC in the upper 1000 m show peaks, more intense at DSL, which could only be explained by in situ production (unpublished data). These results suggest that an important fraction of the POC transported down by migrant zooplankton could be directly (excretion) or indirectly (fecal pellets disaggregation or dissolution) released to the water column as dissolved and suspended organic carbon, decreasing the efficiency of the carbon pump.

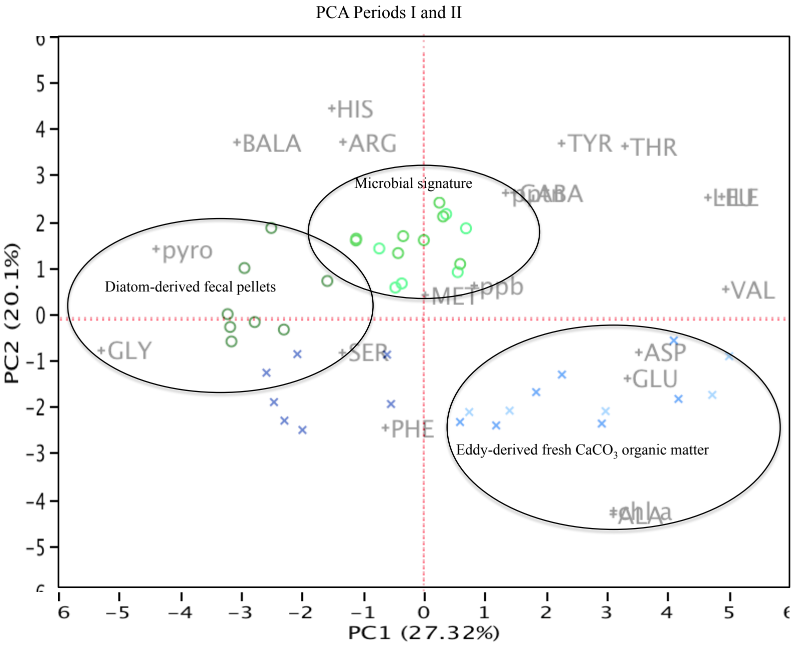

Figure 6.3: Principal Component Analysis (PCA). PCA was used here to quantitatively assess variation in the organic composition of eddy vs. bloom derived sinking particles. PC1 (which explains 27.3% of the variation) split samples in three major groups: 1) stratified period particles, with fresh and $CaCO_3$ algal indicators ASP, GLU and Chl-a located to the right along PC1, 2) bloom-derived particles, indicated by alteration products such as Serine, Glycine and Pyro, which are plotted towards the left on PC1, and 3) particles enriched in microbial indicators BALA, GABA, and ppt.

Figure 6.4 shows a conceptual model of the POC flow during stratified/eddy vs. seasonal bloom conditions. The major differences between the two scenarios are the phytoplankton community structure and the resulting differential microbial and zooplankton pressure. The lower metabolic carbon consumption during stratified/eddy conditions (Figure 6.4a) seems to be the cause of the higher POC T_{eff} and the fresher organic matter exported relative to the bloom period (Figure 6.4b). Overall, these results suggest that the pathways of the POC flow vary seasonally and at the mesoscale level, with profound implications for carbon dynamic.

Our time series observations clearly illustrate how the balance between $CaCO_3$ and opal may drive carbon export. When opal is more abundant (presumably due to a diatom enrichment) there is a higher carbon export at surface (290 m) but also enhanced grazing by zooplankton and microbial remineralization in the mesopelagic waters, which results in a lower POC T_{eff} to the deep ocean. These findings support the hypothesis proposed by Alonso-González et al. (2010a) that the phytoplankton community structure, (particularly the dominance of $CaCO_3$-rich organisms over diatoms), the more efficient ballasting by $CaCO_3$, and hence the lower zooplankton grazing activity are the major factors controlling organic matter export within eddies. But, what are the processes that ultimately determine the relative distribution of diatoms and coccolithophorids? A recent study focused on the processes controlling the phytoplankton community composition in the ocean showed that the balance between coccolithophorids and diatoms (C/D ratio) is correlated with the nutricline depth, a proxy of the nutrient supply to the mixed layer (Cermeño et al. 2008). These authors indicate that coccolithophorids dominate over diatoms as the water column stratifies and the nutricline deepens. According to these findings, the shallower mixed layer registered in this area relative to those at ALOHA and HOT together with the low silica content of the waters, would be the reasons for the high C/D ratio.

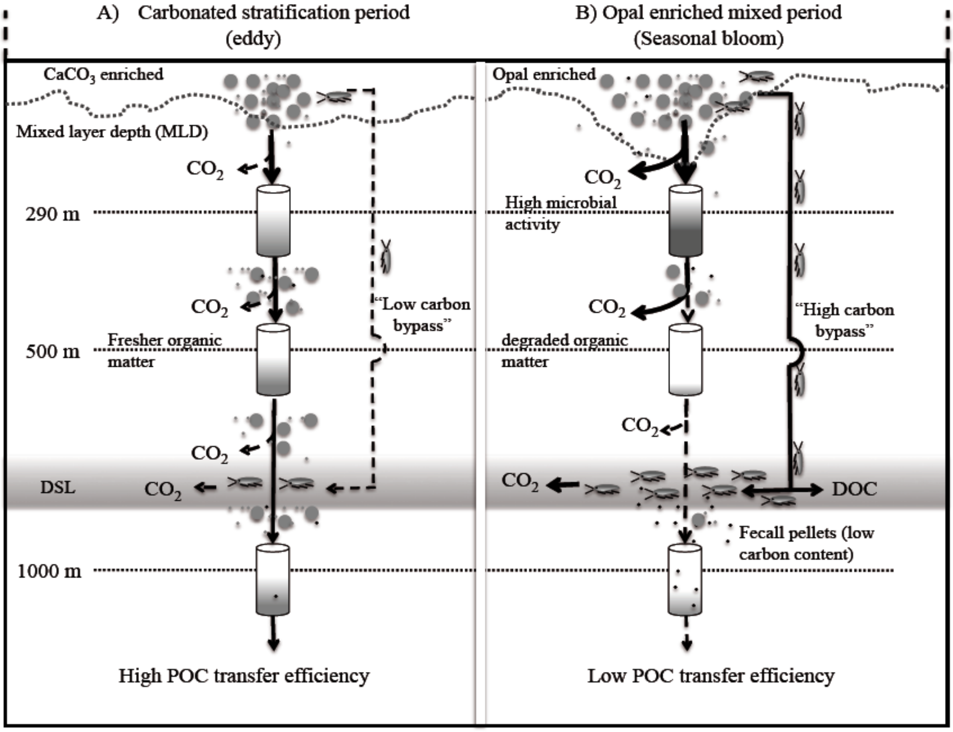

FIGURE 6.4: Conceptual model. Conceptual model of POC flow during (A) stratified/eddy conditions and (B) bloom period. A) The POC flux from the epipelagic to the mesopelagic zone is because of passive sedimentation of $CaCO_3$-enriched organic aggregates. The low zooplankton and microbial pressure result in a high POC transfer efficiency. B) The POC flow is channeled through active transport mediated by migrant zooplankton. A high microbial and zooplankton activity over the opal-enriched organic matter seems to recycle the exported carbon instead of being transported to the deep ocean, yielding a low POC transfer efficiency (see text for details).

6.3.2 Annual influence of cyclonic eddies on carbon sequestration

To evaluate the potential role of cyclonic eddies in the regional carbon budget, we have investigated the annual eddy-induced carbon sequestration below 1000 depth by combining different tools (see Appendix 6.5). In situ observations and results from a ROMS model (Shchepetkin and McWilliams, 2009) were used to estimate the number, age and area of cyclonic eddies generated during the stratified summer-autumn period (when eddies seem to enhance carbon fluxes).

The ROMS model showed 1160 cyclonic eddies within the 40-year climatological dataset, giving an average of 29 cyclonic eddies per summer-autumn period for the whole area (Fig. 6.5). As illustrated in Figure 6.6, the age histogram for cyclonic eddies shows that most of them are structures of less than 150 days (as our sampled eddies).

In order to calculate the annual carbon sequestration (below 1000 m) promoted by the presence of cyclonic eddies within this area, we have used the above data together with the average eddy-induced carbon flux increase obtained in this study (12.5 mg C m^{-2} d^{-1}; see Table 6.1). According to these data, we obtain an annual carbon sequestration induced by cyclonic eddies of 0.34 Tg C/yr (see Apendix II for calculations). For comparison, carbon sequestration below 1000 m for the whole studied area without taking into account cyclonic eddies range between 0.23-0.36 Tg C/yr when using our non-eddy conditions data or those from Neuer et al. (2007) at the ESTOC station, respectively. Our results indicate that cyclonic eddies, which represent a 28% of the total area, sequester a similar amount or 1.5 times more carbon than the whole area, clearly enhancing the biological pump. Moreover, our eddy-induced carbon sequestration estimates are likely conservative because sediment traps tended to undercollect particles when deployed in areas of high mesoscale activity (Alonso-González et al. 2010b).

6.3.3 Role of cyclonic eddies and migrant zooplankton on the mesopelagic carbon imbalance

Estimates of the plankton metabolic carbon demand (MCD) are significantly higher than vertical fluxes of POC measured with sediment traps (Steinberg et al. 2008; Baltar et al. 2009). We asked whether intermittent POC pulses by cyclonic eddies could locally resolve this observational discrepancy. Our results indicate that the overall effect of the eddy activity in our study area is to increase POC fluxes 2-4 times. To examine the balance between eddy-induced vertical POC fluxes and mesopelagic carbon demand, we used reasonable lower and upper values (9 and 68 mmol C m^{-2} d^{-1}), for mesopelagic respiration rates in our region of study (Jenkins and Goldman, 1985 and Arístegui et al. 2005, respectively). Using these respiration rates, our eddy-induced POC fluxes range between 10-50% of the mesopelagic respiration estimates. Thus, we find that cyclonic eddies cannot directly bridge the gap between vertical carbon fluxes and the metabolic carbon demand in mesopelagic waters. This result indicates the existence of alternative mechanisms to fulfill the high carbon demand of mesopelagic waters. Indeed, Baltar et al. (2009) and our chapter 4 indicate a significant correlation between suspended POC (POC_{susp}) and potential respiration in the surface and deep waters of the subtropical Northeast Atlantic. Nevertheless, POC_{susp} concentrations at depth appear to be inadequate to support sustained metabolic demand since a new supply of POC_{susp} would be required to keep up with the demand (Steinberg et al. 2008). Our chapter 3 shows that the lateral flux of POC_{susp} from the continental margin accounted for up to 60% of the total mesopelagic respiration in the Canary Region, giving evidence of an important mechanism supplying POC_{susp} at deep levels. In addition, Baltar et al. (2010) suggest that dissolved inorganic carbon fixation in the dark ocean could contribute between 12-72% to the prokaryotic carbon demand.

Here, we propose a new source of non-sinking organic carbon at depth that may represent an important fraction of the missing carbon respired in the mesopelagic waters. As stated above, the organic matter produced during phytoplankton blooms could be processed by migrant zooplankton and released daily as DOC or POC_{susp} in the DSL. Thus, diel vertical migration by zooplankton in this area is more likely to supply organic carbon for respiration, rather than to sequester it to the deep ocean.

6.4 Conclusions

Our study gives evidence that cyclonic eddies generated south of the Canary Islands enhance organic carbon, amino acid and pigment export with respect to non-eddy conditions. The higher POC T_{eff} observed during eddy conditions together with the fresher organic matter exported make eddies an efficient organic carbon pump to the ocean interior. The fact that the organic matter exported within eddies is less degraded indicates either a faster particle settling velocity (due to differences in particle size or ballasting) or the fact that the organic matter is being physically protected. This finding has profound implications for carbon sequestration since the depth of organic matter decomposition determines whether respired CO_2 may be exchanged quickly with the atmosphere or rather be sequestered over long periods of time (Armstrong et al. 2002). Thus, if fast-sinking or physically-protected particles contribute largely to the carbon flux within cyclonic eddies, the POC transfer efficiency to the mesopelagic waters increases, resulting in an enhanced CO_2 sequestration in the deep ocean (>1000m).

During the seasonal bloom, when the surface waters were more mixed, however, an important change in the dynamic of POC flow was observed. POC biosynthesized during the seasonal bloom was more enriched in diatom-derived compounds than at other times and appeared to be controlled by vertically migrating zooplankton and prokaryotes in the upper mesopelagic zone, and hence exported to higher trophic levels, released as suspended or dissolved organic carbon at the DSL or remineralized in surface waters. This situation indicates that, compared to the stratified/eddy periods, the fate of most of the material generated during the seasonal bloom is to be recycled in the mesopelagic zone instead of being transported to the deep ocean.

The results presented above indicate that cyclonic eddies in this area are more effective at transporting sinking POC to the deep ocean than the ambient waters (including the seasonal bloom), highlighting the important role of these features on the regional biogeochemistry. However, we find that even the highest POC fluxes observed in this study could explain only about 50% of the lowest respiration rates reported for this area. Overall, the apparent metabolic imbalance in the mesopelagic waters cannot be fulfilled by eddy-derived vertical inputs of sinking POC, strengthening the current view that microbial life in the deep ocean is more dependent on the slow-sinking and suspended particles than on the sinking pool.

Acknowledgments

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Appendix II

6.6 Appendix II

6.6.1 Climatological ROMS (Regional Ocean Modeling System) numerical model configuration of the Canary Basin

Figure 6.5 shows the trajectories of simulated cyclonic eddies in the Canary Island region. The trajectories were obtained by applying an eddy tracker to the surface velocity outputs from a climatological ROMS (Regional Ocean Modeling System; Shchepetkin and McWilliams, 2009) numerical model configuration of the Canary Basin. The length of the simulation is 50 years, and the horizontal resolution of is 7.5 km so that it is fully eddy resolving. A full description of the configuration and its validation is given by Mason (2009). Eddies were tracked over a 40-year period. The eddy tracker is based on the Okubo-Weiss parameter, and follows a method that has been applied to the tracking of mesoscale eddies observed by altimetry (Chelton et al. 2007, Sangrá et al. 2009). Further details of the eddy tracking method are given by Mason (2009).

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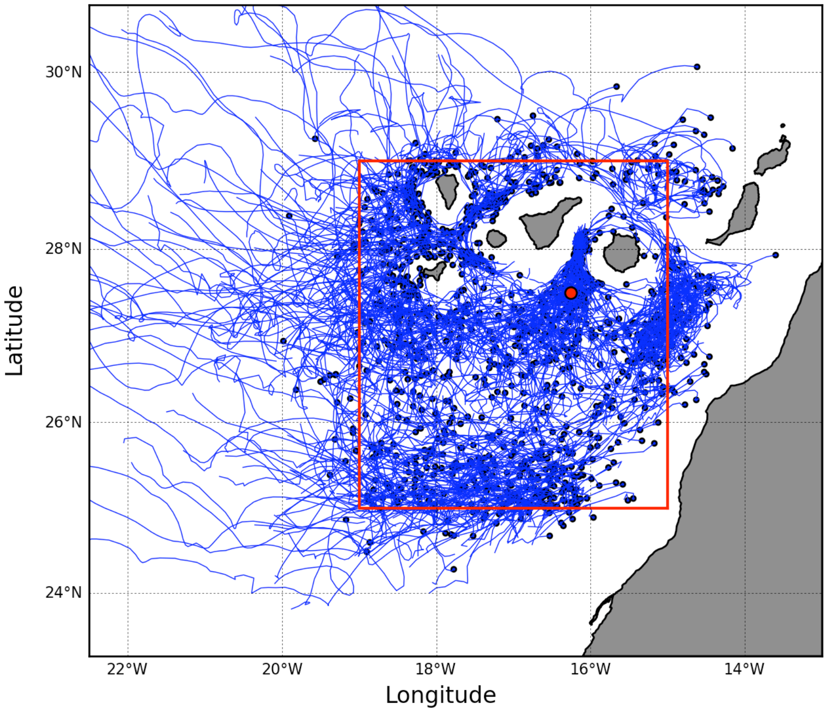

FIGURE 6.5: Trajectories of simulated cyclonic eddies that traverse the Canary Island region identified by the red box over a period of 40 climatological years. 1160 eddies are tracked. Blue circles mark the beginning of each trajectory. The large red circle marks the site of the mooring.

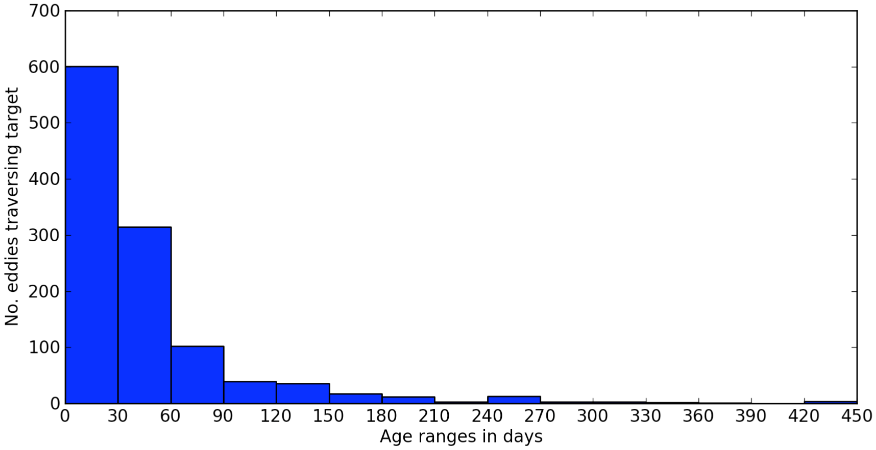

Figure 6.6: Histogram showing the relationship between the frequency at which simulated cyclonic eddies pass through the target region (identified in Figure 6.5) and their age. 30-day bins are shown, and eddies older than 450 days are omitted.

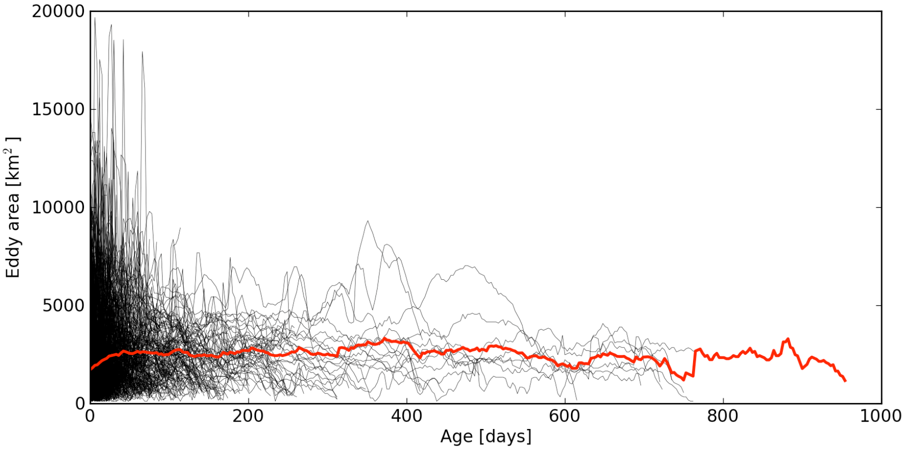

Figure 6.7: Line plots in black showing the areas as a function of age of the 1160 simulated cyclonic eddies identified in Figure 6.5. The average area is plotted in red.

CHAPTER 7

GENERAL DISCUSSION

Contents

7.1 Role of suspended and slowly-sinking POC in the water column biogeochemistry

Traditionally, in oceanic biogeochemistry, the organic matter biosynthesized in the euphotic zone is considered to be transported primarily by sinking particulate material. However, vertical sinking POC fluxes in the deep waters of the North Atlantic have been reported to be inadequate to account for the observed carbon demand [Reinthaler et al. 2006; Steinberg et al. 2008]. These findings have questioned the assumption that sinking POC is the main respiration substrate and invoke the existence of unaccounted sources of organic matter to supply the carbon necessary for the deep water metabolic activity.

Microbial communities in the dark ocean are supplied with dissolved organic matter (DOM) and particulate organic matter (POM) largely formed in the epipelagic zone and transported into the deep ocean [Arístegui et al. 2009]. The relative contribution of dissolved organic carbon (DOC) to total mesopelagic respiration (R), at a global scale, was estimated by Arístegui et al. [2002]. In their study, DOC contributed 10-15% to the total mesopelagic oxygen consumption, a value that cannot fulfill the metabolic imbalance. Surprisingly, previous studies of carbon budgets have not considered the potential role of suspended particulate organic carbon (POC_{susp}), even though this pool is quantitatively far larger than sinking POC [McCave, 1984; Kepkay, 2000]. This huge pool of organic carbon is not represented in the material collected by current sediment traps. Thus, if vertical carbon fluxes derived from sediment traps are used to construct carbon budgets for different biogeochemical processes, strong imbalances may arise. Additionally, other potential source of organic carbon, under-collected by sediment traps, are the slowly-settling particles. Sediment traps may miss a fraction of the exported POC in the small and slowly-settling particles because of lateral advection. In that scenario, a higher percentage of small versus large particles would result in lower average sediment trap collection efficiency, making determining the regional and temporal variability in the shape of the particle velocity spectrum of great interest.

In this section, we discuss the potential contribution of slowly-settling particles (chapter 2) and suspended POC (chapters 3 and 4) to total respiration, as well as, its transport mechanisms.

According to the results obtained from the IRSC sediment traps (chapter 2), at least during half of the year in subtropical waters, more than 60% of total particulate organic carbon is contained in slowly settling particles (0.7-11 m d^{-1}). Moreover, analyses of organic biomarkers (amino acids and chloropigments) reveal that these particles have the same degradation state, or are even fresher than rapidly sinking particles. These characteristics make this carbon pool susceptible of lateral advection and remineralization in the water column without being accounted in carbon balances derived from sediment traps. This finding has profound consequences for organic carbon dynamic (see Figure 9.1).

One we know that slowly-settling particles dominate the "sinking" organic carbon fraction in our region, and that these particles undergo lateral advection

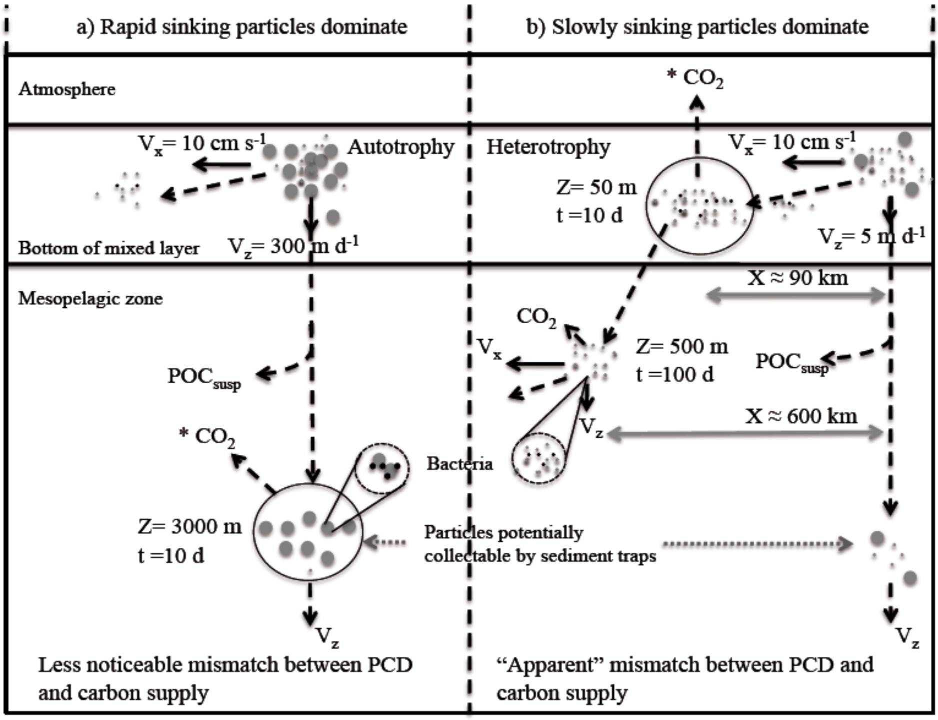

Figure 7.1: Conceptual model of sinking velocity-dependent particle dynamics. (a) In a system where rapidly-settling particles dominate, epipelagic and upper mesopelagic remineralization of sinking POC may be minimal; (b) In a system where slowly-sinking particles dominate, a fraction of POC will undergo lateral advection and may escape collection by standard sediment traps, leading to a mismatch between POC flux and prokaryotic carbon demand. Solid black arrows = particle velocities. Dashed black arrows = carbon trajectories. Solid grey lines illustrate the theoretical horizontal distance reached by slowly settling particles during two different periods (10 and 100 days). The distances were estimated using a zonal velocity of 10 cm s^{-1} and 5 cm s^{-1} for the epipelagic and mesopelagic zones, respectively. Solid circles represent particles with the same "starting point" (Z = 0 m) but different dynamics characteristics. After 10 days, the bulk of POC remains in the euphotic zone (~50 m) in (b), but reaches 3000 m in (a). Dashed grey lines indicate the amount of POC potentially collectable by sediment traps (assuming the same PP) in each scenario.

[Gust and Kozerski, 2000], the interest lies in calculating the lateral transport of suspended and slowly-settling POC. With this purpose, we estimated the lateral transport and consumption, from surface to 3000 m, of suspended particulate organic carbon (POC), through a box model approach (chapter 3). This analysis allows us to conclude that the lateral POC fluxes are 2 or 3 orders of magnitude higher than vertical fluxes depending on water masses, confirming our hypothesis of a more relevant horizontal versus vertical flux of POC per unit area. These findings suggest that in the ocean, no ecosystem is a closed one, so it can receive organic material from, and export material to, adjacent ecosystems. In our work, we also demonstrate that continental margins produce more organic carbon than they respire, being a fraction of this non-respired, neutrally-buoyant organic carbon available for export from the coastal to the open ocean through sloping neutral density layers.

From a biogeochemical point of view, this lateral POC flux accounts for 30-60% of the total mesopelagic respiration (R), on the basis of lower and upper case scenarios of vertical POC inputs and dissolved organic carbon contribution to respiration. However, POC_{susp} concentrations at depth have been reported to be inadequate to support sustained metabolic demand since a new supply of POC_{susp} would be required to keep up with the demand [Steinberg et al. 2008]. Then, our chapter 3 also give evidences of an important and unaccounted mechanism supplying POC_{susp} at deep levels. Additionally, in situ production of organic carbon by prokaryotic chemoautotrophs have been proposed as a mechanism fueling suspended POC in the deep waters of the northeast Atlantic Ocean [Herndl et al. 2005]. Indeed, a recent work conducted in the mesopelagic northeast Atlantic concluded that dissolved inorganic carbon fixation contribute between 12% to 72% to the daily prokaryotic carbon demand [Baltar et al. 2010]. Based on these results, suspended POC seems to play a more important role on the mesopelagic biogeochemistry relative to sinking POC.

With the aim of reinforce the hypothesis of an important correlation between POC_{susp} and respiration we looked at regional gradients and temporal variability in water column respiration (ETS) and suspended particulate organic material (chapter 4). The resulting correlation analysis reveals that POC_{susp} supports between 65% and 74% of plankton respiration in the water column (in agreement with chapter 3), highlighting a low contribution of sinking POC (<20%) to the water column respiration. Thus, the coupling between sinking POC and respiration in the water column is much weaker than has traditionally been assumed. A recent study, based on the algorithm of Antia et al. [2001], also concluded that the potential contribution of the sinking POC amounts to 4-12% to the prokaryotic carbon demand per day when using a surface primary production of 28 and 50 mmol C $m^{-2}d^{-1}$, respectively [Baltar et al. 2010]. To summarize, Figure 9.2 shows the contribution of the different organic carbon sources discussed here to mesopelagic respiration, as well as, the mechanisms of transport of each of them.

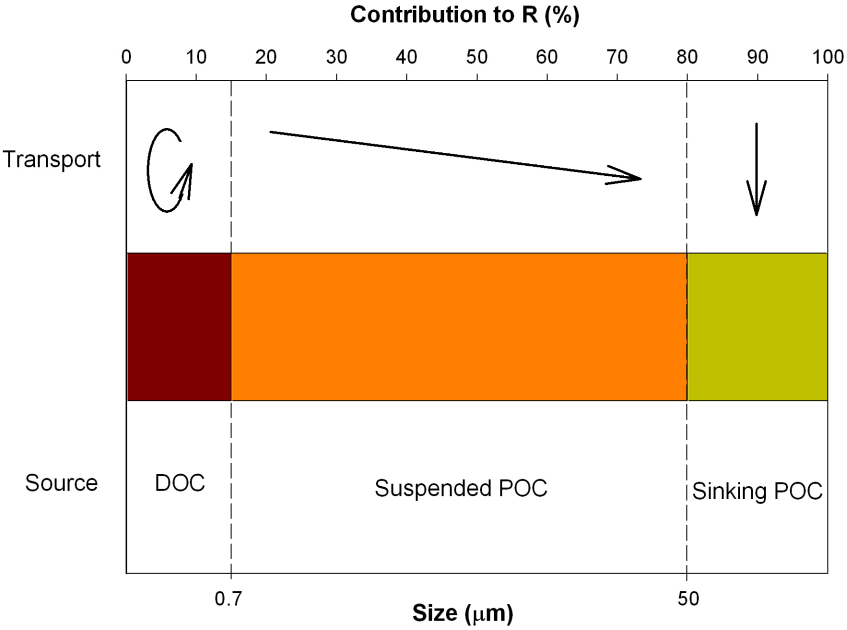

Figure 7.2: Conceptual model of the contribution of different organic carbon sources to mesopelagic respiration. Bottom panel illustrates the different carbon source as a function of size, while upper panel shows the dominant mechanisms of transport of each source.

Taken together, these findings could help to explain the apparent imbalance between the carbon sources and the oxygen utilization rates in the mesopelagic waters when accounting only for the vertical sinking POC collected with sediment traps, and indicate that bacterial activity is linked to suspended POC rather than to vertical POC flux. Ultimately, this work suggests that we must change from the point of view of traditional one-dimensional (vertical) approaches to studies of the ocean carbon cycle in three-dimensions as previously suggested by Michaels et al. [1994].

7.2 Significance of mesoscale eddies to POC dynamic in the subtropical northeast Atlantic

The topographic obstacle that represent the Canary Islands to the Canary Current flow causes the frequent shedding of cyclonic and anticyclonic eddies, in a fashion that resembles a von Karman vortex street, and becomes the major source of mesoscalar variability south of the archipelago [see Sangrá et al. 2007]. These features, accommodate a diverse set of physical, chemical, and biological interactions that influence marine biogeochemistry on a wide range of timescales [Benitez-Nelson and McGillicuddy, 2008]. Enhanced phytoplankton primary production induced by nutrient pumping into the euphotic zone by cyclonic eddies has been reported [Arístegui et al. 1997; Oschlies and Garçon, 1998]. However, the eddy-associated changes in plankton community structure, trophic interactions, impact on organic matter export and biogeochemical significance of eddies in this area is barely know.

The main objective of chapters 5 and 6 was to fill the gap in our knowledge of significance of eddies to carbon dynamic. To achieve this goal we measured, together with total POC fluxes, mesoscale trends in amino acid (THAA) and chloropigment compositions and fluxes obtained from free floating and moored sediment trap deployments in the northeast Atlantic Ocean. Both THAA and chloropigments are useful indicators of decomposition, source and transport in the water column [e.g., Wakeham et al., 1997; Dauwe and Middelburg, 1998;

Lee et al., 2000]. Since inorganic nitrogen can control the biological pump through its role as a limiting nutrient, the decomposition and remineralization of organic nitrogen as amino acids are of particular importance. Chloropigments are key indicators of organic matter diagenesis, since their origin stems from surface water communities. Thus, by following chlorophyll degradation as particles fall from the surface through the water column we can determine the "freshness" of organic matter during its transport to deeper layers.

Under the steady state conditions, the enhanced nutrient fluxes by cyclonic eddies have to be compensated by a stimulation of marine phytoplankton growth rate, and as a consequence, enhanced POC export out of the euphotic zone to balance the supply of incoming nutrients. However, this balance between nutrient injection, production and export is not always reached, as the community response to nutrient inputs is complex [Buesseler et al. 2008]. Indeed, two recently mesoscale programs (E-Flux, North Pacific and EDDIES, North Atlantic), focussed in the role of mesoscale eddies in downward export flux, concluded that eddies did not enhance carbon flux, although they increased the flux of biogenic silica [Benitez-Nelson and McGillicuddy, 2008]. These findings raise a first-order question: *What are the factors controlling carbon export within eddies?*

Based on biomarkers analysis (chapters 5 and 6), we suggest that phytoplankton community structure, particularly the dominance of $CaCO_3$ organisms over diatoms, efficient ballasting, and subsequent low zooplankton grazing activity are the major factors influencing organic matter export within eddies. Several works have indicated that a significant fraction of organic matter produced in surface waters is transported to depth associated with mineral ballast [Armstrong et al. 2002; Francois et al. 2002], and specially with carbonate [Klaas and Archer, 2002]. Therefore, the enhanced POC flux observed in the eddies generated south of the Canary Islands could be due to the increased particle settling velocity in highly carbonate-ballasted systems in comparison to those in opal-ballasted system (like Hawaii). Moreover, chapter 6 and a previous study [Ingalls et al. 2006] suggest that, in diatom-rich areas, the grazing pressure by mesozooplankton is higher than in $CaCO_3$-rich areas, and that the latter areas would have higher aggregate export instead of fecal pellet production. Thus, our findings are consistent with the hypothesis proposed by the above programs of zooplankton grazing as a mechanism to reduce POC export within eddies. In opal enriched eddies, the biomass produced was found to be processed by microzooplankton, which in turn, are grazed by large ciliates and dinoflagellates releasing suspended and dissolved organic matter instead of producing fecal pellets [Landry et al. 2008; Maiti et al 2008].

Our findings (chapter 6) also suggest that an important fraction of the carbon budget generated during mixed and opal-enriched periods (like our seasonal bloom or Hawaiian eddies) is mediated by vertically migrating zooplankton. These organisms feed at surface and upper mesopelagic waters and defecate below 500 m, thus they could potentially contribute significantly to the vertical carbon flux below the mesopelagic zone [Hernández-León et al. 2010]. However, our results show that the POC T_{eff} between 290 and 1000 m during these periods was only 8%, but ranged from 27 to 73% associated with eddies during the stratification period. Therefore, we suggest that strong active transport by migrant zooplankton facilitate particulate organic matter recycling within the mesopelagic zone and results in a weakening of the biological pump. On the contrary, the results presented above indicate that cyclonic eddies in this area are more effective transporting sinking POC to the deep ocean than the ambient waters (including the seasonal bloom), highlighting the important role of these features on the regional biogeochemistry. However, the apparent metabolic imbalance in the mesopelagic waters cannot be fulfilled by eddy-derived vertical inputs of sinking POC, strengthening the current view that microbial life in the deep ocean is more dependent on the slow-sinking and suspended particles than on the sinking pool (chapters 2, 3 and 4).

7.3 Conceptual model of POC flow and decomposition in the Canary Basin

A primary focus of ocean science during the past 3 decades has been the identification of the factors controlling the downward export of biogenic particles, the so called "biological pump" [Boyd and Trull, 2007]. Most of the current knowledge of oceanic biogeochemical processes affecting particulate matter is derived from sediment trap data [Buesseler et al. 2000], nevertheless, several unresolved issues on sediment trap effectiveness prevail to date [see Gardner, 2000]. Sediment traps are thought to under-sample slowly settling particles, which can undergo lateral transport over long distances (chapter 3) as well as trap-related winnowing [Gust and Kozerski, 2000]. As a consequence, construction of global biogeochemical cycles, ocean carbon budgets, trophic interactions, and transport mechanisms has long been guided by the simplification introduced by sediment traps, which give a 1D vision of the whole picture. This thesis, besides the vertical POC fluxes, try to provide information about the lateral POC transport through mass balance and organic biomarkers approaches.

Figure 9.3 illustrates the conceptual POC flow model proposed for the Canary Basin after this thesis research. This model is basically divided into two scenarios according to seasonality, hydrographic conditions and phytoplankton community structure. The left panel shows the summer-autumn conditions, where the water column is stratificated, the calcium carbonate phytoplanktonic organism dominate and the cyclonic eddies are more intense. On the contrary, the right panel displays the winter-spring conditions, where the surface water layers are mixed and a relative enhancement of diatoms occur. These two different situations force a temporal-dependence POC flow dynamic that has not previously established.

Summer-Autumn conditions

During this period of time the pathway of POC flow is mainly via slowly-settling and suspended particles which undergo lateral transport (chapter 3).

This situation leads to a layered POC distribution with maximums localized at water masses interfaces and micro-gradients of density due to accumulation of this quasi-neutrally buoyant organic pool. Additionally, such layered distribution is fueled by suspended carbon laterally exported from the NW African continental margin. According to this distribution, these particles have longer residence times in the water column compared with the faster sinking particles. Therefore, is reasonable to think that respiration could match or exceeds primary production rates as frequently reported for this area [Duarte et al. 2001; González et al. 2001; Marañón et al. 2007]. However, the exception to this distribution is found within eddies, where vertical mixing is more pronounced and POC flow is more vertical and efficient. Taking eddies into account, our results show an important POC flow at 1000 m depth during this period (Figure 6.1), indicating that, if it is evaluated as a whole system, the balance between production and respiration should be positive. These findings also suggest that a carbon deficit during the summer-autumn period should exist in absence of mesoscale eddies, highlighting the important role of these features.

The phytoplankton community structure within eddies is mainly dominated by calcium carbonate organisms, resulting in a low zooplankton grazing pressure and also in a low active transport by migrant mesozooplakton.

Winter-Spring conditions

During the winter-spring period the trophic structure and pathways of biogenic POC are determined by the degree of vertical mixing of the surface waters. Our results are suggestive of surface silica enrichment because of winter mixing (see deeper mixed layer depth, MLD; Figure 6.1a), relative enhancement of diatoms and subsequent increase in POC export at the base of the euphotic zone. This conditions are favorable to the production of larger and fast settling particles (as reported in chapter 2), therefore one would expect that these particles could potentially contribute significantly to the vertical carbon flux below the mesopelagic zone. However, compared to the summer-autumn period, we found a low sinking POC transfer efficiency between 290 and 1000 m, suggesting that POC biosynthesized during the late-winter bloom have fates other than sinking particles. Based on POC fluxes and biomarkers we conclude that sinking POC is rapidly processed by the microbial community, bypassed by migrants to the deep scattering layer (DSL) and transformed to non-sinking POC, which is in agreement with the low sinking POC transfer efficiency at 1000 m. This also can explain the paradox that organic matter at diatom-rich stations is removed by mechanisms that do not result in the appearance of sinking organic matter degradation indicators [Ingalls et al. 2006]. Overall, these findings indicate that the fate of the material generated during the seasonal bloom is to be recycled in the mesopelagic zone instead of being transported to the deep ocean. Then, the significance of diel vertical migration by zooplankton in this area is more likely to supply organic carbon for mesopelagic respiration, rather than to sequester it to the deep ocean.

In terms of the association of sinking organic matter with mineral ballast (calcium carbonate and opal) our data concur with Armstrong et al. [2002] and Klaas and Archer [2002] that organic carbon sinking fluxes correlate more with calcium carbonate than with opal. They argued that most of the organic carbon flux to the deep ocean is carried by calcium carbonate, because it is denser than opal and more abundant than terrigenous material. We also suggest that organic matter associated with opal is more bioavailable than organic matter associated to calcium carbonate. A possible explanation for this is that about 50% of the opal dissolves in the upper 100 m of the water column whereas for calcium carbonate this fraction is much smaller [Tréguer et al. 1995]. As a result, net export of calcium carbonate and associated organic matter from the surface ocean is higher than the corresponding fluxes of opal-organic matter.

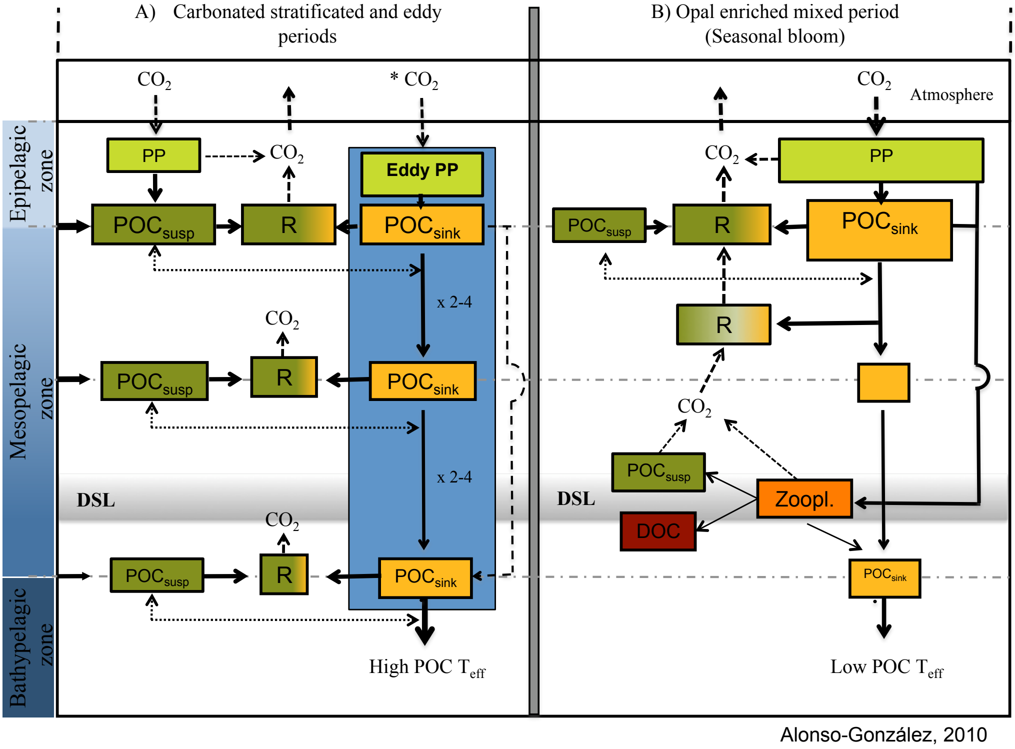

FIGURE 7.3: Conceptual model of the temporal evolution of POC flow and decomposition for the Canary Basin. The model comprises four basic layers: atmosphere, epipelagic, mesopelagic and bathypelagic zones. Organic carbon (POC) fluxes are illustrate by black solid lines, while inorganic carbon (CO_2) fluxes are displayed by black dashed lines. Black dotted lines represent exchange between sinking and suspended POC. During summer-autumn (panel A)) POC presents a layered distribution, except within eddies, where vertical mixing is more pronounced. An external input of suspended POC is represented by three black solid arrows located at the left. $^*CO_2$ represent a net input of CO_2 from the atmosphere to the ocean induced by the presence of cyclonic eddies. The vertical black dashed line indicate a low POC bypass by migrant zooplankton. During winter-spring (panel B)) POC presents a patched distribution with most of the particles traveling vertically. Migrant mesozooplankton bypass an important fraction of the epipelagic POC releasing it as dissolved and suspended organic matter near the bottom of the mesopelagic zone. This results in a lower POC transfer efficiency (T_{eff}) to the bathypelagic zone compared to the panel A).

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CHAPTER 8

CONCLUSIONS

"Es débil porque no ha dudado bastante y ha querido llegar a conclusiones"

Miguel de Unamuno, 1864-1936

The main conclusions that arise from this thesis are:

1. The shape of the particle settling velocity spectrum in our region is dominated by slowly settling particles (0.7-11 m d^{-1}) during summer and autumn and by rapidly settling particles ($>$ 326 m d^{-1}) during winter and spring. This finding has profound implications for carbon dynamics:
   (a) During summer and autumn, sediment traps may miss a fraction of the exported POC in the slowly settling particles. Thus, if vertical carbon fluxes derived from sediment traps are used to construct budgets for different biogeochemical processes, strong imbalances may arise.
   (b) When slowly settling particles dominate the exportable carbon pool, most organic matter would be respired in the epipelagic and upper mesopelagic zones, acting as a biological source of CO_2 susceptible to exchange with the atmosphere. On the contrary, if fast-sinking particles contribute largely to the carbon flux, the carbon transfer efficiency to the mesopelagic waters increases, resulting in an enhanced carbon sequestration in the deep ocean.

2. A significant fraction of the mesopelagic carbon budget in the western Canary Current region is fuelled by lateral suspended carbon advection from continental margins or mesoscale activity in the eastern boundary region. However, a large part of this mesopelagic carbon would be remineralized in the upper 1000 m instead of being transported to the ocean interior.

    (a) The lateral POC fluxes are 2 or 3 orders of magnitude higher than vertical fluxes depending on water masses, confirming the hypothesis of a more relevant horizontal versus vertical flux of particulate organic matter per unit area.

    (b) The influence of the lateral advected particulate carbon from the NW African coast on the oligotrophic subtropical gyre region can reach more than 1000 km offshore.

    (c) This lateral flux accounts for 28-59% of the total mesopelagic respiration, on the basis of lower and upper case scenarios of vertical POC inputs and dissolved organic carbon contribution to respiration.

3. Plankton respiration is mainly (65-74%) supported by seasonal fluctuations in the laterally advected suspended organic matter, highlighting a low contribution of sinking POC (<20%) to the water column respiration. This finding could help to explain the apparent imbalance between the carbon sources and the oxygen utilization rates in the mesopelagic waters when accounting only for the vertical sinking POC collected with sediment traps.

4. The eddy field generated south of the Canary Islands enhance POC export with respect to surrounding waters by 2 to 4 times. Flux increases of 2 times to one order of magnitude in chloropigment and amino acids are also observed in the eddy field relative to non-eddy conditions.

5. The phytoplankton community structure, particularly the dominance of $CaCO_3$-rich organisms over diatoms, the more efficient ballasting by $CaCO_3$, and hence the lower zooplankton grazing activity are suggested to be the major factors controlling organic matter export within eddies.

6. Analyses of organic biomarkers reveal that organic matter exported during eddy conditions have a less degradation state relative to non-eddy conditions.

7. During the late-winter phytoplankton bloom, an important change in the sinking POC dynamic presumably mediated by vertically migrating zooplankton results in a lower POC transfer efficiency to the deep ocean ($>$1000 m), compared to the effect due to cyclonic eddies.

8. The material transferred during the late-winter bloom is mainly recycled in the mesopelagic zone, whereas cyclonic eddies during the stratification period enhance carbon sequestration below 1000 m depth, highlighting the important role of these features on the regional biogeochemistry.

9. The apparent metabolic imbalance in the mesopelagic waters cannot be fulfilled by eddy-derived vertical inputs of sinking POC, strengthening the view that microbial life in the deep ocean is more dependent on the slow-sinking and suspended particles than on the sinking pool.

CHAPTER 9

Spanish summary/ Resumen en español

9.1 INTRODUCCIÓN GENERAL

9.1.1 La materia orgánica en el océano

La Producción Primaria (PP) por parte de las células fitoplanctónicas es considerada la fuente principal de materia orgánica en el océano [Mopper y Degens, 1979]. Esta flora microscópica juega un papel fundamental en el ciclo del carbono en el océano ya que convierte el carbono inorgánico en carbono orgánico mediante el proceso de fotosíntesis. Otros fuentes menores, pero localmente importantes, además de la producción primaria por parte del plancton y macrófitas, incluyen los aportes terrestres por parte de los ríos, deposisión atmosférica, resuspensión de materia orgánica desde los sedimentos marinos, emisiones hidrotermales, quimioautotrofía y vertidos de petroleo. Por el contrario, la respiración oceánica (R) es el proceso por el cual los organismos obtienen energía a través de la oxidación de la materia orgánica convirtiéndola en sus constituyentes inorgánicos. Debido a que el ciclo de la materia orgánica recae en el balance entre estos dos procesos, PP y R están ampliamente aceptados como factores críticos en el control del ciclo del carbono en el océano [Arístegui et al. 2005]. Sin embargo, los mecanismos que controlan la distribución de la materia orgánica en la columna de agua han recibido menos atención presumiblemente debido a la dificultad de cuantificar tales procesos in situ. Conocer como funcionan estos mecanismos de transporte es crucial para una predicción cuantitativa de los flujos y rutas de la materia orgánica en diferentes ambientes.

Un aspecto esencial para intentar comprender los mecanismos involucrados en el transporte de carbono es identificar los diferentes pools de carbono presentes en la columna de agua. Tradicionalmente, la materia orgánica en el océano ha sido operacionalmente dividida en dos pools diferentes de acuerdo a técnicas de filtración. La meria orgánica que pasa a través de filtros de fibra de vidrio con un poro nominal de 0,2-0,7 micras se asume que es materia orgánica disuelta (DOM), mientras que el material retenido en el filtro es considerado materia orgánica particulada (POM). Otro aspecto clave que afecta a la dinámica del carbono en la columna de agua es la composición de la materia orgánica. El DOM en aguas superficiales se compone de una mezcla DOM refractario muy antiguo y una pequeña fracción de DOM lábil y nuevo [Benner, 2002] producido in situ por las comunidades planctónicas. En áreas tropicales y subtropicales, la mayoría del DOM biodisponible es respirado en aguas superficiales y mesopelágicas superiores contribuyendo poco al metabolismo procariota profundo o secuestro de carbono en el océano profundo. De hecho, el DOC exportado con la circulación termohalina contribuye sólamente entre un 10 y un 20% a la utilización aparente de oxígeno global en el océano profundo [Arístegui et al. 2002]. Este hecho sostiene la visión actual de que la vida microbiana en el océano profundo está principalmente impulsada por el pool de carbono orgánico particulado [Honjo 1996; Bendtsen et al. 2002; Arístegui et al. 2009]. Con respecto al pool orgánico particulado, la composición orgánica del POM está dominada por compuestos derivados del fitoplancton [Lee et al. 2004]. Sim embargo, durante su viaje a niveles más profundos, la materia orgánica sufre alteraciones de su composición original debido a la actividad heterotrófica. Tal alteración de la firma original es dependiente del tamaño de partícula, de ahí el interés en determinar las diferentes clases de tamaños de partículas.

Las partículas portadoras de carbono orgánico en el océano son parte de un contínuo de tamaños [Verdugo et al. 2004], sin embargo, son operacionalmente divididas por los oceanógrafos en dos clases distintas de acuerdo a sus propiedades: i) carbono orgánico particulado suspendido (POC$_{susp}$), y ii) carbono orgánico particulado que se hunde (POC$_{sink}$). La diferencia entre estas dos fracciones es esencial puesto que cada una de ellas presenta un comportamiento diferente en la columna de agua. Se asume que el POC$_{susp}$ comprende las partículas que van desde 0,7 a 50 micras, mientras que el POC$_{sink}$ comprende aquellas mayores a 50 micras [McCave, 1975; 1984]. El POC$_{susp}$ domina el stock permanente de material particulado en el océano [McCave, 1975; Kepkay 2000], aunque, sorprendentemente, nuestro conocimiento acerca de su importancia biogeoquímica es escaso. Esta falta de información ha sido debida al hecho de que los investigadores tradicionalmente se han centrado en el carbono orgánico que se hunde [Suess, 1980; Boyd and Trull, 2007]. Por el contrario, la transferencia de carbono que se produce desde las aguas superficiales hacia el océano profundo via POC$_{sink}$ es crítica, a larga escala, para la eliminación de elementos climáticamentente activos, como el dióxido de carbono de la atmósfera.

Evidencias recientes sugieren que el comportamiento de las partículas en la columna de agua no sólo depende del tamaño de las mismas, sino también de la diferencia entre su densidad promedio y aquella de las aguas que las rodean [Burd and Jackson, 2009]. Entonces, la velocidad de sedimentación es llamada a ser un aspecto clave el cual influencia los flujos verticales y la remineralización del carbono, sin embargo poco se conoce acerca de su variabilidad espacio-temporal. La velocidad de sedimentacin de las partículas determina si el carbono orgánico sufre transporte lateral o vertical, viajando con o a través de las masas de agua, respectivamente. Por tanto, surge una interesante cuestión: *Cuál es la variabilidad regional y temporal en la forma del espectro de velocidades de sedimentación de las partículas?*

9.1.2 Balance entre síntesis y destrucción de carbono orgánico particulado en la aguas epipelágicas

A escala del océano global y en estado estacionario, la cantidad de materia orgánica fijada fotosintéticamente por organismos autótrofos tiene que ser balanceada por la materia orgánica consumida por los organismos heterotróficos. Sin embargo, estudios regionales sobre el metabolismo del plancton sugieren una variabilidad regional en el balance metabólico entre los procesos autotróficos y heterotróficos. De hecho, numerosos experimentos sobre el metabolismo del plancton llevados a cabo en el Océano Atlántico noreste subtropical han reportado que este sistema es un ecosistema hetrotrófico [Duarte et al. 2001; González et al. 2001; Serret et al. 2002]. Una posible explicación a este desbalance es que la producción primaria bruta puede estar subestimada debido a aspectos metodológicos [Robinson and Williams, 2005]. Duarte et al. [2001] sugieren que el carbono orgánico que se necesita para sustentar este desbalance debe ser suministrado por aportes externos (ej. transporte lateral y deposición atmosférica). Otra posibilidad expuesta por otros autores es que estas tasas puedes estar desviadas debido a sus diferentes escalas temporales asi como por su diferente variabilidad espacio-temporal, especialmente PP [del Giorgio et al. 1997; Arístegui and Harrison, 2002; Karl et al. 2003; Williams et al. 2004]. Al sur de Las Islas Canarias, Arístegui et al. [2003] sugieren que las tasas de respiración medidas en Las Islas Canarias son alimentadas por remolinos mesoescalares y aportes externos de materia orgánica.

A pesar de la aparente consistencia de esta anomalía, un desbalance metabólico heterotrófico (P<R) puede difícilmente ser explicado cuando se recogen partículas por debajo de la zona fótica, si sólo tenemos en cuenta la producción y exportación de carbono desde la superficie. Como ejemplo, la Tabla 9.1 muestra los resultados de un estudio llevado a cabo en el Océano Atlántico noreste subtropical (resultados sin publicar) dónde estudiamos tendencias regionales y mesoescalares en el metabolismo del plancton y en los flujos de POC que se hunde obtenidos a partir de cambios in vitro en oxígeno disuelto y fondeos de trampas de sedimento a la deriva, respectivamente.

Como se puede observar, las tasas de NCP fueron siempre negativas durante la campaña RODA I (agosto, 2006). Por ello, esperaríamos que la exportación de carbono desde la zona fótica fuera practi-

Table 9.1: Tasas integradas diarias (mmol O_2 m^{-2} d^{-1}) de producción primaria bruta (GPP), producción neta comunitaria (NCP) y respiración comunitaria (R) de la campaña de agosto (RODA I). Profundidad de integración, 120 m. Flujo de POC (mmol C m^{-2} d^{-1}) en la base de la capa fótica (150 m).

Stación	Lat. N	Long. W	GPP	NCP	R	P/R	Flujo POC
1	29.42	20.02	58.8	-47.3	106.5	0.55	5.53
2	28.75	18.27	112.2	-7.2	119.2	0.94	6.06
3	27.59	17.33	89.2	-16.4	105.5	0.85	13.09
4	27.58	15.60	113.5	-7.7	121.0	0.94	6.38
5	27.71	16.00	73.0	-11.6	84.7	0.86	9.63

camente nula. Sin embargo, estas estaciones presentaron tasas considerables de exportación de carbono, las cuales oscilaban entre 5,5 y 13 mmol C m^{-2} d^{-1} planteando la cuestión de cuál es el origen de esta materia exportada por debajo de la zona fótica. Este interrogante nos permite plantearnos la segunda cuestión que nos gustaría contestar en este estudio: *Estamos interpretando correctamente los balances de carbono en aguas superficiales simplemente teniendo en cuenta las tasas de producción in situ?*

9.1.3 Balance de carbono en las aguas mesopelágicas

Durante las dos últimas décadas numerosas evidencias indican que los procariotas mesopelágicos representan un componente metabólico mayoritario del océano [ver trabajo de revisión de Arístegui et al. 2009]. De acuerdo con la visión clásica de la bomba biológica, las comunidades procarióticas de las aguas mesopelágicas son suministradas con materia orgánica particulada mayoritariamente formada en aguas superficiales y transportada hacia el océano via partículas que se hunden. Este hecho es corroborado por la evidencia de que el carbono orgánico disuelto (DOC) contribuye sólo un 10-20%, a escala global, a las tasas de remineralización en el océano profundo [Arístegui et al. 2002]. Sin embargo, el POC que se hunde recolectado con las trampas de sedimento actuales no explican el restante 80-90% de las tasas de utilización de oxígeno en el océano profundo [Reinthaler et al. 2006; Steinberg et al. 2008; Baltar et al. 2009]. Este aparente desbalance es una de las más excitantes paradojas aún sin resolver en el ciclo del carbono e indica que la existencia de mecanismos alternativos para cumplir con la alta demanda de carbono de las aguas mesopelágicas o que la actividad metabólica en el océano profundo está siendo sobreestimada. El cálculo de los factores de conversión usados para estimar las tasas metabólicas en las aguas profundas presenta numerosas incertidumbres [Burd et al. 2010], así que la sobreestimación de las tasas metabólicas podría ser posible. No obstante, las estimas de actividad metabólica bacteriana en aguas profundas del Noroeste Mediterráneo son sugeridas a ser superiores en aquellas muestras mantenidas a presión in situ que aquellas medidas bajo condiciones de despresurización [Tamburini et al. 2003], indicando ésto que deben existir fuentes de carbono no tenidas en cuenta [ver Burd et al. 2010 para más detalles].

Una de estas fuentes de carbono no tenidas en cuenta podría ser la presencia de carbono orgánico suspendido o de baja tasa de sedimentación submuestreado por las trampas de sedimento actuales. La mayoría de la materia orgánica particulada en la columna de agua está formada de partículas suspendidas de flotabilidad neutra [Kepkay 2000; Verdugo et al. 2004], aunque, paradójicamente, los mecanismos de transporte advectivo y remineralización del carbono suspendido son escasamente conocidos [Bauer and Druffel, 1998], al contrario que con el POC que se hunde [ver revisión en Boyd and Trull 2007]. Recientemente, Baltar et al. [2009] encontró una correlación significativa entre el POC suspendido y la respiración potencial en aguas batipelágicas del Atlántico Noreste subtropical. Sin embargo, las concentraciones de POC suspendido en profundidad han sido reportadas como inadecuadas para sustentar una demanda de carbono sostenida debido a que un aporte nuevo de POC suspendido sería requerido para mantener la demanda [Steinberg et al. 2008]. *Existe por tanto algún mecanismo capaz de suministrar suficiente POC suspendido para satisfacer la demanda metabólica de carbono de las aguas mesopelágicas?*

9.1.4 Impacto de los remolinos mesoescalares en los flujos de carbono orgánico

Se conoce que los remolinos tienen un gran impacto en la biogeoquímica del océano superficial debido a los pulsos de nutrientes que inyectan en la zona fótica [Oschlies and Garçon, 1998] y a la estimulación de la actividad biológica [Falkowski et al. 1991; Sweeney, 2001; McGillicuddy et al. 2007]. Sin embargo, nuestro conocimiento acerca del impacto de los remolinos en el balance metabólico planctónico y subsecuente exportación de carbono istá limitado a unos pocos estudios y reportan resultados contradictorios. Con respecto al metabolismo del plancton, González et al. [2001] concluyen que el déficit de carbono orgánico el el Giro Subtropical del Atlántico Norte debiera aumentar entre un 14% y un 52% en ausencia de estructuras mesoescalares. Maixandeau et al. [2005], trabanjo en la parte noreste de la Cuenca Atlántica, reportaron que la variabilidad espacial de los procesos biológicos en invierno fue controlada por estructuras mesoescalares. En un estudio mesoescalar más reciente llevado a cabo en el Mar de Los Sargasso, los autores proveen nuevos datos que sugieren que el tipo y edad de los remolinos muestreados son factores importantes en el control del signo de la producción neta comunitaria [Mouriño and McGillicuddy, 2006]. A pesar de estos importantes estudios, nuestro conocimiento acerca de los complejos mecanismos que controlan la síntesis y respiración en los remolinos es escaso.

En relación a los flujos de carbono orgánico en los remolinos, un número limitado de estudios ha mostrado evidencias directas de un aumento de exportación de POC mediado por remolinos mesoescalares [e.j. Sweeney, 2003; Bidigare et al. 2003; McGillicuddy et al. 2007]. Sin embargo, programas interdisciplinares recientes (E-Flux (Pacífico Norte) y EDDIES (Atlántico Norte)) centrados en el efecto de los remolinos en la exportación de carbono han mostrado resultados inesperados. Sorprendentemente, ambos programas concluyen que los remolinos estudiados no aumenaron el flujo de carbono, aunque si el sílice biogénico [e.j. Benitez-Nelson and McGillicuddy, 2008; Maiti et al. 2008]. Estos nuevos descubrimientos ponen de manifiesto nuestra falta de conocimiento acerca de los mecanismos que controlan la exportación de carbono fuera de la zona fótica en los remolinos mesoescalares.

La mayoría de los estudios de trampas de sedimento en remolinos han medido las propiedades brutas de los flujos, como son el carbono y nitrógeno total, mientras que los compuestos individuales han recibido menos atención. Aunque los valores de carbono y nitrógeno total son provechosos, el conocimiento de los compuestos específicos provee información más precisa acerca de la labilidad, interacción con otros elementos, y mecanismos de degradación [Lee et al. 2000; Sheridan et al. 2002; Ingalls et al. 2006]. Aquí hemos intentado resolver alguna de las incertidumbres relacionadas con el papel que los remolinos pueden jugar en el transporte de materia orgánica hacia el océano profundo: *Podemos dilucidar cuáles son los factores que controlan la exportación de carbono en los remolinos usando biomarcadores? Pueden los remolinos cambiar la composición de la materia orgánica exportada? Pueden los remolinos aumentar el secuestro de carbono en el océano profundo o son estructuras superficiales con poca relevancia biogeoquímica?*

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9.2 Objetivos de la tesis y organización

El objetivo general de esta tesis fue profundizar en el conocimiento de la dinámica del carbono orgánico particulado (POC) en el Océano Atlántico Noreste Subtropical, así como determinar la importancia biogeoquímica de las dos fracciones que conforman el total del POC (el POC que no se hunde y el que se hunde). Para la consecución de este objetivo general, numerosos objetivos específicos fueron abordados. Básicamente, tratamos de responder a las preguntas planteadas en la introducción general:

- 1. *Cuál es la variabilidad regional y temporal en la forma del espectro de velocidades de sedimentación de las partículas?*

- 2. ál es la contribución del carbono orgánico suspendido a la demanda de carbono en el océano profundo? *Existe algún mecanismo capaz de suministrar suficiente* POC_{susp} *para satisfacer la demanda metabólica de carbono en las aguas mesopelágicas?*

- 3. *Cuál es el grado de acoplamiento entre el POC suspendido y la respiración?*

- 4. *Podemos dilucidar cuáles son los factores que controlan la exportación de carbono en los remolinos usando biomarcadores?*

- 5. *Pueden los remolinos cambiar la composición de la materia orgánica exportada?*

- 6. *Pueden los remolinos aumentar el secuestro de carbono hacia el océano profundo?*

∗ Para abordar la primera pregunta, desplegamos un fondeo en la región de la Corriente de Canarias durante un periodo de un año y medio. Este fondeo estaba compuesto de trampas de sedimento (IRSC) [Peterson et al., 2005] ancladas a 260 m de profundidada. Estas trampas poseen la capacidad de separar las partículas en clases discretas en función de su velocidad de sedimentación. Para conocer el papel biogeoquímico potencial de cada una de las fracciones de velocidad, llevamos a cabo análisis de flujos y composición de aminoácidos y cloropigmentos. **(Capítulo 2)**

Este trabajo resultó en la siguiente publicación:

- *"El papel de las partículas de sedimentación lenta en el ciclo del carbono oceánico"* publicado en **Geophysical Research Letters (GRL)**.

∗ Para intentar resolver el aparente desbalance de carbono en aguas superficiales y mesopelágicas (preguntas 2 y 3), se presentan dos capítulos. En el primer estudio, para responder a la pregunta 2, estimamos el transporte y consumo horizontal, desde la superficie hasta 3000 m de profundidad, de carbono orgánico suspendido recogido con botellas oceanográficas. El análisis fue realizado usando una aproximacin de modelo de caja, con fronteras físicas que se extienden desde 20° a 29° 10'N y 20° 35' a 26°W (1000 x 600 Km) en la región de la Corriente de Canarias. **(Capítulo 3)**

∗ En el segundo estudio, para responder a la pregunta 3, la variabilidad espacio-temporal de la respiración del microplancton en aguas epipelágicas y mesopelágicas fue analizada a través de la actividad enzimática del sistema de transporte de electrones (ETS). este estudio fue llevado a cabo a lo largo de dos secciones zonales (21°N y 26°N) que se extendían desde el afloramiento costero del noroeste de África hasta las aguas de océano abierto del Atlántico noreste subtropical. **(Capítulo 4)**

Estos trabajos resultaron en las siguientes publicaciones:

- *"Transporte lateral y consumo de POC en aguas superficiales y profundas de la región de la Corriente de Canarias: un estudio de modelo de caja"* publicado en **Global Biogechemical Cycles (GBC)**.

- *"Variabilidad espacio-temporal de la respiración de la columna de agua en la Cuenca Canaria: el papel del carbono orgánico suspendido"* sometido a **Journal of Marine Systems (JMS)**

∗ Para delucidar los factores que controlan la exportación de carbono en los remolinos reportamos, junto con los flujos de POC y PON, patrones regionales y mesoescalares de la composición y flujos de aminoácidos y cloropigmentos obtenidos a partir de trampas de sedimento a la deriva y fijas en el Océano Atlántico noreste. **(Capítulo 5)**

Este trabajo resultó en la siguiente publicación:

- *"Variabilidad regional y temporal de los flujos de materia orgánica en el Océano Atlántico noreste subtropical: un diagnóstico por biomarcadores"* publicado en **Biogeosciences (BG)**.

∗ Para abordar los objetivos específicos número 5 y 6, medimos flujos y composición de POC, aminoácidos y cloropigmentos en muestras recogidas en un fondeo anclado en el área de generación de los remolinos ciclónicos que se generan al sur de Las Islas Canarias durante un periodo de 1.5 años. Los efectos de la presencia de los remolinos fueron investigados desde la superficie hasta los 1000 m.

(Capítulo 6)

Este trabajo resultó en la siguiente publicación:

- *"Secuestro de carbono incrementado por los remolinos mesoescalares en el Océano Atlántico noreste"* sometido a **Proceedings of the National Academy of Sciences, (PNAS)**.

9.3 METODOLOGÍA

Cálculo del flujo exportado de materia orgánica particulada (POM): se estima a partir del material recolectado en trampas de sedimento flotantes. Se desplegaron dos trampas situadas a 100 y 200 m de profundidad. Estas trampas se dejan a la deriva durante 14-15 horas en las diferentes estaciones de 16 h. El material recolectado en las trampas, situadas justo por debajo de la zona eufótica, representa (teóricamente) la producción exportada particulada. La MOP se concentró en filtros de fibra de vidrio mediante filtración, y se congelaron hasta su análisis. Se analiza la composición de C y N en los filtros mediante combustión a alta temperatura en un analizador elemental (CHN, Perkin Elmer).

Cálculo del balance metabólico (P/R): se cuantificó el balance metabólico (producción bruta vs. respiración comunitaria) en aguas superficiales (0-90 m) de las siguientes estaciones: R2, T1, T2, T5, T6, T9, T11, T14, T15, T18 y T21. Para ello se desarrolla un sistema de incubación de muestras en la oscuridad y en la luz que reproduce las condiciones ambientales. De esta manera se eliminan posibles errores de irradiancia y temperatura de incubación. El procedimiento de muestreo fue el siguiente: en el CTD de recogida del agua para las incubaciones se determinaban las temperaturas de las cinco profundidades (5, 15, 30, 60, y 90 m) y se ajustaban los baños termostáticos a las mismas. Se llenaban todas las botellas de incubación (iniciales, claras y oscuras) con el agua de sus respectivas profundidades, previamente homogeneizada. Posteriormente las claras eran ubicadas en su respectivo sistema de incubación, las oscuras en los baños termostáticos correspondientes y las iniciales fijadas para la determinación del oxígeno inicial. Transcurridas 24 horas se fijaban las claras y las oscuras y el oxígeno se determinaba por valoraciones Winkler, con un sistema automatizado de gran precisión con punto final colorimétrico (microwinkler) (Arístegui Harrison 2002).

Distribución y concentración de materia orgánica particulada (POM): se realizaron perfiles para obtener la distribución y las concentraciones de materia orgánica particulada (POC y PON). En estos perfiles se recolectaron muestras cada 50 m, desde la superficie hasta 1000 m de profundidad. Dichas muestras (entre 3 y 4 litros de agua) se concentraron en filtros de fibra de vidrio GF/F y se congelaron a -80°C hasta que sean analizadas en el laboratorio de la Facultad de Ciencias del Mar. En cada estación, y a diferentes profundidades, se ponía un doble filtro GF/F baja el primero, para medir la adsorción de carbono orgánico disuelto (DOC) y restárselo al valor total del POC. Se ha visto que el carbono debido a la adsorcin de DOC por el filtro puede llegar a ser >1uM. Por otro lado, las concentraciones de materia orgánica particulada, estiamadas a partir de muestras recogidas con botellas oceanográficas, se compararán con concentraciones obtenidas a partir de muestras recogidas con bombas de filtracin in situ (SAPs).

Cuantificación de la respiración del microplancton (R) en la columna de agua: se estima a partir de la actividad enzimática respiratoria del sistema de transferencia de electrones (actividad ETS; Packard, 1985). Se utilizan índices R/ETS calculados durante esta campaña para transformar la respiración potencial (ETS) en respiración real (R). Con el fin de obtener perfiles verticales con la resolución necesaria para ver la contribución de las comunidades mesopelágicas a la respiración se recolectaron muestras cada 50 m, desde la superficie hasta 1000 m de profundidad. Las muestras (entre 4 y 5 litros de agua) se concentran en filtros de fibra de vidrio y se congelan en nitrógeno líquido hasta que sean analizadas en el laboratorio de la Facultad de Ciencias del Mar.

Clorofila a, feofitina a, feofórbido a, y pirofeofórbido a fueron determinados mediante Cromatografía Líquida de Alta Resolución en fase inversa (HPLC) [Lee et al., 2000; Wakeham et al., 2009]. Los aminoácidos fueron medidos por HPLC en los mismos filtros analizados para pigmentos, usando una precolumna y derivatización con o?pthaldialdehyde (OPA) después de la hidrólisis [Lee et al., 2000; Wakeham et al., 2009].

Los Análisis Principales de Componentes son comúnmente utilizados en el análisis de complejas bases de datos orgánicas [Goñi et al., 2000; Ingalls et al., 2006; Goutx et al., 2007]. Es un análisis de regresión multivariante que reduce un largo número de variables a unos pocos componentes. El PCA fue usado en esta tesis para calcular cuantitativamente variaciones en la composición de las partículas que se hunden. El PCA fue aplicado a los datos de composición de pigmentos y amioácidos. Antes de realizar el PCA, los datos de abundancia en mol% de cada muestra son estandarizadas restando la media de todos los valores y dividiendo por la desviación estándar de todos los valores [Dauwe and Middelburg, 1998; Dauwe et al., 1999; Sheridan et al., 2002]. El primer componente principal del PCA es el eje de máxima variación del conjunto de datos, mientras que el segundo es equivalente a el eje de máxima variación residual.

Todos los PCA fueron realizados en Sirius en Windows (versión 7.0).

9.4 RESULTADOS Y DISCUSIÓN GENERAL

9.4.1 Papel del carbono suspendido y de baja tasa de sedimentación en la biogeoquímica de la columna de agua

Tradicionalmente, en biogeoquímica oceánica, la materia orgánica biosintetizada en la zona fótica se considera que es transportada principalmente por el material particulado que se hunde. Sin embargo, los flujos verticales de carbono orgánico que se hunde en las aguas profundas del Atlántico Norte han sido reportados como inadecuados para soportar la demanda de carbono observada [Reinthaler et al. 2006; Steinberg et al. 2008]. Estos descubrimientos han cuestinado la asunsión de que el carbono que se hunde es el principal sustrato para la respiración e invocan la existencia de fuentes no tenidas en cuenta de materia orgánica para suministrar el carbono necesario para la actividad metabólica de las aguas profundas.

Las comunidades microbianas en el océano profundo son suministradas con materia orgánica disuelta (DOM) y materia orgánica particulada (POM) mayoritariamente formada en la zona epipelágica la cual es transportada hacia el océano profundo [Arístegui et al. 2009]. La contribución relativa del carbono orgánico disuelto (DOC) a la respiración mesopelágica total (R), a escala global, fue estimada por Arístegui et al. [2002]. En su estudio, el DOC contribuyó entre un 10 y un 15% al consumo de oxígeno total en la zona mesopelágica, un valor que no puede satisfacer el desbalance metabólico. Sorprendentemente, los estudios previos de balances de carbono no han considerado el papel potencial que puede jugar el carbono orgánico particulado suspendido (POC_{susp}), incluso sabiendo que este pool de carbono es cuantitativamente mucho mayor que el POC que se hunde [McCave, 1984; Kepkay, 2000]. Este enorme pool de carbono no está representado en el material capturado por las trampas de sedimento actuales. Entonces, si los flujos verticales de carbono derivados de trampas de sedimento son usados para construir balances de carbono para diferentes procesos biogeoquímicos, fuertes desbalances pueden surgir. De forma adicional, otra fuente potencial de carbono orgánico, submuestreada por las trampas de sedimento, son las partículas de sedimentación lenta. Las trampas de sedimento pueden perder una fracción del POC exportado en las partículas pequeñas y de sedimentación lenta debido a la advección lateral. En este escenario, un mayor porcentaje de partículas pequeñas frente a grandes resultaría en una menor eficiencia promedio de recolección por parte de las trampas de sedimento. Esto hace que la determinación de la variabilidad espacio-temporal de la forma del espectro de velocidades de las partículas sea de vital importancia.

En esta sección, discutimos la contribución potencial de las partículas de sedimentación lenta (Capítulo 2) y del POC suspendido

(Capítulos 3 y 4) a la respiración total, así como sus mecanismos de transporte.

De acuerdo con los resultados obtenidos por las trampas de sedimento IRSC (Capítulo 2), al menos durante la mitad del año en en estas aguas subtropicales, más del 60% del total del carbono orgánico particulado se encuentra contenido en las partículas de sedimentación lenta (0,7-11 m d^{-1}). Además, los análisis de biomarcadores orgánicos (aminoácidos y cloropigmentos) revelan que estas partículas tienen un estado de degradación similar, o incluso más fresco que las partículas de sedimentación rápida. Estas caracteristicas hacen a este pool de carbono susceptible a la advección lateral y remineralización en la columna de agua sin ser tenido en cuenta en los balances de carbono derivados de las trampas de sedimento. Este descubrimiento tiene profundas consecuencias para la dinánica del carbono (ver Figura 9.1).

Una vez que conocemos que las partículas de sedimentación lenta dominan la fracción del POC que se "hunde" en esta región, y que estas partículas sufren advección lateral [Gust y Kozerski, 2000], el interés reside en calcular el transporte lateral del POC suspendido y de aquel que se hunde muy lentamente. Con este proósito, estimamos el transporte lateral y consumo, desde la superficie hasta los 3000 m, del carbono orgánico pariculado suspendido, a través de una aproximación de modelo de cajas (Capítulo 3). Este análisis nos permite concluir que los flujos laterales de POC son 2 o 3 órdenes de magnitud superior a los flujos verticales dependiendo de las masas de agua, confirmando nuestra hipótesis de un flujo de carbono lateral más relevante que el vertical por unidad de área. Estos resultados sugieren que en el océano, ningún ecosistema es cerrado, así que puede recibir y exportar material orgánico hacia ecosistemas adyacentes. En nuestro trabajo, también demostramos que los márgenes continentales producen más carbono orgánico del que ellos pueden respirar, siendo una fracción de este carbono orgánico no respirado y de flotación neutra disponible para ser exportado desde la costa hacia océano abierto a través de capas de densidad neutral inclinadas.

Desde un punto de vista biogeoquímico, este flujo lateral de POC soporta entre un 30 y un 60% de la respiración total mesopelágica (R), en base a bajos o altos escenarios de contribución de los flujos verticales de POC y la contribución del carbono orgánico disuelto a la respiración. Sin embargo, las concentraciones de POC_{susp} en profundidad han sido reportadas como inadecuadas para soportar una demanda metabólica sostenida, ya que un nuevo suministro de POC_{susp} es requerido para mantener la demanda [Steinberg et al. 2008]. Entonces, nuestro Capítulo 3 también da evidencias de un importante y no tenido en cuenta mecanismo que suministra POC_{susp} a niveles profundos. Adicionalmente, producción in situ de carbono orgánico por parte de quimioautótrofos procariotas ha sido propuesto como un mecanismo que suministra POC suspendido en las aguas profundas del Océano Atlántico Noreste [Herndl et al. 2005]. De hecho, un trabajo reciente llevado a cabo en la zona mesopelágica del Atlántico Noreste concluye que la fijación de carbono inorgánico disuelto contribuye entre un 12% y un 72% a la demanda de carbono procariota diaria [Baltar et al. 2010]. En base a estos resultados, el POC suspendido parece jugar un papel más importante en la biogeoquímica mesopelágica que el POC que se hunde.

Con el propósito de reforzar la hipótesis de una importante correlación entre el POC_{susp} y la respiración estudiamos los gradientes regionales y la variabilidad temporal en la respiración de la columna de agua (ETS) y el carbono particulado orgánico suspendido (Captulo 4). El análisis de correlación resultante revela que el POC_{susp} soporta entre el 65% y el 74% de la respiración del plankton en la columna de agua (de acuerdo con el Capítulo 3), poniendo de manifiesto una baja contribución (<20%) a la respiración de la columna de agua por parte del POC que se hunde. Entonces, el acoplamiento entre el POC que se hunde y la respiración en la columna de agua es mucho más débil de lo que tradicionalmente ha sido asumido. Un estudio reciente, basado en el algoritmo de Antia et al. [2001], también concluyó que la contribución potencial del POC que se hunde recae entre el 4 y el 12% de la demanda procariota de carbono diaria al usar una producción primaria superficial de 28 y 50 mmol C $m^{-2}d^{-1}$, respectivamente [Baltar et al. 2010]. Resumiendo, la Figura 9.2 muestra la contribución relativa de las diferentes fuentes de carbono orgánico discutidas aquí a la respiración mesopelágica, así como los mecanismos de transporte de cada una de ellas.

Como un todo, estos descubrimientos podrían ayudar a explicar el desbalance aparente entre las fuentes de carbono y las tasas de utilización de oxígeno en las aguas mesopelágicas cuando sólo se tienen en cuenta el flujo vertical de POC recojido con las trampas de sedimento, e indican que la actividad bacteriana está más ligada al POC suspendido que al POC que se hunde. Finalmente, este trabajo sugiere que debemos cambiar de punto de vista de aproximaciones tradicionales en una dimensión (vertical) a estudios del ciclo del carbono en el océano in tres dimensiones como previamente fue sugerido por Michaels et al. [1994].

9.4.2 Importancia de los remolinos mesoescalares en la dinámica del POC en el Atlántico Noreste subtropical

El obstáculo topográfico que representan Las Islas Canarias al flujo de La Corriente de Canarias causa la frecuente aparicón de remolinos ciclónicos y anticiclónicos, de una manera similar a las calles de von Karman y los cuales representan la mayor fuente de variabilidad mesoescalar al sur del archipiélago [ver Sangrá et al. 2005]. Estas estructuras, acomodan un diverso conjunto de interacciones físicas, químicas, y biológicas las cuales influencian la biogeoquímica marina en un amplio rango de escalas temporales [Benítez-Nelson and McGillicuddy, 2008]. Aumento de la producción primaria, inducida por un bombeo de nutrientes en la zona fótica por parte de los remolinos ciclónicos ha sido reportado [Arístegui et al. 1997; Oschlies and Garçon, 1998]. Sin embargo, los cambios asociados a la presencia de los remolinos en en la estructura del plankton, interacciones tróficas, impacto sobre la exportación de materia orgánica e importancia biogeoquímica en esta área son escasamente conocidos.

El objetivo principal de los capítulos 5 y 6 fue completar el hueco en nuestro conocimiento acerca de la importancia de los remolinos en la dinámica del carbono. Para abarcar este objetivo medimos, junto con los flujos totales de POC, patrones mesoescalares en la composición y flujos de aminoácidos (THAA) y cloropigmentos obtenidos por fondeos de trampas de sedimentos a la deriva y fijas en el Océano Atlántico Noreste. Ambos, THAA y cloropigmentos son prácticos indicadores de descomposición, fuentes y transporte en la columna de agua [e.g., Wakeham et al., 1997;

Dauwe and Middelburg, 1998; Lee et al., 2000]. Como el nitrógeno inorgánico puede controlar la bomba biológica a través de su papel de nutriente limitante, la descomposición y remineralización del nitrógeno orgánico a aminoácidos son de particular importancia. Los cloropigmentos son indicadores clave de la diagénesis de la materia orgánica, puesto que su origen está en las comunidades de aguas superficiales. Entonces, siguiendo la degradación de la clorofila a medida que las partículas caen desde la superficie a través de la columna de agua podemos determinar la "frescura" de la meria orgánica durante su transporte hacia capas más profundas.

Bajo condiciones de estado estacionario, el aumento en los flujos de nutrientes inducidos por los remolinos tiene que ser compensado por una estimulación de la tasa de crecimiento del fitoplancton marino, y como consecuencia, un aumento de la exportación de POC desde la zona fótica para balancear el aporte de nutrientes entrante. Sin embargo, este balance entre inyección de nutrientes, producción y exportación no siempre es alcanzado, debido a que la respuesta de la comunidad a la entrada de nutrientes es compleja [Buesseler et al. 2008]. De hecho, dos programas mesoescalares recientes (E-Flux, Pacífico Norte y EDDIES, Atlántico Norte), centrados en el papel de los remolinos mesoescalares en el flujo exportado de materia, concluyeron que los remolinos no aumentan el flujo de carbono, aunque si incrementaron el flujo de sílice biogénica [Benitez-Nelson and McGillicuddy, 2008]. Estos resultados plantean un cuestión de primer orden: *Cuáles son los factores que controlan la exportación de carbono en los remolinos?*

En base a los análisis de biomarcadores (capítulos 5 y 6), nosotros sugerimos que la estructura de la comunidad del fitoplancton, particularmente el predominio de organismos de carbonato cálcico sobre diatomeas, un "lastrado" eficiente y una consecuente menor actividad de pastaje por parte del zooplancton son los mayores factores que influencian la exportación de materia orgánica en los remolinos. Numerosos trabajos han indicado que un fracción importante de la materia orgánica producida en aguas superficiales es transportada a profundidad asociada con minerales de "lastre" [Armstrong et al. 2002; Francois et al. 2002], especialmente con los carbonatos [Klaas and Archer, 2002]. Por tanto, el aumento del flujo de POC observado en los remolinos generados al sur de Las Islas Canarias puede ser debido a un aumento de la velocidad de sedimentación de las partículas en un sistema altamente lastrado por carbonatos en comparación con esos sistemas lastrados por ópalo (como Hawaii). Además, nuestro capítulo 6 y un estudio previo [Ingalls et al. 2006] sugieren que, en áreas ricas en diatomeas, la presión de pastaje por parte del zooplancton es mayor que en áreas ricas en organismos de $CaCO_3$, teniendo estas últimas una mayor exportación de agregados en lugar de empaquetados fecales.

Entonces, nuestros resultados son consistentes con la hipótesis propuesta por los programas mencionados anteriormente de el pastaje del zooplancton como un mecanismo para reducir la exportación de POC en los remolinos. En los remolinos enriquecidos en ópalo, se encontr que la biomasa producida es procesada por el microzooplancton, los cuales a su vez son predados por ciliados grandes y dinoflagelados liberando materia orgánica suspendida y disuelta en lugar de producir empaquetados fecales [Landry et al. 2008; Maiti et al 2008].

Nuestros resultados (capítulo 6) también sugieren que una importante fracción del carbono generado durante los periodos de mezcla y enriquecidos en ópalo (como nuestro bloom estacional o los remolinos de Hawaii) es mediada por el zooplancton migrador vertical. Estos organismos se alimentan en superficie y zona mesopelágica superior y defecan por debajo de 500 m, por ello podrían potencialmente contribuir de manera significativa a el flujo vertical de carbono por debajo de la zona mesopelágica [Hernández-León et al. 2010]. Sin embargo, nuestros resultados muestran que la eficiencia de transferencia de POC entre 290 y 1000 m durante estos periodos fue sólo del 8%, mientras que fue del 27 al 73% asociada a los remolinos durante el periodo de estratificación. Por tanto, nosotros sugerimos que un transporte activo importante por parte de los migradores verticales facilita el reciclado del carbono orgánico particulado en la zona mesopelágica, por lo que resulta en un debilitamiento de la bomba biológica. Por el contrario, los resultados presentados arriba indican que los remolinos ciclónicos en esta área son más efectivos transportando POC al océano profundo que las aguas ambientales (incluyendo el bloom estacional), poniendo de manifiesto el importante papel que tienen estas estructuras en la biogeoquímica regional. No obstante, el aparente desbalance metabólico en las aguas mesopelágicas no puede ser satisfecho por aportes verticales de POC que se hunde derivados de los remolinos, reforzando la visión actual de que la vida microbiana en el océano profundo es más dependiente de las partículas de sedimentación lenta y suspendidas que del POC que se hunde (capítulos 2, 3 y 4).

9.4.3 Modelo conceptual de flujos y descomposición de POC en la Cuenca Canaria

Un foco principal de las ciencias marinas durante las 3 últimas décadas ha sido la identificación de los factores que controlan la exportación de las partículas biogénicas hacia el océano profundo, la conocida "bomba biológica" [Boyd and Trull, 2007]. La mayor parte de nuestro conocimiento actual de los procesos biogeoquímicos oceánicos que afectan a la materia particulada es derivado de datos de trampas de sedimento [Buesseler et al. 2000], sin embargo, numerosos aspectos sin resolver acerca de la efectividad de las trampas de sedimentos prevalecen hoy en dia [ver Gardner, 2000]. Se piensa que las trampas de sedimento submuestrean las partículas de sedimentación lenta, las cuales pueden sufrir advección lateral durante largas distancias (capítulo 3) así como resuspensión en el interior de las trampas de sedimento [Gust and Kozerski, 2000]. Como consecuencia, la construcción de los ciclos biogeoquímicos globales, balances de carbono oceánicos, interacciones tróficas, y mecanismos de transporte han sido ampliamente guiados por la simplificación introducida por las trampas de sedimento, las cuales dan una visión en una dimensión del "panorama" total.Esta tesis, además de los flujos verticales de POC, trata de proveer información acerca del transporte lateral de POC a través de aproximaciones de balances de masa y biomarcadores orgánicos.

Figura 9.3 ilustra el modelo conceptual de flujo de POC propuesto para la Cuenca Canaria después de esta tesis de investigación. Este modelo está básicamente dividido en dos escenarios de acuerdo a la estacionalidad, condiciones hidrográficas y estructura de la comunidad del plancton. El panel de la izquierda muestra las condiciones de verano-otoño, dónde la columna de agua está estratificada, dominan los organismos fitoplanctónicos de carbonato cálcico y los remolinos ciclónicos son más intensos. Por el contrario, el panel de la derecha muestra las condiciones de invierno-primavera, dónde las aguas superficiales están mezcladas y ocurre un eriquecimiento relativo de diatomeas. Estas dos situaciones diferentes fuerzan a la dinámica del POC a una dependencia temporal que no había sido préviamente establecida.

Condiciones de Verano-Otoño

Durante este periodo de tiempo la ruta del flujo de POC es principalmente via partículas de sedimentación lenta y suspendidas las cuales sufren transporte lateral (capítulo 3). Esta situación da lugar a una ditribución de POC en capas con máximos localizados en las interfaces de las masas de agua y microgradientes de densidad debido a la acumulación de este pool orgánico con características de flotabilidad casi neutra. Adicionalmente, esta distribución en capas es alimentada por carbono suspendido lateralmente exportado desde margen continental del Noroeste de África. De acuerdo con esta distribución, estas partículas tienen tiempos de residencia mayores en la columna de agua en comparación con las partículas de sedimentación rápida. Por tanto, es razonable pensar que la respiración pueda igualar o superar las tasas de producción primaria como ha sido frecuentemente reportado para esta área [Duarte et al. 2001; González et al. 2001; Marañón et al. 2007]. Sin embargo, la exepción a esta distribución se encuentra en los remolinos, donde la mezcla vertical es más pronunciada y el flujo de POC es más vertical y eficiente. Teniendo los remolinos en cuenta, nuestros resultados muestran un flujo importante de POC a 1000 m de profundidad durante este periodo (Figura 6.1), indicando que, si el sistema es evaluado como un todo, el balance entre la producción y la respiración tiene que ser positivo. Estos descubrimientos también sugieren que un déficit de carbono durante en verano-otoño debiera existir en ausencia de remolinos, resaltando el importante papel de estas estructuras.

La estructura de la comunidad del fitoplancton en los remolinos está principalmente dominada por organismos de carbonato cálcico, resultando en una baja presión de pastaje por parte del zooplancton y también en un bajo transporte activo por el mesozooplancton migrador.

Condiciones de Invierno-Primavera

Durante el periodo de invierno-primavera la estructura trófica y rutas del POC biogénico están determinadas por el grado de mezcla vertical de las aguas superficiales. Nuestros resultados sugieren un enriquecimiento superficial en silice debido a la mezcla invernal (ver capa de mezcla más profunda, MLD; Figura 6.1a), aumento relativo de diatomeas y consiguiente incremento en la exportación de POC en la base de la capa fótica. Estas condiciones son favorables para la producción de partículas de mayor tamaño y con mayores tasas de sedimentación (como fue reportado en el capítulo 2), por ello uno esperaría que estas partículas pudieran potencialmente contribuir al flujo vertical por debajo de la zona mesopelágica. Sin embargo, en comparación con el periodo de verano-otoño, encontramos una baja eficiencia de transferencia de POC entre 290 y 1000 m, lo que sugiere que el POC biosintetizado durante el bloom tardío de invierno tiene otro destino que la exportación en forma de partículas. En base a los flujos de POC y biomarcadores, concluimos que el POC que se hunde es rápidamente procesado por la comunidad microbiana, baipaseada a la capa de reflecxión profunda (DSL) por los organismos migradores y transformada en POC que no se hunde, lo que está de acuerdo con la baja eficiencia de transferencia de POC registrada a 1000 m. Esto también puede explicar la paradoja de que la materia orgánica en estaciones ricas en diatomeas es eliminada por mecanismos que no resultan en la aparicón de marcadores de degradación en la materia que se hunde [Ingalls et al. 2006]. En conjunto, estos descubrimientos indican que que el destino del material generado durante el bloom estacional es ser reciclado en la zona mesopelágica en lugar de ser transportado hacia el océano profundo. Entonces, la importancia de los migradores verticales diários en este área está más ligada al suministro de carbono orgánico para la respiración mesopelágica, que al secuestro de carbono hacia el océano profundo.

En términos de la asociación de la materia orgánica que se hunde con los minerales "lastre" (carbonato cálcico y ópalo) nuestros datos coinciden con Armstrong et al. [2002] y Klaas and Archer [2002] en que los flujos de carbono orgánico que se hunde se correlacionan más con el carbonato cálcico que con el ópalo. Ellos argumentan que la mayoría del flujo de carbono orgánico hacia el océano profundo es llevado a cabo por el carbonato cálcico, debido a que es más denso que el ópalo y más abundante que el material terrígeno. Nosotros sugerimos también que la materia orgánica asociada con ópalo es más biodisponible que la materia orgánica asociada al carbonato cálcico. Una posible explicación para esto es que aproximadamente el 50% del ópalo se disuelve en los primeros 100 m de la columna de agua, mientras que para el carbonato cálcico este porcentaje es mucho menor [Tréguer et al. 1995]. Como consecuencia, la exportación neta de carbonato cálcico y materia orgánica asociada desde la superficie del océano es mayor que los flujos correspondientes de materia orgánica asociada con ópalo.

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9.5 CONCLUSIONES

"Es débil porque no ha dudado bastante y ha querido llegar a conclusiones"

Miguel de Unamuno, 1864-1936

Las principales conclusiones que surgen de esta tesis son:

(a) La forma del espectro de velocidades de sedimentación de las partículas en nuestra región esta dominada por las partículas de sedimentación lenta (0.7-11 m d^{-1}) durante el verano y el otoño y por partículas de sedimentación rápida durante invierno y primavera. Esta descubrimiento tiene profundas implicaciones para la dinámica del carbono:

   i. Durante el verano y el otoño, las trampas de sedimento pueden perder una fracción del POC exportado en las partículas de sedimentación lenta. Entonces, si los flujos verticales de carbono derivados de trampas de sedimento son usados para construir balances para diferentes procesos biogeoquímicos, fuertes desbalances pueden surgir.

   ii. Cuando las partículas de sedimentación lenta dominan el pool de carbono exportable, la mayoría de la materia orgánica sería respirada en la zona epipelágica y mesopelágica superior, actuando como una fuente biológica de CO_2 susceptible de ser intercambiada con la atmósfera. Por el contrario, si las partículas de sedimentación rápida contribuyen mayoritariamente al flujo de carbono, la eficiencia de transferencia de carbono a la zona mesopelágica incrementa, resultando en un aumento del secuestro de carbono hacia el océano profundo.

(b) Una fracción significativa del balance de carbono mesopelágico en la región oeste de la Corriente de Canarias es alimentada por advección lateral de carbono suspendido desde el márgen continental o de la actividad a mesoescla en la región de frontera este. Sin embargo, una gran parte de este carbono mesopelágico podría ser remineralizado en los primeros 1000 m en lugar de ser transportado hacia océano abierto.

   i. Los flujos laterales de POC son 2 o 3 órdenes de magnitud superiores a los flujos verticales dependiendo de las masas de agua, confirmando la hipótesis de que el flujo horizontal de materia orgánica particulada es más relevante por unidad de área que el vertical.

   ii. La influencia del carbono orgánico particulado advectado horizontalmente desde la costa Noroeste de África hacia la región del giro subtropical puede llegar a más de 1000 Km de distancia.

   iii. Este flujo lateral de POC soporta entre un 28 y un 59% de la respiración total mesopelágica, en base a una baja o alta contribución de los flujos verticales de POC y del carbono orgánico disuelto a la repiración.

(c) La respiración del plancton es principalmente (65-74%) soportada por las fluctuaciones de la materia orgánica suspendida advectada lateralmente, resaltando una baja contribución del POC que se hunde (<20%) a la respiración de la columna de agua. Este conclusión podría ayudar a explicar el aparente desbalance entre las fuentes de carbono y las tasas de utilización de oxígenoen las aguas mesopelágicas cuando sólo se tienen en cuenta los flujos verticales de POC que se hunde recogido con trampas de sedimento.

(d) El campo de remolinos generados al sur de Las Islas Canarias aumenta entre 2 y 4 veces el flujo de POC con respecto a las aguas ambientales. Incrementos de entre 2 y 10 veces en los flujos de cloropigmentos y aminoácidos son observados en el campo de remolinos con respecto a condiciones de no remolino.

(e) La estructura de la comunidad del fitoplancton, particularmente, el predominio de organismos enriquecidos en $CaCO_3$ sobre diatomeas, el "lastrado" más eficiente por parte del $CaCO_3$, y por tanto la menor presión por parte del zooplancton son sugeridos como los mayores factores de control sobre la exportación de materia orgánica en los remolinos.

(f) Los análisis de biomarcadores orgánicos revela que la materia orgánica exportada durante condiciones de remolino tiene un estado de degradación menor con respecto a las condiciones de no remolino.

(g) Durante el bloom de fitoplancton tardío de invierno, un cambio importante en la dinámica del POC que se hunde, presumiblemente mediado por el zooplancton migrador vertical resulta en una menor eficiencia de transferencia de POC hacia el océano profundo ($>$1000 m), respecto a el efecto debido a los remolinos ciclónicos.

(h) El material transferido durante el bloom tardío de invierno es principalmente reciclado en la zona mesopelágica, mientras que los remolinos ciclónicos durante el periodo de estratificación aumentan el secuestro de carbono, resaltando así la importancia de estas estructuras en la biogeoquímica de la columna de agua a nivel regional.

(i) El aparente desbalance metabólico en las aguas mesopelágicas no puede ser satisfecho por aportes verticales de POC que se hunde derivados de los remolinos, reforzando la visión actual de que la vida microbiana en el océano profundo es más dependiente de las partículas de sedimentación lenta y suspendidas que del POC que se hunde.

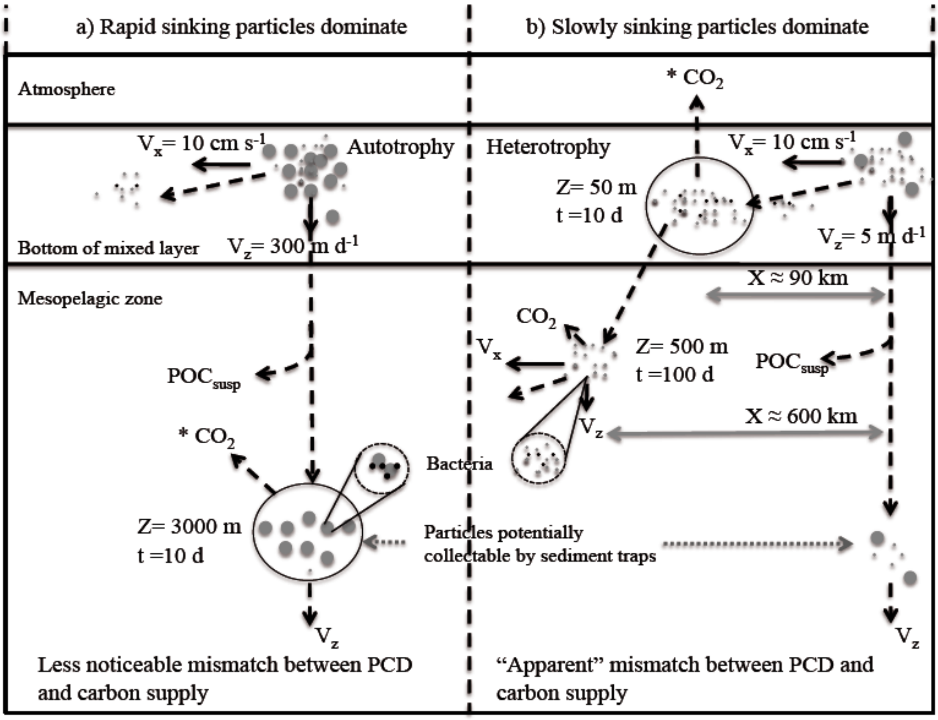


FIGURE 9.1: Modelo conceptual dependiente de la velocidad de la dinámica de las partículas. (a) En un sistema donde las partículas de sedimentación rápida dominan, la remineralización epipelágica y mesopelágica del POC que se hunde debe ser mínima; (b) En un sistema donde las partículas de sedimentación lenta dominan, una importante fración del POC sufrirá advección lateral y puede escapar de las trampas de sedimentos, dando lugar a un desacoplamiento entre el flujo de POC y la demanda de POC procariota. Flechas contínuas negras = velocidad de las partículas. Flechas discontínuas negras = trajectorias del carbono. Líneas contínuas grises ilustran la distancia horizontal teórica alcanzada por las partículas de sedimentación lenta durante dos periodos diferentes de tiempo (10 y 100 dias). Las distancias fueron estimadas usando una velocidad zonal de la corriente de 10 cm s^{-1} y 5 cm s^{-1} para las zonas epipelágica y mesopelágicas, respectivamente. Los círculos representan partículas con el mismo "punto de partida" (Z = 0 m) pero con diferentes características dinámicas. Después de 10 dias, la mayor parte del POC permanece en la zona fótica (~50 m) en (b), pero alcanza 3000 m en (a). Las líneas discontínuas grisesindican la cantidad de POC potencialmente recolectable por las trampas de sedimento (asumiendo la misma PP) en cada escenario.

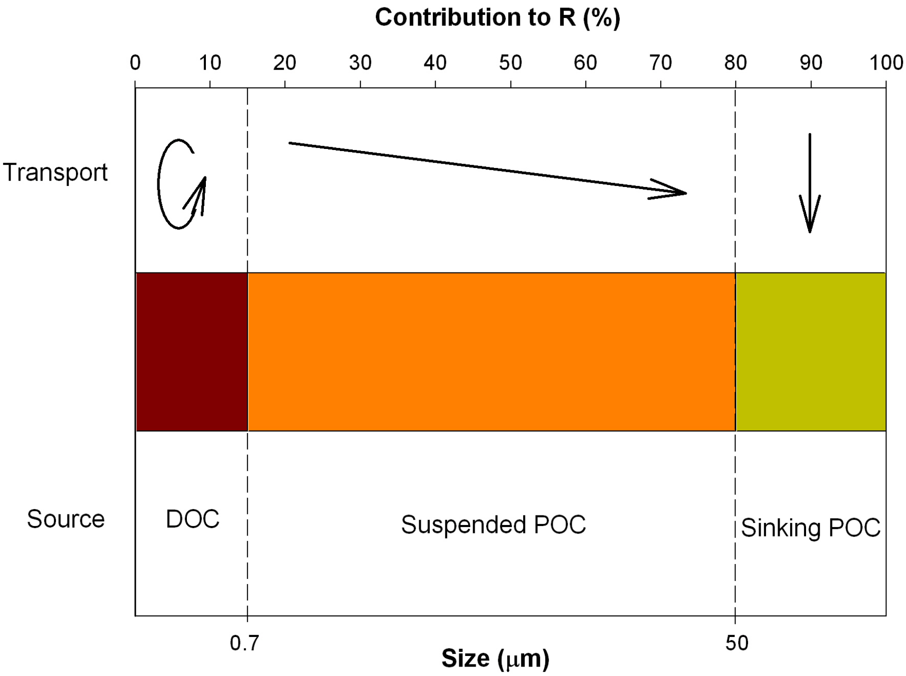
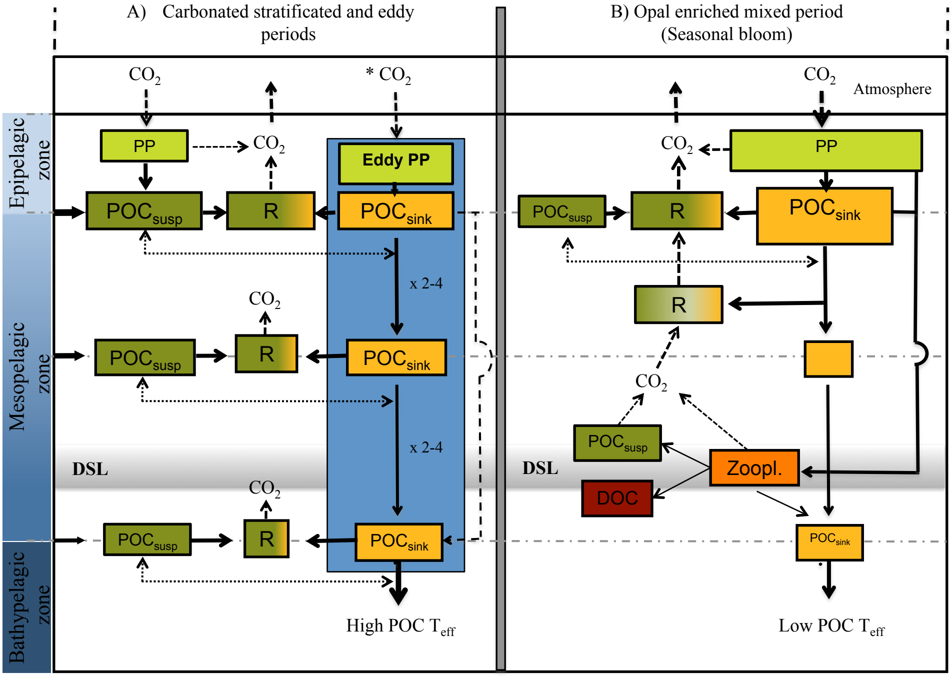


FIGURE 9.2: Modelo conceptual de la contribución de las diferentes fuentes de carbono orgánico a la respiración mesopelágica. Los paneles de abajo ilustran las diferentes fuentes de carbono en función del tamaño de partícula, mientras que los paneles superiores muestran el mecanismo de transporte dominante de cada una de ellas.



Alonso-González, 2010

FIGURE 9.3: Modelo conceptual de la evolución temporal del flujo y descomposición de POC para la Cuenca Canaria. El modelo comprende cuatro capas básicas: atmósfera, zona epipelágica, zona mesopelágica y zona batipelágica. Los flujos de carbono orgánico (POC) son ilustrados por líneas contínuas negras, mientras que los flujos de carbono inorgánico (CO_2) son mostrados por líneas discontínuas negras. Las líneas negras a puntos representan el intercambio entre el POC que se hunde y el suspendido. Durante verano-otoño (panel A)) el POC presenta una distribucón en capas, excepto en los remolinos, dónde la mezcla vertical es más pronunciada. La entrada externa de carbono suspendido es representada por tres flechas negras contínuas localizadas en la izquierda. *CO_2 representa una entrada neta de CO_2 desde la atmósfera a el océano inducida por la presencia de los remolinos ciclónicos. La línea negra vertical discontínua indica un bajo baipas de POC por parte del zooplancton. Durante invierno-primavera (panel B)) el POC presenta una distribución parcheada con la mayor parte de las partículas viajando verticalmente. El mesozooplancton migrador realiza un baipas de una importante fracción del POC epipelágico liberándolo como materia orgánica disuelta o suspendida cerca del fondo de la zona mesopelágica. Esto resulta en una menor eficiencia de transferencia de POC (T_{eff}) hacia la zona batipelágica comparado con el panel A).