



Off-shelf fluxes of labile materials by an upwelling filament in the NW Iberian Upwelling System

X.A. Álvarez-Salgado ^{a,*}, M.D. Doval ^a, A.V. Borges ^b, I. Joint ^c,
M. Frankignoulle ^b, E.M.S. Woodward ^c, F.G. Figueiras ^a

^a CSIC, Instituto de Investigaciones Mariñas, Eduardo Cabello 6, 36208-Vigo, Spain

^b Univ. of Liège, Unité d'Océanographie Chimique, Sart Tilman B5, B-4000 Liège, Belgium

^c NERC, Plymouth Marine Laboratory, Prospect Place, Plymouth PL1 3DH, UK

Abstract

Daily changes in the concentrations of carbon and nitrogen species were monitored during the course of a Lagrangian drifter experiment in a recurrent upwelling filament south of Cape Finisterre (NW Iberian Upwelling System). A drifting buoy released at the southern edge of the upwelling centre generated by the Cape moved 60km southwestwards from 3 to 7 August 1998. Organic matter in the 50m deep study water mass (average $77 \pm 2 \mu\text{M C}$) consisted of: $57 \mu\text{M C}$ of dissolved organic matter (DOM) with a C/N molar ratio of 19 ± 2 ; $6 \mu\text{M C}$ of DOM with a C/N ratio of 9 ± 2 , and $14 \mu\text{M C}$ of 50% DOM and 50% suspended organic matter (POM_{susp}) with a C/N ratio of 6.0 ± 0.4 .

Net conversion of consumed inorganic salts into accumulated $\text{TOM} = \text{POM}_{\text{susp}} + \text{DOM}$ was $\sim 40\%$ for nitrogen and $\sim 30\%$ for carbon. Since the parcel of water crossed the shelf-edge, these conversion efficiencies are equivalent to net horizontal export-ratio of 0.4 and 0.3 respectively. A second drifter was deployed in the offshore-end of the filament, and was displaced 20km west between 14 and 17 August 1998. Nitrate was exhausted in the surface water and no significant changes were observed in the variables measured during the course of the second experiment. Low C/N ratios (6.5 ± 0.4) and rapid $\text{POM}_{\text{susp}}/\text{DOM}$ inter-conversion in the $20 \mu\text{M C}$ excess observed in the study volume points to the persistence of the labile materials formed on the shelf during transport to the ocean. Our data demonstrate

- a) the key role of upwelling filaments in off-shelf export of organic materials and
- b) the major contribution of DOM to this horizontal export, a previously unaccounted amount.

The high nitrogen content of the materials exported make them attractive organic substrates for use by microbial populations in the adjacent oligotrophic ocean. © 2001 Elsevier Science Ltd. All rights reserved.

Contents

1. Introduction	322
---------------------------	-----

* Corresponding author. Tel.: +34-986-231930; fax: +34-986-292762.

E-mail address: xsalgado@iim.csic.es (X.A. Álvarez-Salgado).

2. Materials and methods	323
2.1. The Lagrangian study	323
2.2. CO ₂ system, nutrients, dissolved oxygen, chlorophyll and microplankton determinations	323
2.3. Dissolved and suspended organic matter measurements	325
3. Results	326
3.1. The coastal upwelling study	326
3.2. The filament study	331
4. Discussion and conclusions	332
4.1. Off-shelf export of primary production mediated through an upwelling filament	333
4.2. Lability of the exported materials	334
Acknowledgements	335
References	335

1. Introduction

Ocean margins are important sites for high net primary production by phytoplankton responding to the enhanced nutrient fluxes from adjacent continental and ocean waters. Although ocean margins cover only 8% of the total ocean surface, according to different estimates they support 18–33% of the global net primary production and 27–50% of the global export production (Walsh, 1991; Chavez & Toggweiler, 1995; Wollast, 1998). Considerations of the fate of exported materials have centred on sinking particulate organic matter (POM_{sink}), either deposited on the shelf (Falkowski et al., 1988; Biscaye, Flagg, & Falkowski, 1994) or transported offshore and deposited on the slope (Walsh, Rowe, Iverson, & McRoy, 1981). Despite the recognition of the importance of fresh suspended (POM_{susp}) and dissolved (DOM) organic matter to marine carbon cycling (e.g. Kirchman et al., 1993; Hansell & Carlson, 1998), their contributions to the export production of ocean margins have not been quantified (Wollast, 1998).

The ecosystems of ocean margins affected by wind-driven upwelling react to the increased nutrient inputs from the ocean by enhancing organic matter production, recycling and export (Walsh, 1991). Horizontal offshore transport of the export production is favoured, especially at sites where large upwelling filaments develop (e.g. Brink & Cowles, 1991; Gabric et al., 1993; Barton et al., 1998). However, even recent modelling approaches to horizontal carbon export by upwelling filaments (Gabric, Eifler, & Schrimpf, 1996; Moisan, Hofmann, & Haidvogel, 1996) have neglected the key contribution of fresh DOM.

Recent work in the NW Iberian upwelling system has confirmed the major contribution of DOM to the excess of phytogenic materials accumulating in surface waters on the shelf to the south of Cape Finisterre (Álvarez-Salgado, Doval, & Pérez, 1999). A large filament is regularly observed at that position (Haynes, Barton, & Pilling, 1993). The westward extension of this filament depends on the intensity of the recurrent upwelling episodes (~2 week period; Álvarez-Salgado, Rosón, Pérez, & Pazos, 1993) during April/May to September/October, which is the upwelling season at our latitudes, 42–43°N (Wooster, Bakun, & McClain, 1976). The aim of this work was to study the short time-scale evolution of the dissolved and suspended, organic and inorganic, carbon and nitrogen stocks in a parcel of recently upwelled Eastern North Atlantic Central Water (ENACW) (referred to as the parcel below), which was subsequently advected offshore along a filament that occurs recurrently south of Cape Finisterre. The net ecosystem metabolism (NEM) of carbon and nitrogen species in the parcel, i.e. the net balance of production minus the respiration of autotrophs and heterotrophs will be inferred. The horizontal export ratio (e-ratio) of organic materials

across the shelf-edge, i.e. the fraction of the NEM in the upwelling centre off Cape Finisterre that is exported to the adjacent ocean, will be estimated. Although horizontal export of dissolved organic matter has recently been taken into account in the estimation of e-ratio of the oceanic equatorial upwelling (e.g. Archer, Peltzer, & Kirchman, 1997), this is the first time it has been assessed in a study of ocean margins. Finally, the simultaneous determinations of carbon and nitrogen stocks allows us to discuss on the key issue of the lability of the exported materials, as assessed from the study of the C/N ratios.

2. Materials and methods

2.1. *The Lagrangian study*

Upwelling filaments off the western Iberian Peninsula are frequently observed in early July. They reach their maximum offshore extent in late September, but have usually disappeared by late October, after the development of the poleward-flowing slope current of warm subtropical water that characterises the downwelling season at these latitudes (Haynes et al., 1993). The filament selected for study occurs recurrently south of Cape Finisterre during the upwelling season, and it is the longest one off the western Iberian Peninsula, both in terms of its mean (150–170km) and maximum (245–280km) lengths. It probably originates as a result of topographic forcing and shelf induced wind-stress variation in the area, where the Rías Baixas funnel the wind to the south-west.

Rapid offshore advection of shelf surface waters carried by an upwelling filament has been observed by both direct current measurements and by drifter trajectories (Brink & Cowles, 1991; Haynes et al., 1993). Entrainment and subsequent offshore transport of recently upwelled water near the coast occurs in parallel to filament development (Moisan & Hofmann, 1996). Lagrangian drifters have been used to track water masses, allowing the construction of budgets with the assumption of reduced vertical and horizontal advection within the volume under investigation (e.g. Moisan & Hofmann, 1996). In this study, a surface drifting buoy carrying sediment traps was used to track the parcel. Daily discrete water samples were collected nearby at ~02:00, ~09:00 and ~12:00 GMT from 6–8 depths throughout the upper 150m (see Fig. 1 for 02:00 GMT stations position). The buoy was released at the southern edge of Cape Finisterre upwelling centre on 3 August and it drifted southwards until 7 August, crossing the shelf-edge. On 14 August, a second drifter was deployed in the core filament, and moved south-westwards until 17 August. During the filament study additional seawater samples from a depth of 500m were collected at selected stations to give reference values of the chemical characteristics of waters below ENACW. A detailed description of the two drifter studies can be found in Joint et al. (2001), together with justifications for the assumption that the experiments were Lagrangian and provided a consistent temporal sequence of the evolving characteristics of the water.

2.2. *CO₂ system, nutrients, dissolved oxygen, chlorophyll and microplankton determinations*

The measurements of pH were made using a Ross combination electrode (ORION) calibrated on the Total Hydrogen Ion Concentration Scale ($\text{mol} \cdot \text{kg}^{-1} \text{SWS}^{-1}$) with the TRIS and AMP buffers (Dickson, 1993). Total Alkalinity (TA) was measured using classical Gran electro-titration. TA calculation was made with corrections for fluoride and sulphate according to Hansson and Jagner (1973). Total Inorganic Carbon (C_T) contents were calculated using the dissociation constants of carbonic acid from Roy et al. (1993) and the dissociation constant of HSO_4^- from Dickson (1990). C_T and TA have been normalised to salinity 35.0 to produce the corresponding NC_T and NTA parameters, which depend only on the biological and geochemical activity in the parcel. The contribution of CaCO_3 fixation unrelated to nitrate consumption and O_2 production, has to be subtracted from NC_T . For systems where NO_3^- is the dominant inorganic

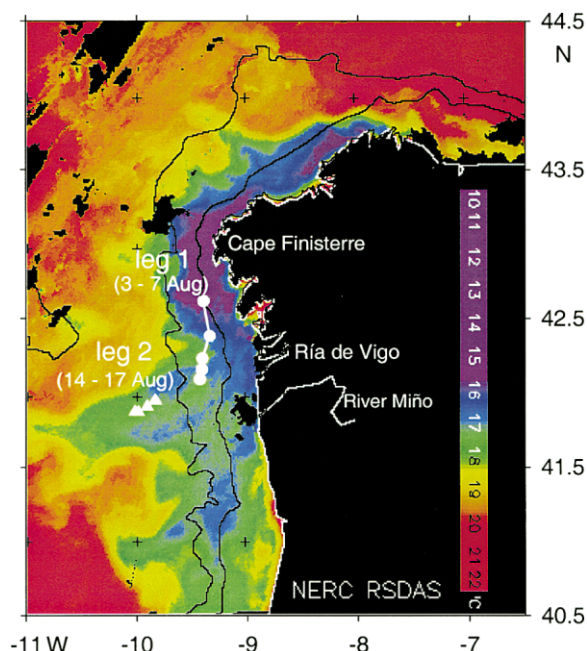


Fig. 1. SST satellite image of the study area (Iberian upwelling system, SW Europe) showing the buoy track during the inshore (3–7 August 1998) and the offshore (14–17 August 1998) studies of the upwelling filament south of Cape Finisterre. The symbols (Leg 1, circles, Leg 2, triangles) indicate the position of the buoy at the daily 02:00 GMT sampling site. The satellite image is from 12 August 1998, at the midpoint of the experiment, and shows the SST imprint of the upwelling filament. Black lines are the 200 and 2000m isobaths.

nitrogen species, as in the present study, the CaCO_3 -corrected NC_T ($\text{NC}_{T\text{cor}}$) can be calculated according to Broecker and Peng (1982):

$$\text{NC}_{T\text{cor}} = \text{NC}_T - 0.5 \cdot (\text{NTA} + \text{NO}_3^-)$$

Analyses of dissolved nutrient concentrations were performed immediately after sampling. Water samples were carefully transferred from the rosette sampler to clean Nalgene bottles, with every effort being made to minimise contamination. Nutrient concentrations were measured by colorimetric autoanalysis in a Technicon segmented flow colorimetric autoanalyser. Nitrate was measured using the method of Brewer and Riley (1965), nitrite by the procedure of Grasshoff (1976), silicate and phosphate by the methods of Kirkwood (1989), and ammonia by the method of Mantoura and Woodward (1983).

In addition, when present in low concentrations ($<50\text{nM N}$), nitrate and ammonium were measured using more sensitive analytical procedures. Nitrate and nitrite concentrations were determined by the chemiluminescence method of Garside (1981), and low nanomolar concentrations of ammonia were measured by the fluorescence analytical method of Jones (1991). Dissolved oxygen was measured by the Winkler method using a potentiometric end-point determination. Apparent oxygen utilisation, $\text{AOU} = \text{O}_2\text{sat} - \text{O}_2$, was calculated using Benson and Krause's equation (UNESCO, 1986) for oxygen saturation (O_2sat).

Chlorophyll concentrations were measured by spectrophotometric (Parsons, Maita, & Lalli, 1984) and fluorometric (Holm-Hansen, Lorenzen, Holmes, & Strickland, 1965) analyses of extracted pigments. Either aliquots of 1 to 2 litres of water from the above experiments were filtered through Whatman GF/F filters for spectrophotometric analysis, or 100ml samples were filtered through polycarbonate filters for fluorometric determination of chlorophyll concentration of three size fractions ($>5\mu\text{m}$, <5 to $>2\mu\text{m}$ and $<2\mu\text{m}$); all

filters were frozen until return to the laboratory. Pigments were extracted by addition of 90% acetone and then stored in the dark at 4°C for ~12 h prior to analysis.

Samples for microplankton counts were preserved in Lugol's iodine and sedimented in 100ml composite chambers. Diatoms, dinoflagellates, flagellates and ciliates were identified and counted using an inverted microscope. Cell numbers were converted into carbon biomass as described by Joint et al. (2001).

2.3. Dissolved and suspended organic matter measurements

DOM ($\phi < 0.8 \mu\text{m}$) and POM_{susp} ($> 0.8 - < 200 \mu\text{m}$) concentrations in the water column were determined during the course of the experiment. Seawater for the analysis of POM_{susp} was drawn from the Niskin bottles into 2 l polycarbonate flasks. It was immediately filtered through 25 mm Whatman GF/F filters (precombusted 450°C, 4h) using an oil-less vacuum filtration system (filtration pressure $< 0.3 \text{ kg} \cdot \text{cm}^{-2}$) to collect the suspended material. The filters were dried over silica gel and frozen at -20°C until analysed in the laboratory. Suspended organic carbon (POC_{susp}) and nitrogen (PON_{susp}) measurements were carried out with a Perkin Elmer 2400 CHN analyser. Catalytic combustion of POC_{susp} and PON_{susp} to CO_2 and NO_x , respectively was performed at 900°C and reduction of NO_x to N_2 at 640°C . Acetanilide was used to calibrate the system. The analytical error of the method is $\pm 0.1 \mu\text{M C}$ for POC_{susp} and $\pm 0.04 \mu\text{M N}$ for PON_{susp} .

Samples for the analyses of dissolved organic matter (DOM) were collected into 250ml acid-cleaned all-glass flasks. They were immediately filtered through 47 mm Whatman GF/F filters (precombusted 450°C , 4 hours) in an acid-cleaned all-glass filtration system, and collected in 10ml glass ampoules (precombusted 450°C , 12 hours). After acidification with H_3PO_4 to $\text{pH} < 2$, the ampoules were heat-sealed and preserved in the dark at 4°C , until analysed in the laboratory. A nitrogen-specific Antek 7020 nitric oxide (NO^\bullet) chemiluminescence detector was coupled in series with the carbon specific Infra-red Gas Analyser (IRGA) of a Shimadzu TOC-5000 organic carbon analyser, in conjunction with a PC-based integration software package (Integrador v1.2, Fractal Info, Spain) as described in Álvarez-Salgado and Miller (1998). An injection cycle took ~4 min. As each sample was injected 3–4 times, ~12–16 min were necessary for completion. The system was standardised daily with a mixture of potassium hydrogen phthalate and glycine. The system blank was obtained by frequent injection (every 4–6 samples) of UV Milli-Q water, and was equivalent to $10 \mu\text{M C}$ and $0.4 \mu\text{M N}$. Precision of the simultaneous measurements were respectively $\pm 1 \mu\text{M C}$ and $\pm 0.3 \mu\text{M N}$. The accuracy of our DOC measurements was tested daily with the reference materials provided by J. Sharp (University of Delaware). We obtained an average concentration of $45.1 \pm 0.7 \mu\text{M C}$ ($n=52$) for the DEEP OCEAN reference (Sargasso Sea deep water, 2600m) and $0.4 \pm 0.6 \mu\text{M C}$ ($n=52$) for the BLANK reference material. The nominal values provided by the reference laboratories were 44.0 ± 1.5 and $0.0 \pm 1.5 \mu\text{M C}$ respectively.

Dissolved organic nitrogen (DON) concentration in the samples was obtained by subtracting the independently measured NO_3^- from the HTCO-TDN . A problem with the precision of DON measurements remains in nitrate-rich upwelled waters, where the DON contribution to the TDN signal is small ($\sim 3.5 \mu\text{M N}$ DON from $\sim 12 \mu\text{M N}$ TDN). The standard deviation of the DON concentration can be calculated as

$$\sigma_{\text{DON}} = \sqrt{\sigma_{\text{TDN}}^2 + \sigma_{\text{DIN}}^2}$$

Since the analytical error of NO_3^- measurements is $\pm 0.1 \mu\text{M N}$, the precision of DON estimation for upwelled waters would be ~10% or $\pm 0.3 \mu\text{M N}$.

3. Results

3.1. The coastal upwelling study

Nitrogen species ($\text{NO}_3^- + \text{NO}_2^-$, DON and $\text{TON} = \text{PON}_{\text{susp}} + \text{DON}$) have been chosen to present the time evolution of the chemical setting during the Lagrangian experiment (Fig. 2). A DON and TON excess and $\text{NO}_3^- + \text{NO}_2^-$ (hereinafter NO_3^-) deficit was observed in the parcel (shaded area in Fig. 2) compared with the levels recorded in the cold and nutrient-rich upwelled ENACW below: $\sim 3.7 \mu\text{MN}$ TON and $\sim 7.5 \mu\text{MN}$ NO_3^- at 150m depth respectively. Nitrate concentrations reduced dramatically from 3 to 7 August, with a concomitant accumulation of DON and TON. Average NO_3^- concentrations in the parcel decreased from $\sim 3 \mu\text{MN}$ to $< 0.4 \mu\text{MN}$ (Fig. 3a); the majority of the consumption occurred during 3 August, at a rate of $\sim 2 \mu\text{MN.d}^{-1}$. No changes of NH_4^+ concentrations (not shown) were observed during the course of the experiment. Net inorganic carbon (NC_{Tcor}) consumption and oxygen production (c.f. AOU) followed the NO_3^- trend (Fig. 3b). The $\text{NC}_{\text{Tcor}}/\text{NO}_3^-$ molar ratio was 9 ± 2 , indicating there was production of organic matter with an excess of carbohydrate, compared with the Redfield composition of planktonic organic matter with a C/N ratio of 6.7 (Anderson, 1995). Accumulation of PON_{susp} and DON accompanied NO_3^- consumption (Fig. 3a). PON_{susp} peaked on 4 August and a short-lived DON maximum was recorded a day later, suggesting there was partial conversion of recently formed PON_{susp} into DON. The efficiency of the system to convert NO_3^- into TON was $\sim 40\%$ while the buoy was inshore over the shelf. Fig. 4a shows the conspicuous time evolution of the C/N molar ratios of POM_{susp} and DOM being transported within the parcel. C/N ratios were high in the recently upwelled ENACW at the upwelling centre, but decreased as POM_{susp} and DOM reached their maxima, indicating an increased contribution of N-rich labile material. The subsequent increase in C/N ratios suggests there was partial consumption of this N-rich material. The evolution of chlorophyll concentrations in the parcel (average $1.2 \pm 0.2 \text{ mgChl.m}^{-3}$; Fig. 4b) paralleled the trend of PON_{susp} (Fig. 3a) and denoted a progressive increase in the size of the $> 5 \mu\text{m}$ fraction (average 43% of the total). Diatoms contributed $< 2\%$ to the total microplankton carbon on 3 August but this contribution had increased to 24% on 7 August (Fig. 4c). Dinoflagellates were the most abundant microplankton group. They represented 67% of the total microplankton carbon from 3 to 7 August.

Results shown in Figs. 3 and 4 are reinforced by the analysis of the correlation between the measured chemical parameters presented in Fig. 5. All the individual samples from the surface to 150m at the three daily sampling times have been considered. Throughout the experiment the contribution of continental runoff to surface waters was negligible. Average salinity in the parcel was 35.68 ± 0.02 , which represents an additional content of $< 0.4\%$ of freshwater compared to the salinity of upwelled ENACW (< 35.80). This is expected from the climate of the study area. Average August 1987–96 continental runoff and offshore Ekman transport off the Rías Baixas was $25 \text{ L.s}^{-1}.\text{km}^{-2}$ of drainage basin and $385 \text{ m}^3.\text{s}^{-1}.\text{km}^{-1}$ of coast (Nogueira, Pérez, & Ríos, 1997). Considering the total area of the drainage basin to be 6800 km^2 and the length of the coast to be 110km, 99.6% of surface waters on the shelf came from the adjacent ocean mediated through upwelling. Consequently, the origin intercept and slope of the correlations presented in Fig. 5 indicate the chemical transformations occurring in the ENACW, which flows from the ocean onto the shelf; where it upwells, enters the offshore flow in photic layer, and in which there is the upwelling-enhanced production, recycling and export of phytogenic materials. This kind of approach has been successfully applied by Hansell and Carlson (1998) to the study of the NEM of the Equatorial Pacific and other marine systems.

Spatial and temporal NC_{Tcor} and NO_3^- changes are coupled throughout the water column ($r = +0.95$). The $\text{NC}_{\text{Tcor}}/\text{NO}_3^-$ slope of $7.7 \pm 0.3 \text{ molC/molN}$ (Fig. 5(a)) is comparable with the value of $9 \pm 2 \text{ molC/molN}$ obtained from the time changes in the parcel (Fig. 3b). Changes in the TOC and TON pools (Fig. 5b) are also well correlated ($r = +0.88$) with a TOC/TON slope of $6.0 \pm 0.4 \text{ molC/molN}$, i.e. about 23% lower than the stoichiometric ratio of net nutrient utilisation ($7.7 \pm 0.3 \text{ molC/molN}$). The direct correlation of POC_{susp}

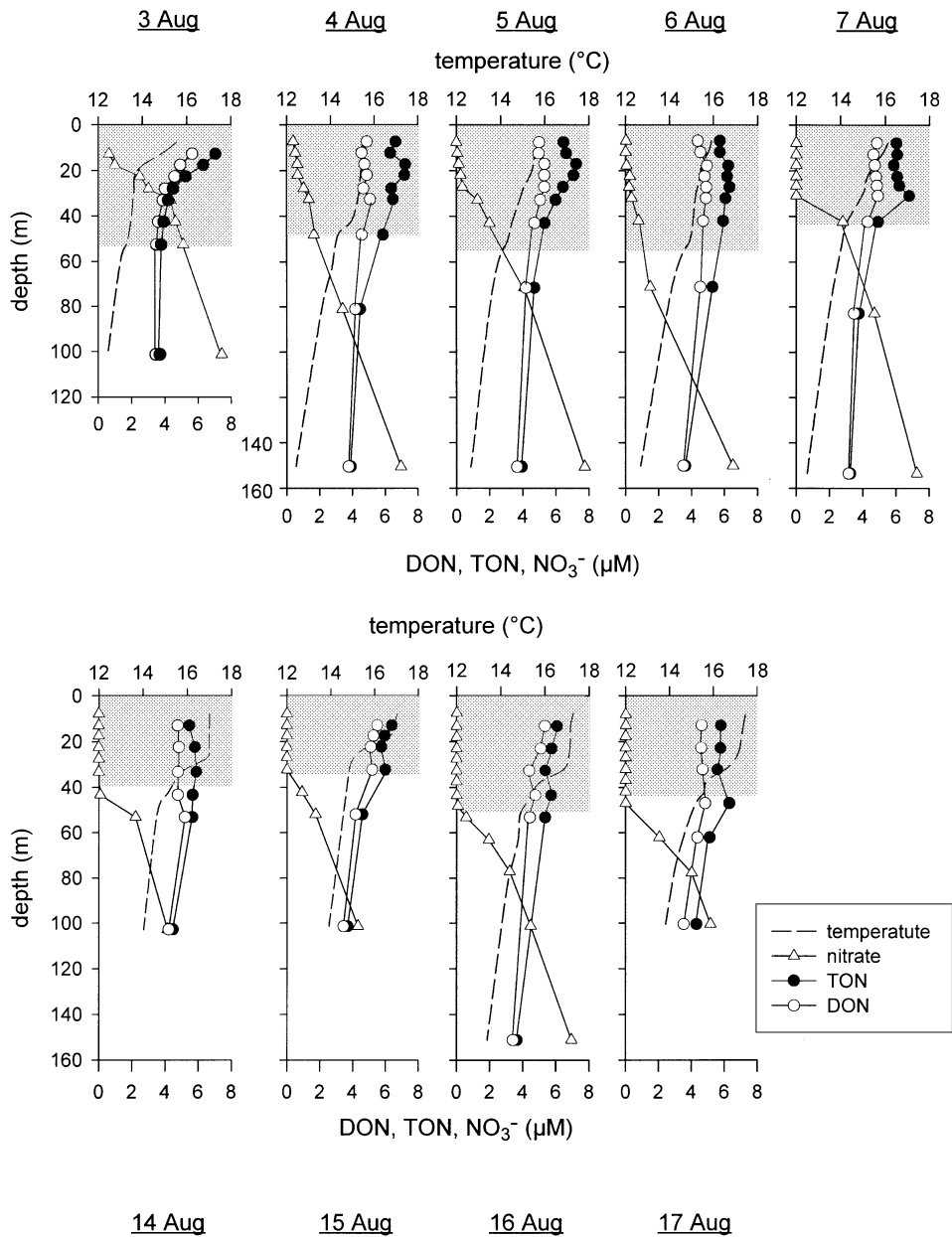


Fig. 2. Time evolution of the 02:00 GMT temperature, nitrate (NO_3^-), dissolved organic nitrogen (DON) and total organic nitrogen ($\text{TON} = \text{PON}_{\text{susp}} + \text{DON}$) profiles during the coastal upwelling (a) and filament study (b) of the filament. Shaded areas indicate the study water volume, with the 1% photosynthetic available radiation (PAR) defining the lower limit of depth.

and PON_{susp} is very good ($r = +0.96$), with a slope of $5.9 \pm 0.2 \text{ molC/molN}$ (Fig. 5c), the same as for the total organic material. Consequently, the fraction of DOM that forms simultaneously with POM_{susp} has about the same C/N ratio and could be considered as labile as POM_{susp} . This labile fraction of DOM can be obtained from the linear regressions between $\text{TOC}/\text{POC}_{\text{susp}}$ ($r = +0.89$; Fig. 5d) and $\text{TON}/\text{PON}_{\text{susp}}$

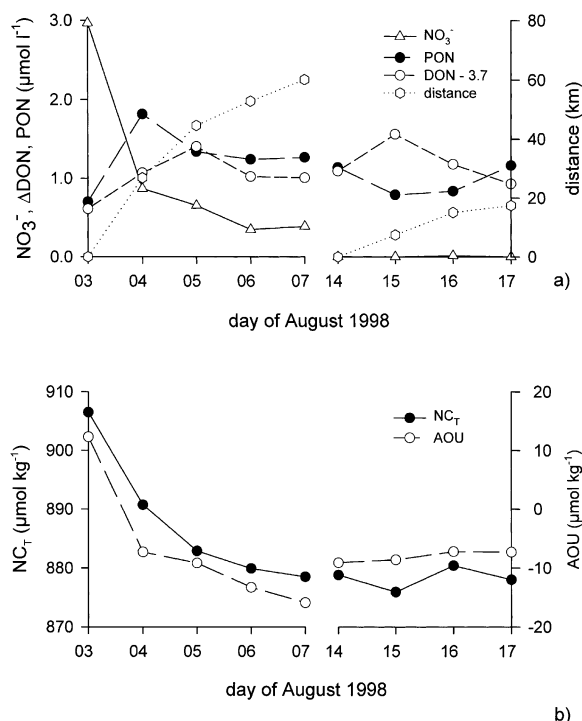


Fig. 3. Time evolution of (a) the average concentrations of NO_3^- , PON_{susp} and $\text{DON} - 3.7$ ($\mu\text{M N}$); and (b) CaCO_3 -corrected total inorganic carbon (NC_T , $\mu\text{M C}$) and apparent oxygen utilisation ($\text{AOU} = \text{O}_2 - \text{O}_2 \text{ saturation}$, $\mu\text{M O}_2$) in the study water mass during the coastal upwelling and filament study. (a) includes the total distance covered by the drifting buoy. $\text{DON} - 3.7$ represents the DON excess compared with DON levels in upwelled ENACW ($3.7 \mu\text{M N}$).

($r=+0.92$; Fig. 5e). The slopes $\text{TOC}/\text{POC}_{\text{susp}} = \text{TON}/\text{PON}_{\text{susp}} = 1.9 \pm 0.1$ indicate that the fraction of DOM formed at the same time-scale as POM_{susp} is of about the same magnitude as POM_{susp} . The intercepts of these regressions ($63 \pm 1 \mu\text{MC}$ and $3.7 \pm 0.1 \mu\text{MN}$) represent the constant amount of DOC and DON in POM -free upwelled water. The C/N molar ratio of this dissolved material, 17 ± 1 , is about 3-times the ratio of the labile material. These numbers agree very well with the DOC and DON concentrations found by Álvarez-Salgado et al. (1999) in recently upwelled ENACW in the same study area. The labile fraction of DOC and DON represents only 8% and 19% of the average DOC and DON concentrations in the water column. DOC and DON in upwelled ENACW (150m depth) is $\sim 10\%$ and $\sim 20\%$ above the constant concentration of $57 \pm 1 \mu\text{M C}$ and $3.0 \pm 0.3 \mu\text{M N}$ observed at 500m depth (not shown). The C/N molar ratio of DOM at 500m increases to $\sim 19 \pm 2$, indicating the refractory nature of this material.

An inverse linear correlation ($r=-0.86$) is observed between TON and NO_3^- (Fig. 5f). The TON/NO_3^- slope of -0.43 ± 0.03 is comparable with the value of 0.4 obtained from the time changes in the parcel (Fig. 3a). It indicates that the conversion efficiency of 40% is applicable both at the time-scale of the study volume (~ 1 wk) and the time-scale of the flushing time of upwelled ENACW on the shelf during upwelling episodes (~ 4 wk). The latter number has been obtained assuming a volume of $\sim 250 \text{ km}^3$ for shelf waters off the Rías Baixas, an offshore Ekman transport of $1000 \text{ m}^3 \cdot \text{s}^{-1} \cdot (\text{km of coast})^{-1}$ during upwelling episodes (Álvarez-Salgado et al., 1993) and a coast $\sim 110 \text{ km}$ long. An inverse linear correlation ($r=-0.85$) is also observed between TOC and $\text{NC}_{T\text{cor}}$ (not shown), with a resultant $\text{TOC}/\text{NC}_{T\text{cor}}$ slope of -0.29 ± 0.03 . Consequently, the conversion efficiency reduces to 0.3 for the case of carbon. Considering the $\text{TOC}/\text{NC}_{T\text{cor}}$, TON/NO_3^- , TOC/TON and $\text{NC}_{T\text{cor}}/\text{NO}_3^-$ slopes in Fig. 5, a C/N ratio of 9 ± 2 mol C/mol N for the organic

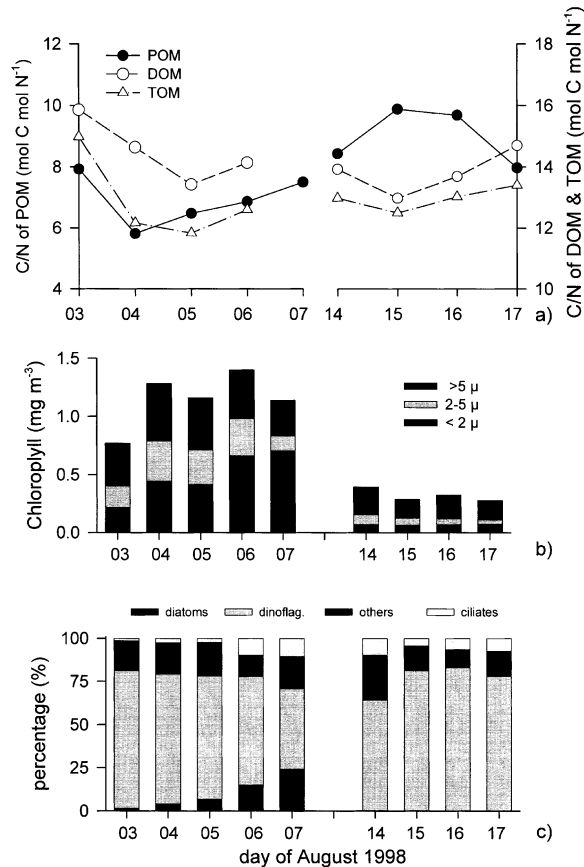


Fig. 4. Time evolution of (a) the average C/N molar ratio of the suspended (POM_{susp}) dissolved (DOM) and total (TOM) organic matter; (b) chlorophyll concentration (mg m⁻³) of three size fractions (<2 μm, 2–5 μm, >5 μm); and (c) the percentage of diatoms, dinoflagellates, ciliates and others (referred to total microplankton carbon) in the parcel at the start during its inshore phase and later at the offshore end of the filament. Small flagellates and Cryptophyceae (small cells) mainly compose the group of 'others'.

material trapped in the shelf can be inferred. This number is in good agreement with the 7.82 reported by Olli et al. (2001).

Fig. 6 summarises the information in the previous paragraphs to produce a tentative partitioning into refractory, labile and semi-labile organic matter in waters upwelled onto the shelf and then being advected offshore. The average TOC concentration at 500m (~100% DOC) is 57 μM C with a C/N molar ratio of 19 ± 2. This depth is just below the lower limit of ENACW off the NW Iberian Peninsula (Pérez, Mouriño, Fraga, & Ríos, 1993). The origin intercept of the regressions in Fig. 5d (63 μM C) and Fig. 5e (3.7 μM N) can be considered as the mixture of refractory (90%, C/N ~ 19 ± 2) and semi-labile materials (10%, C/N ~ 9 ± 2) being transported onshore in the shallower ENACW bodies, and are then upwelled over the shelf. A TOC excess of +14 μM C, with a C/N molar ratio of 6.0 ± 0.4, is observed in the parcel outwelling into the adjacent ocean. It consists of labile materials, 50% POC and 50% DOC. The labile materials represent 18% of the organic carbon that were being transported by the parcel. To produce this tentative partition we made three basic assumptions.

1. DOM in oceanic ENACW does not undergo any transformation (biological or photochemical) during

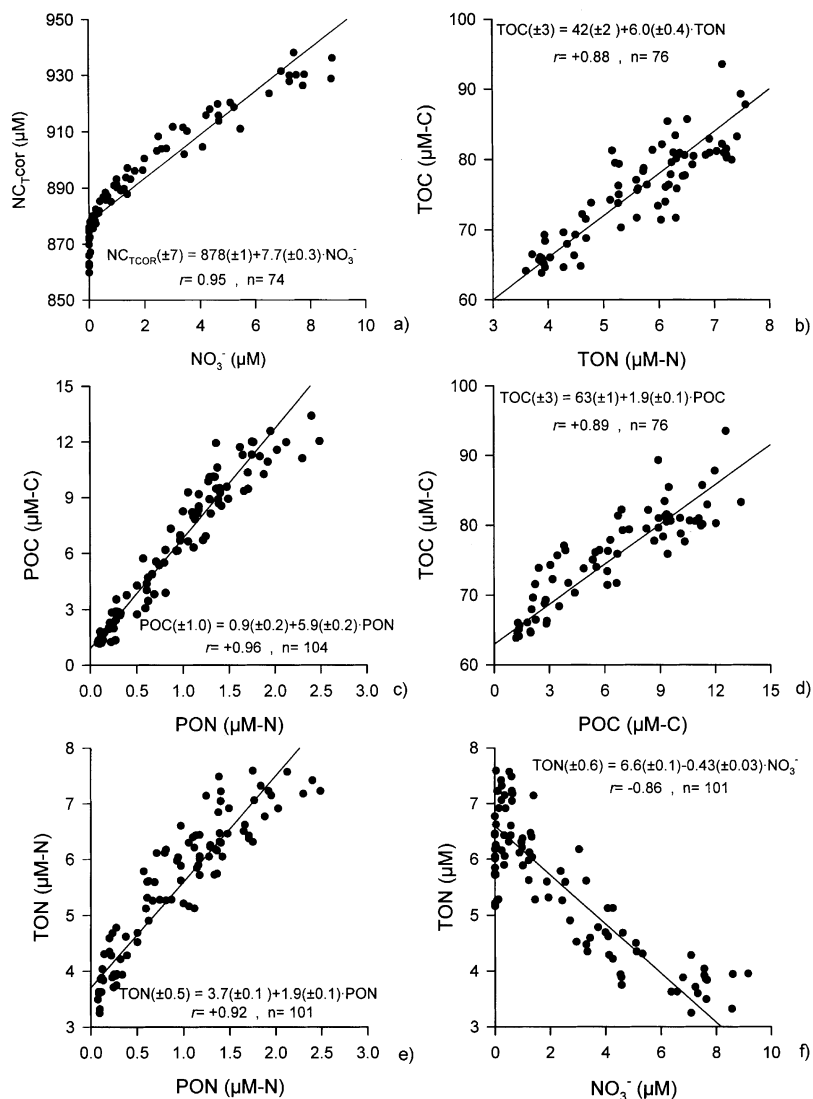


Fig. 5. X–Y plots and linear regression equations (model II; Sokal & Rohlf, 1995) for NC_{Tcor} versus NO_3^- (a), TOC versus TON (b), POC_{susp} versus PON_{susp} (c), TOC versus POC_{susp} (d) TON versus PON_{susp} (e) and TON versus NO_3^- (f) for all bottle data during the coastal upwelling study (3–7 August 1998).

upwelling to the surface and subsequent outwelling to the adjacent ocean. Photochemical labilisation of coloured refractory DOM has been described when deep waters are brought to surface UV-B (e.g. Moran & Zepp, 1997). During an upwelling event, ENACW resides in the UV-B affected shelf surface layer (<20m) for about 5 days. Therefore, it is likely that we have underestimated this contribution to the labile DOM fraction.

2. POM accumulated in the parcel can be considered as labile material. The slope of the direct correlation between POC_{susp} and PON_{susp} , 5.9 ± 0.2 mol C mol N⁻¹, supports this statement. The origin intercept, i.e. the fraction of POC_{susp} that does not co-vary with PON changes, only represents ~10% of the average POC_{susp} content in the parcel.

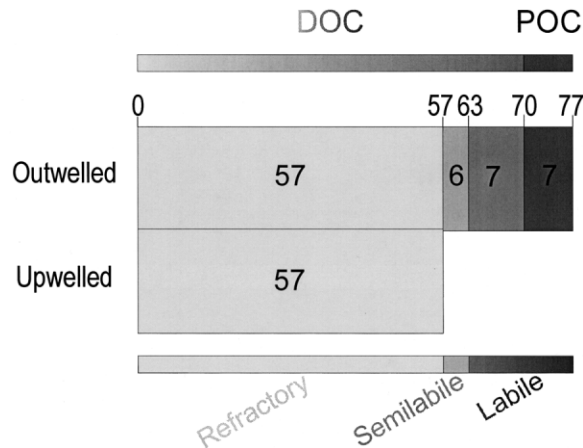


Fig. 6. Tentative partitioning of refractory, semi-labile and labile organic carbon transported by the upwelled ENACW and the outwelled parcel of surface waters when inshore at the start of the study of the filament (3–7 August 1998). Concentrations in μMC .

- The fractions of DOC and DON that co-vary with POC_{susp} and PON_{susp} (Fig. 5d and e) also contribute to the labile fraction. It should be noticed that the terms ‘refractory’, ‘semi-labile’ and ‘labile’ in Fig. 6 are introduced to identify the three organic matter fractions with contrasting C/N molar ratios. Therefore, they represent a relative rather than an absolute scale of reactivity.

3.2. The filament study

Hydrographic and chemical conditions in the filament were quite distinct from those observed during the coastal upwelling study. A well-developed pycnocline at $\sim 40\text{m}$ depth separated the warm ($>16^\circ\text{C}$) and NO_3^- exhausted water at the surface from the underlying cold and NO_3^- rich ENACW (Fig. 2). Shipboard $\text{NO}_2^- + \text{NO}_3^-$ and NH_4^+ measurements in the nanomolar range confirmed that nitrogenous nutrients were exhausted at the offshore end of the filament ($<7 \text{ nmol l}^{-1} \text{ NO}_2^- + \text{NO}_3^-$, $<20 \text{ nmol l}^{-1} \text{ NH}_4^+$). It is worth noting a transient ($<0.15 \mu\text{M N}$) primary NO_2^- maximum observed below the pycnocline (Joint et al., 2001). DON and TON behave oppositely to NO_3^- ; their concentrations were maximum in the surface mixed layer and decreased with depth to $\sim 3.5 \mu\text{M N}$ at 150m. There was no significant change in NO_3^- or TON ($=\text{PON}_{\text{susp}} + \text{DON}$) concentrations between 14 and 17 August (Fig. 3a). After 14 August, DON increased ($+0.5 \mu\text{M N}$) and PON_{susp} decreased ($-0.4 \mu\text{M N}$). From 15 to 17 August, DON consumption ($-0.6 \mu\text{M N}$) accompanied PON_{susp} accumulation ($+0.4 \mu\text{M N}$). Increases of POM_{susp} and decreases of DOM C/N ratios followed the initial conversion of PON_{susp} into DON (Fig. 4a). Conversely, the POM C/N ratio decreased after 15 August while the DOM C/N ratio increased, which could be related to the release of carbohydrate (Norrman, Zweifel, Hopkinson, & Fry, 1995; Søndergaard et al., 2000). Therefore, the fresh organic matter produced inshore at the origin of the filament was still present off-shore. The evolution of NC_T and AOU (Fig. 3b) was also consistent with NO_3^- concentration and no significant variations were measured between 14 and 17 August. Chlorophyll concentration in the off-shore filament (Fig. 4b) was only a quarter of that measured in the coastal upwelling study. The phytoplankton assemblage in the filament was dominated by smaller cells; 60% of the chlorophyll was in the $<2 \mu\text{m}$ fraction. Dinoflagellates dominated (77%) the biomass of the microplankton (Fig. 4c), and diatoms were absent. It should be emphasised that these microplankton counts were only for cells $>5 \mu\text{m}$.

4. Discussion and conclusions

Cold, nutrient-rich waters upwelled on the shelf of coastal upwelling systems may evolve into meso-scale cyclonic structures, ‘upwelling centres’, or elongated plumes or ‘filaments’ (Traganza, Conrad, & Braker, 1981). Our study in the NW Iberian upwelling system began at the southern edge of the Cape Finisterre upwelling centre, where the water parcel was captured at an intermediate state of its development, i.e. after the spin-up phase of an upwelling event. The eyes of upwelling centres are characterised by high nutrients and low temperatures and low chlorophyll concentrations. The small numbers of phytoplankton cells brought to the surface initially have to adapt to the higher light and nutrient conditions (e.g. MacIsaac, Dugdale, Barber, Blasco, & Packard, 1985; Dugdale & Wilkerson, 1989). Covariation between high NO_3^- and low temperature was still persisting at the intermediate state at which we began the observations, when chlorophyll levels were relatively high, $>0.5\text{mg}\cdot\text{m}^{-3}$. The initial C/N ratio of POM_{susp} ($>8\text{ mol C mol N}^{-1}$) suggests that significant amounts of detritus were already suspended in the water, as has been observed in freshly upwelled waters off Point Conception, California (Jones et al., 1983). Subsequently, the water in the parcel evolved towards an advanced state of the upwelling cycle at which the thermal signal still persisted but the nutrients had become depleted. The time evolution of chlorophyll fractions during the inshore study indicated that there was a succession to larger phytoplankton species, as shown by progressive increase in diatom abundance. This is consistent with observations by Abbott et al. (1990) in the California upwelling system, who described how the phytoplankton assemblage became progressively dominated by large slow-growing centric diatoms as their drifter moved offshore. In fact, this is the time development of a typical coastal upwelling system (Jones et al., 1993; MacIsaac et al., 1985; Dugdale & Wilkerson, 1989). In contrast, in the filament study NO_3^- was already depleted in surface waters, phytoplankton numbers were low and were dominated by cells $<2\mu\text{m}$, and there was at the deep chlorophyll maximum (DCM). Microplankton biomass was almost exclusively composed of dinoflagellates and small flagellates, many of them heterotrophic. This is consistent with the dominance of small flagellates in warm, stratified and NO_3^- depleted oceanic waters (Cushing, 1989). Therefore, it seems that the food web in the parcel of coastal water entrained in the filament underwent the transition from being a eutrophic coastal environment to an oligotrophic offshore environment as suggested by Abbott et al. (1990).

This contrast in patterns, according to Hood, Abbott, Huyer, and Kosro (1990), results primarily from there being two ecosystems separated by a strong front, rather than a reflection of the temporal decline of phytoplankton biomass as it is exported offshore. In this sense, Wilkerson and Dugdale (1987) presented a ‘conveyor belt’ scheme where small species are selectively removed by the surface offshore flux of the 2-layer cross-shelf circulation, and larger species are retained in the deeper onshore flow and returned to the shelf. In addition, Brink and Cowles (1991) suggested that subduction of coastal waters entrained by the filament during offshore transport may account for the changes in surface nutrient concentrations and phytoplankton populations observed by Abbott et al. (1990). Floating drifters are constrained to stay at a constant near-surface depth, so they will lose track of the original water parcel if subduction occurs. Subduction rates in the giant upwelling filament off Point Conception (California) ranges from 10 to $40\text{m}\cdot\text{d}^{-1}$ (Kadko, Washburn, & Jones, 1991) and so affects the distribution of chlorophyll, phytoplankton and particle abundance (Jones, Morrers, Reinecker, Stanton, & Washburn, 1991). Downwelling rates in the relatively small (65km wide, 150km long) filament we observed off the Rías Baixas are not comparable with those observed in the giant (200km wide, 500km long) filament off Point Conception. In addition, our drifter was positioned in the centre of the offshore flow of the filament and not along its northern margin where the downwelling velocity was at its maximum (Swenson, Niiler, Brink, & Abbott, 1992). We considered the time evolution of average changes from the surface to the 1% PAR or the nutricline ($\sim 50\text{m}$), which integrates possible vertical displacements. In this sense, the simulation of a Lagrangian drifter entrained by an upwelling filament (Moisan & Hofmann, 1996) shows offshore subduction up to the level of the nutricline. This makes a difference with studies based on continuous records measured by a fixed depth

drifter entrained by the filament (Abbott et al., 1990). These considerations, together with the demonstration of the Lagrangian nature of the two drifter studies by Joint et al. (2001), allow us to assume that the time evolution of the chemical variables resulted from the NEM of the whole community of micro-organisms in the parcel.

4.1. Off-shelf export of primary production mediated through an upwelling filament

Net consumption of NO_3^- by the community of organisms in the study coastal water mass transforms into:

1. DON ($<0.8\mu\text{m}$) and PON_{susp} ($>0.8\text{--}<200\mu\text{m}$), which accumulated in the parcel, and
2. PON_{sink} ($>200\mu\text{m}$), which either sank out of the parcel and was deposited on the shelf and/or slope or was actively transported by mesozooplankton.

The time evolution of nitrogen species during the upwelling study showed the expected chemical succession starting with NO_3^- consumption, followed by PON_{susp} (phytoplankton) growth, and culminating with DON accumulation. The observed change in C/N ratios of POM_{susp} and DOM also supports this view. Although this time segregation has been observed in cultures (e.g. Norrman et al., 1995), this is the first observation of it in the field. The efficiency of conversion of NO_3^- consumption into TON accumulation during the transit of the surface coastal waters from Cape Finisterre upwelling centre to the ocean was $\sim 40\%$. After the parcel crossed the shelf-edge (Fig. 1), this conversion efficiency was equivalent to a net ecosystem horizontal export ratio (e-ratio) of 0.4. The e-ratio reduced to 0.3 for the case of carbon, indicating that the shelf is trapping carbon more efficiently than nitrogen.

It is worth noting that DOC and DON represent about half of the organic carbon and nitrogen exported by the filament. The $-\Delta\text{DOC}/\Delta\text{NC}_{\text{Tcor}}$ ratio is ~ 0.15 and the $-\Delta\text{DON}/\Delta\text{NO}_3^-$ ratio is ~ 0.20 . These numbers agree very well with the 20% of $\Delta\text{C}_{\text{T}}$ assumed by Hansell and Carlson (1998) for the coastal upwelling zone in their global estimates of DOC net community production. Although the key role of labile DOC and DON in the regeneration and new production of marine systems is recognised nowadays (e.g. Bronk, Glibert, & Ward, 1994; Hansell & Carlson, 1998), it has not been incorporated yet into debates about the fate of phytogenic materials in the coastal zone. Horizontal transport of recently produced POM_{susp} and DOM to the adjacent relatively barren offshore waters constitutes an alternative route for the export of organic materials produced along ocean margins. Estimates of these exports need to supplement the traditional estimates of POM sinks through deposition onto shelf and slope sediments. Filaments provide a mechanism whereby organic material produced in shelf waters can be transported hundreds of kilometres offshore into the ocean, and are features common to all the major coastal upwelling regions of the World Ocean (e.g. Brink & Cowles, 1991; Gabric et al., 1993). If the e-ratios determined here for the NW Iberian Upwelling System can be applied to other filaments, export fluxes have been dramatically underestimated because the contribution of DOM has not been included in the budgets.

Average westward displacement of the parcel during the offshore study was $\sim 7\text{cm.s}^{-1}$, which is only half the speeds reported for the giant upwelling filaments off California (Brink & Cowles, 1991). Velocities are larger in the offshore than in the onshore part of the flows so that depth-integrated (to 1% PAR) offshore POC_{susp} fluxes on the northern side of the filament are much greater than the onshore carbon flux to the south (Moisan et al., 1996). Considering the size of the offshore flowing section of the study water mass ($\sim 50\text{m}$ deep, $\sim 32\text{km}$ wide) and the labile/semi-labile $\text{POC}_{\text{susp}} + \text{DOC}$ ($20\mu\text{M C}$) and chlorophyll (0.31mg m^{-3}) concentrations, the filament we studied was transporting $\sim 27\text{ kgC.s}^{-1}$ and 35gChl.s^{-1} . If this rough calculation is extrapolated to the whole period when the filament is active (May–September, ~ 150 days), then $\sim 3.5 \times 10^8\text{kgC}$ of labile $\text{POM}_{\text{susp}} + \text{DOM}$ and $4.5 \times 10^5\text{kgChl}$ are being exported per year to the adjacent ocean. Since this filament is a major route for the export of primary production in shelf waters

off the Rías Baixas (3400km²), the resultant export per unit of shelf area is roughly 100gC.m⁻².y⁻¹. This represents as much as 45% of the total annual primary production in the study area estimated by Bode et al. (1996) to be ~220gC.m².y⁻¹. Our estimates are small compared with transport values obtained in the giant filaments off California (100–200km wide, 100m deep), whose export ranges from 170 to 506gChl.s⁻¹ (Jones et al., 1991; Strub, Kosro, & Huyer, 1991; Moisan et al., 1996). Obviously, carbon export values are also small when compared with POC_{susp} fluxes of 158–1890gC.m⁻².y⁻¹ calculated by Moisan et al. (1996). If the 1:1 relative contribution of POC_{susp} and DOC to labile TOC exported by the study filament can be extrapolated to other upwelling systems, previous calculations have probably underestimated the offshore flux of biogenic carbon by a 50%.

4.2. Lability of the exported materials

The organic pool exported consists of suspended particles (living phytoplankton and microheterotrophs, detritus) and dissolved materials that will serve as new resources for the growth and respiration of populations in the adjacent oceanic waters. The importance of DOM export for ecological function will depend on the lability of the transported materials and the trophic status of the region that receives that material. The community of heterotrophic bacteria living in the receptor ecosystem will use any labile materials rapidly (Kirchman et al., 1993). In addition, phytoplankton is able to use urea and some amino acids (Wafar, Le Corre, & L'helguen, 1995). In contrast, semi-labile materials will tend to persist and so be transported horizontally (Legendre & Le Fèvre, 1995) or vertically (Vidal, Duarte, & Agustí, 1999). It has also been suggested that labile DOC will accumulate when there is nutrient limitation (oligotrophic systems) or when bacterial populations are being controlled by microzooplankton grazing (Williams, 1995; Thingstad, Hagström, & Rassoulzadegan, 1997). The conversion efficiency of labile DOC into bacterial biomass reduces from 30–50% in nutrient-rich to <5% in nutrient-limited systems (e.g. Fuhrman, 1992; Kirchman, Suzuki, Garside, & Ducklow, 1991; Hansell, Bates, & Gundersen, 1995). This has clear implications for the global carbon balance. If the exported DOC is incorporated into higher trophic levels via the microbial loop, then it could be transferred to the deep ocean where it will contribute to the temporary sequestration of anthropogenic CO₂. If it is mineralised >500m, the CO₂ produced will be isolated from the atmosphere for at least a few hundred years (Broecker & Peng, 1982).

In the case of the study filament, the question of the lability of the exported materials has been approached through the C/N ratio. The average composition of the initial products of phytoplankton production and early degradation (Anderson, 1995) is C₁₀₆H₁₇₅O₄₂N₁₆P (54.5% proteins, 25.5% carbohydrates, 16.1% lipids and 4.0% nucleic acids), has a molar C/N ratio of 6.6. The average C/N ratios of the POM_{susp}+DOM excess was 6.8±1.0 in the coast and 6.5±0.4 in the filament. Therefore, this has to be considered as a pool of labile materials. In contrast, the C/N ratio of the more refractory DOM in waters from 150 and 500m was 17±1 and 19±2 respectively. The high nitrogen content of the exported materials is likely to make it an attractive organic substrate for microbial populations in the adjacent oligotrophic ocean, but our study does not allow rising any conclusion regarding this point.

Offshore export of labile POM_{susp}+DOM from upwelling systems is relevant to the controversy on the autotrophic (Williams, 1998) or heterotrophic (Del Giorgio, Cole, & Cimbleris, 1997; Duarte & Agustí, 1998) status of oligotrophic surface waters. Assuming that 45% of the ~1 Gt year⁻¹ primary production in coastal upwelling systems worldwide (Wollast, 1998) is exported offshore, then 0.45 GtC y⁻¹ of bio-reactive organic matter will be entering the food web of the oligotrophic ocean. This flux of new POC_{susp}+DOC represents >25% of the estimated export of semi-labile DOC from the surface to the deep ocean (assuming that it represents 30% of the total downward flux of organic carbon; Yamanaka & Tajika, 1997) and >10% of the global sinking flux in the open ocean (4.2GtC.y⁻¹; Wollast, 1998). Recent observations by Bauer and Druffel (1998) indicate injection of old POC_{susp}+DOC from ocean margins directly

into the deep ocean. Our work shows that ocean margins are also significant sources of recent materials to the surface ocean.

Acknowledgements

We are very grateful to the captain and the crew of RRS Charles Darwin, who assisted us during the sampling programme. D. Cummings and A.P. Rees (PML) participated in nutrient analyses, P. Mendes (UAlg) collected POM and DOM samples, T. Rellán and A.F. Ríos (IIM) performed the POM analyses, and P. Pazos (IIM) did the phytoplankton counts. The satellite image has been provided by the NERC RSDAS group at PML (CCMS), UK. Support for this work came from the EU project OMEX II-II (MAST3-CT97-0076) and the Spanish CICYT grant No. MAR97-1729-CE and MAR97-2068-CE.

References

- Abbott, M. R., Brink, K. H., Booth, C. R., Blasco, D., Codispoti, L. A., Niiler, P. P., & Ramp, S. R. (1990). Observations of phytoplankton and nutrients from a Lagrangian drifter off Northern California. *Journal of Geophysical Research*, 95, 9393–9409.
- Álvarez-Salgado, X. A., Rosón, G., Pérez, F. F., & Pazos, Y. (1993). Hydrographic variability off the Rías Baixas (NW Spain) during the upwelling season. *Journal of Geophysical Research*, 98, 14447–14455.
- Álvarez-Salgado, X. A., & Miller, A. E. J. (1998). Simultaneous determination of dissolved organic carbon and total dissolved nitrogen in seawater by high temperature catalytic oxidation: conditions for accurate shipboard measurements. *Marine Chemistry*, 62, 325–333.
- Álvarez-Salgado, X. A., Doval, M. D., & Pérez, F. F. (1999). Dissolved organic matter in shelf waters off the Ría de Vigo (NW Iberian upwelling system). *Journal of Marine Systems*, 18, 383–394.
- Anderson, L. A. (1995). On the hydrogen and oxygen content of marine phytoplankton. *Deep-Sea Research I*, 42, 1675–1680.
- Archer, D., Peltzer, E. T., & Kirchman, D. L. (1997). A time-scale for dissolved organic carbon production in the equatorial Pacific surface water. *Global Biogeochemical Cycles*, 11, 435–452.
- Barton, E. D., Arístegui, J., Tett, P., Cánton, M., García-Braun, J., Hernández-León, S., Nykjaer, L., Almeida, C., Almunia, J., Ballesteros, S., Basterretxea, G., Escáñez, J., García-Weill, L., Hernández-Guerra, A., López-Laatzén, F., Molina, R., Montero, M. F., Navarro-Pérez, E., Rodríguez, J. M., van Lenning, K., Vélez, H., & Wild, K. (1998). The transition zone of the Canary Current upwelling region. *Progress in Oceanography*, 41, 455–504.
- Bauer, J. E., & Druffel, E. R. M. (1998). Ocean margins as a significant source of organic matter to the deep open ocean. *Nature, London*, 392, 482–485.
- Biscaye, P. E., Flagg, C. N., & Falkowski, P. G. (1994). The Shelf Edge Exchange Processes experiment, SEEP-II: an introduction to hypothesis, results and conclusions. *Deep-Sea Research II*, 41, 231–252.
- Bode, A., Casas, B., Fernández, E., Maraño, E., Serret, P., & Varela, M. (1996). Phytoplankton biomass and production in shelf waters off NW Spain: spatial and seasonal variability in relation to upwelling. *Hydrobiologia*, 341, 225–234.
- Brewer, P. G., & Riley, J. P. (1965). The automatic determination of nitrate in seawater. *Deep-Sea Research*, 12, 765–772.
- Brink, K. H., & Cowles, T. J. (1991). The coastal transition zone program. *Journal of Geophysical Research*, 96, 14367–14648.
- Broecker, W. S., & Peng, T.-H. (1982). *Tracers in the sea*. New York: Eldigio Press.
- Bronk, D. A., Glibert, P. M., & Ward, B. B. (1994). Nitrogen uptake, dissolved organic nitrogen release, and new production. *Science*, 265, 1843–1846.
- Chavez, F. P., & Toggweiler, J. R. (1995). Physical estimates of global new production: the upwelling contribution. In C. P. Summerhayes, K.-C. Emeis, M. V. Angel, R. L. Smith, & B. Zeitzschel (Eds.), *Upwelling in the ocean. Modern processes and ancient records* (pp. 13–32). New York: Wiley and Sons.
- Cushing, D. H. (1989). A difference in structure between ecosystems in strongly stratified water and in those that are weakly stratified. *Journal of Plankton Research*, 11, 1–13.
- Del Giorgio, P. A., Cole, J. J., & Cimbleris, A. (1997). Respiration rates in bacteria exceed plankton production in unproductive aquatic systems. *Nature*, 385, 148–151.
- Dickson, A. G. (1990). Standard potential of the reaction: $\text{AgCl(s)} + 1/2\text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$, and the standard acidity constant of the ion HSO_4 in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics*, 22, 113–127.
- Dickson, A. G. (1993). pH buffers for sea water media based on the total hydrogen ion concentration scale. *Deep-Sea Research I*, 40, 107–118.

- Duarte, C. M., & Agustí, S. (1998). The CO₂ balance of unproductive aquatic ecosystems. *Science*, 281, 234–236.
- Dugdale, R. C., & Wilkerson, F. P. (1989). New production in the upwelling center at Point Conception, California: Temporal and spatial patterns. *Deep-Sea Research*, 36, 985–1007.
- Falkowski, P. G., Flagg, C. N., Rowe, G. T., Smith, S. L., Whitedge, T. E., & Wirick, C. D. (1988). The fate of a spring phytoplankton bloom: export or oxidation? *Continental Shelf Research*, 8, 457–484.
- Fuhrman, J. A. (1992). Bacterioplankton roles in cycling of organic matter: the microbial food web. In P. G. Falkowski, & A. D. Woodhead (Eds.), *Primary productivity and biogeochemical cycles in the sea* (pp. 361–383). New York: Plenum Press.
- Gabric, A. J., García, L., Camp, L. V., Nykjaer, L., Eifler, W., & Schrimpf, W. (1993). Offshore export of shelf production in the Cape Blanc (Mauritania) giant filament as derived from coastal zone colour scanner imagery. *Journal of Geophysical Research*, 98, 4697–4712.
- Gabric, A. J., Eifler, W., & Schrimpf, W. (1996). A Lagrangian model of phytoplankton dynamics in the northwest African coastal upwelling zone. *Advances in Space Research*, 18, 99–115.
- Garside, C. (1981). Nitrate and ammonium uptake in the apex of the New York Bight. *Limnology and Oceanography*, 26, 731–739.
- Grasshoff, K. (1976). *Methods of seawater analysis*. Weinheim: Verlag Chemie.
- Hansell, D. A., Bates, N. R., & Gundersen, K. (1995). Mineralization of dissolved organic carbon in the Sargasso Sea. *Marine Chemistry*, 51, 201–212.
- Hansell, D. A., & Carlson, C. A. (1998). Net community production of dissolved organic carbon. *Global Biogeochemical Cycles*, 12, 443–453.
- Hansson, I., & Jagner, D. (1973). Evaluation of the accuracy of Gran plots by means of computer calculations. *Analytica Chimica Acta*, 65, 363–373.
- Haynes, R., Barton, E. D., & Pilling, I. (1993). Development, persistence and variability of upwelling filaments off the Atlantic Coast of the Iberian Peninsula. *Journal of Geophysical Research*, 98, 22681–22692.
- Holm-Hansen, O., Lorenzen, C. J., Holmes, R. W., & Strickland, J. D. H. (1965). Fluorometric determination of chlorophyll. *Journal du Conseil Permanent International pour l'Exploration de la Mer*, 30, 3–15.
- Hood, R., Abbott, M., Huyer, A., & Kosro, P. (1990). Surface patterns in temperature, flow, phytoplankton biomass and species composition in the coastal transition zone off northern California. *Journal of Geophysical Research*, 95, 18081–18094.
- Joint, I., Inall, M., Torres, R., Figueiras, F.G., Álvarez-Salgado, X.A., Rees, A.P., & Woodward, M. (2001). Two Lagrangian experiments in the Iberian upwelling system: tracking an upwelling event and an off-shore filament. *Progress in Oceanography*, 51 (2-4), 221–248.
- Jones, B. H., Brink, K. H., Dugdale, R. C., Stuart, D. W., Van Leer, J. C., Blasco, D., & Kelly, J. C. (1983). Observations of a persistent upwelling center off Point Conception, California. In E. Suess, & J. Thiede (Eds.), *Coastal upwelling: its sediment record. Responses of the sedimentary regime to present coastal upwelling* (pp. 37–60). Plenum Press.
- Jones, B. H., Morrers, C. N. K., Reinecker, M. M., Stanton, T., & Washburn, L. (1991). Chemical and biological structure and transport of a cool filament associated with a jet-eddy system off Northern California in July 1986 (OPTOMA21). *Journal of Geophysical Research*, 96, 22207–22225.
- Jones, R. D. (1991). An improved fluorescence method for the determination of nanomolar concentrations of ammonium in natural waters. *Limnology and Oceanography*, 36, 814–819.
- Kadko, D. C., Washburn, L., & Jones, B. (1991). Evidence of subduction within the cold filaments of the northern California coastal transition zone. *Journal of Geophysical Research*, 96, 14909–14926.
- Kirchman, D. L., Suzuki, Y., Garside, C., & Ducklow, H. W. (1991). High turnover rates of dissolved organic carbon during a spring phytoplankton bloom. *Nature*, 352, 612–614.
- Kirchman, D. L., Lancelot, C., Fasham, M., Legendre, L., Radach, G., & Scott, M. (1993). Dissolved organic material in biogeochemical models of the ocean. In G. T. Evans, & M. J. R. Fasham (Eds.), *Towards a model of ocean biogeochemical processes. NATO series I: Global environmental change 10* (pp. 209–225). Berlin: Springer.
- Kirkwood, D.S. (1989). Simultaneous determination of selected nutrients in seawater. ICES CM:C:29.
- Legendre, L., & Le Fèvre, J. (1995). Microbial food webs and the export of biogenic carbon in the oceans. *Aquatic Microbial Ecology*, 9, 69–77.
- MacIsaac, J. J., Dugdale, R. C., Barber, R. T., Blasco, D., & Packard, T. T. (1985). Primary production cycle in an upwelling center. *Deep-Sea Research*, 32, 503–529.
- Mantoura, R. F. C., & Woodward, E. M. S. (1983). Optimization of the indophenol blue method for the automated determination of ammonia in estuarine waters. *Estuarine, Coastal and Shelf Science*, 17, 219–224.
- Moisan, J. R., Hofmann, E. E., & Haidvogel, D. B. (1996). Modelling nutrient and plankton processes in the California coastal transition zone 2. A three-dimensional physical-bio-optical model. *Journal of Geophysical Research*, 101, 22677–22691.
- Moisan, J. R., & Hofmann, E. E. (1996). Modelling nutrient and plankton processes in the California coastal transition zone 3. Lagrangian drifters. *Journal of Geophysical Research*, 101, 22677–22691.
- Moran, M. A., & Zepp, R. G. (1997). Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. *Limnology and Oceanography*, 42, 1307–1316.

- Nogueira, E., Pérez, F. F., & Ríos, A. F. (1997). Seasonal patterns and long-term trends in an estuarine upwelling ecosystem (Ría de Vigo, NW Spain). *Estuarine, Coastal and Shelf Science*, 44, 285–300.
- Norrman, B., Zweifel, U. L., Hopkinson, C. S., & Fry, B. (1995). Production and utilisation of dissolved organic carbon during an experimental diatom bloom. *Limnology and Oceanography*, 40, 898–907.
- Olli, K., Wexels Riser, C., Wassmann, P., Ratkova, A., Arashkevich, E., & Pasternak, A. (2001). Vertical flux of biogenic matter during a Lagrangian study off the NW Spanish continental margin. *Progress in Oceanography*, 51 (2–4), 443–466.
- Parsons, T. R., Maita, Y., & Lalli, C. M. (1984). *A manual of chemical and biological methods for sea-water analysis*. Pergamon: Oxford.
- Pérez, F. F., Mouriño, C., Fraga, F., & Ríos, A. F. (1993). Displacement of water masses and remineralization rates off the Iberian Peninsula by nutrient anomalies. *Journal of Marine Research*, 51, 869–892.
- Roy, R. N., Roy, L. N., Vogel, K. M., Porter-Moore, C., Pearson, T., Good, C. E., Millero, F. J., & Cambell, D. J. (1993). Determination of the ionization constants of carbonic acid in seawater in salinities 5 to 45 and temperatures 0 to 45°C. *Marine Chemistry*, 44, 249–267.
- Sokal, R. R., & Rohlf, F. J. (1995). *Biometry*. New York: Freeman and Company.
- Søndergaard, M., Williams, P. J. le B., Cauwet, G., Riemann, B., Robinson, C., Terzic, S., Woodward, E. M. S., & Worm, J. (2000). Net accumulation and flux of dissolved organic carbon and dissolved organic nitrogen in marine plankton communities. *Limnology and Oceanography*, 45, 1097–1111.
- Strub, P. T., Kosro, P. M., & Huyer, A. (1991). The nature of cold filaments in the California Current system. *Journal of Geophysical Research*, 96, 14743–14768.
- Swenson, M. S., Niiler, P. P., Brink, K. H., & Abbott, M. R. (1992). Drifter observations of a cold filament off Point Arena, California, in July 1988. *Journal of Geophysical Research*, 97, 3593–3610.
- Thingstad, T. F., Hagström, A., & Rassoulzadegan, F. (1997). Accumulation of degradable DOC in surface waters: Is it caused by a malfunctioning microbial loop? *Limnology and Oceanography*, 42, 398–404.
- Traganza, E. D., Conrad, J. C., & Braker, L. C. (1981). Satellite observations of a cyclonic upwelling system and a giant plume in the California Current. In F. A. Richards (Eds.), *Coastal upwelling, coastal estuarine science* (Vol. 1) (pp. 228–241). Washington: AGU.
- UNESCO (1986). *Progress on oceanographic tables and standards 1983–1986. Work and recommendations of the UNESCO/SCOR/ICES/IAPSO Joint Panel*. UNESCO Technical Papers in Marine Sciences, 50.
- Vidal, M., Duarte, C. M., & Agustí, S. (1999). Dissolved organic nitrogen and phosphorus pools and fluxes in the central Atlantic Ocean. *Limnology and Oceanography*, 44, 106–117.
- Wafar, M. V. M., Le Corre, P., & L'helguen, S. (1995). F-ratios calculated with and without urea uptake in nitrogen uptake by phytoplankton. *Deep-Sea Research I*, 9, 1669–1674.
- Walsh, J. J., Rowe, G. T., Iverson, R. L., & McRoy, C. P. (1981). Biological export of shelf carbon: a neglected sink of the global CO₂ cycle. *Nature*, 291, 196–201.
- Walsh, J. J. (1991). Importance of continental margins in the marine biogeochemical cycling of carbon and nitrogen. *Nature*, 359, 53–55.
- Wilkerson, F. P., & Dugdale, R. C. (1987). The use of large shipboard barrels and drifters to study the effect of coastal upwelling on phytoplankton nutrient dynamics. *Limnology and Oceanography*, 32, 368–382.
- Williams, P. J. le B. (1995). Evidence for the seasonal accumulation of carbon-rich dissolved organic material, its scale in comparison with changes in particulate material and the consequential effect on net C/N assimilation ratios. *Marine Chemistry*, 51, 17–29.
- Williams, P. J. le B. (1998). The balance of plankton respiration and photosynthesis in the open oceans. *Nature*, 394, 55–57.
- Wollast, R. (1998). Evaluation and comparison of the global carbon cycle in the coastal zone and in the open ocean. In K. H. Brink, & A. R. Robinson (Eds.), *The sea* (Vol. 10) (pp. 213–252). New York: John Wiley and Sons.
- Wooster, W. S., Bakun, A., & McClain, D. R. (1976). The seasonal upwelling cycle along the eastern boundary of the North Atlantic. *Journal of Marine Research*, 34, 131–141.
- Yamanaka, Y., & Tajika, E. (1997). Role of dissolved organic matter in the marine biogeochemical cycle: studies using an ocean biogeochemical general circulation model. *Global Biogeochemical Cycles*, 11, 599–612.