

Effect of upwelling pulses on excess carbohydrate synthesis as deduced from nutrient, carbon dioxide and oxygen profiles

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ABSTRACT: The coupling between upwelling intensity off the NW Iberian coast and differential carbohydrate synthesis and utilisation in the water column has been investigated using the conservative chemical parameters 'NO', 'CO' and 'NCO'. Differences between the observed vertical distribution of 'NO' and 'CO' and that expected from Redfield stoichiometry indicate that an excess of carbohydrate synthesis occurs in the surface layer when nutrients become depleted during upwelling relaxation periods. Excess carbohydrate synthesised in upper layers is consumed at subsurface levels. This consumption can be attributed to the presence of autotrophic migratory organisms like the photosynthetic ciliate *Mesodinium rubrum* and several dinoflagellates which produce carbohydrates in the upper, well illuminated layers and take up nutrients in the subphotic zone. Conversely, situations of intense upwelling are associated with production of organic matter following the Redfield ratio and with a decrease in carbohydrate synthesis. Deviations from Redfield stoichiometry found in other marine areas could be explained by processes comparable to those occurring in the NW Iberian upwelling, suggesting that vertical migration by photosynthetic organisms may play a greater role in the vertical transport of nitrogen and carbon than generally recognized.

KEY WORDS: Upwelling · Carbohydrate · Redfield ratio

INTRODUCTION

Vertical advection of nutrients supports high population densities of phytoplankton in coastal upwelling areas. However, the structure and function of these populations fluctuate at a wide range of time scales in response to changes of the upwelling intensity and associated physical characteristics (Estrada & Blasco 1979, Figueiras & Ríos 1993, Kudela et al. 1997). Variability of upwelling intensity over a timescale of several days, typically associated with fluctuations in wind stress, is characteristic of all major upwelling areas. The alternation of periods of strong upwelling (or 'events'), which introduce cold and nutrient-rich waters from deep layers into the upper euphotic zone, and

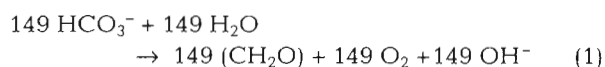
periods of relaxation affects both the temporal and spatial variability of the upwelling ecosystem. During relaxation periods, exhaustion of nutrients in the euphotic zone may favour the development of phytoplankton forms able to migrate vertically and to take advantage of the nutrient content in subsurface waters (Raven & Richardson 1984, Cullen 1985, Cullen et al. 1985, Villarino et al. 1995). This behaviour is shown by many dinoflagellates and other motile forms, like the autotrophic ciliate *Mesodinium rubrum*. These organisms are typical components of the upwelling community (Smith & Barber 1979, Estrada & Blasco 1985) and may develop dense populations reaching the category of red tides. During the day, migratory dinoflagellates remain in the euphotic zone and synthesise mainly carbohydrates, due to a lack of N and P for building other compounds. During the night, the organisms descend

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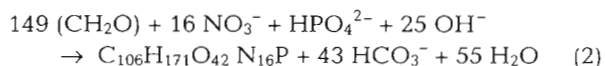
to the nutricline, in the subphotic zone, and synthesise proteins and other necessary compounds, using part of the carbohydrates produced and stored during the day both as an energy source and as a supplier of carbon for biosynthesis (Cullen 1985). *M. rubrum* presents a very active vertical migration (Wilkerson & Grunseich 1990, Passow 1991) and probably uses the same strategy to capture nutrients when these disappear from the euphotic zone. In addition, recent studies have shown that even non-motile organisms, like *Rhizosolenia* sp. and other large diatoms, may accumulate carbohydrates in upper, nutrient-poor water layers; these may be used to regulate their buoyancy to sink down into the nutrient-rich subphotic zone (Villareal et al. 1993, 1996, 1999, Villareal & Carpenter 1994, Richardson et al. 1996). Richardson & Cullen (1995) observed that *Thalassiosira weissflogii* showed a similar behaviour in cultures.

Due to migration, as described above, the synthesis of carbohydrates in the nutrient-exhausted euphotic zone produces an increase of oxygen and a utilisation of CO_2 without uptake of NO_3^- and HPO_4^{2-} . Conversely, in the nutrient-rich subphotic zone, NO_3^- and HPO_4^{2-} are used up without equivalent oxygen production and CO_2 utilisation. Fraga et al. (1992) modelled this differential synthesis using the following stoichiometric scheme:

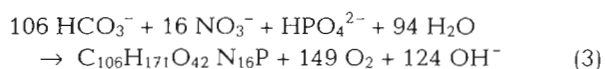
Euphotic layer



Subphotic layer



Considering a whole water column, with both euphotic and subphotic layers, the sum of processes (1) and (2) will fulfil the Redfield ratio according to the following stoichiometric equation:



However, as a consequence of the vertical separation between the production and consumption of carbohydrates, the relation of Redfield et al. (1963) will hold neither in the euphotic nor in the subphotic layers and the deviations from it will be stronger with increased synthesis and utilisation of carbohydrates. In summary, the processes described in (1) and (2) consume 141 mol of CO_2 from the euphotic zone to convert 100 mol of carbon into biomass with a C/N ratio of 6.6 and release 41 mol of CO_2 in the subphotic zone. The 15 mol of nitrogen (100/6.6) needed for biomass synthesis are taken up from the subphotic zone. The combination of

processes (1) and (2) has different implications than the deviations of the Redfield ratio described by Banse (1994) for a 6.1 m diameter plastic sphere, which were due to excess carbohydrate synthesis with respect to that of nitrogenated compounds, within the euphotic zone.

The spatial uncoupling between synthesis and consumption in the photic zone could be a scenario more widespread than previously recognized. This could explain the abnormal patterns of C and N utilisation found in marine areas like the Southern Benguela Upwelling System (Probyn et al. 1996), the subtropical waters of the NE Pacific (Emerson & Hayward 1995) and the North Atlantic (Sambrotto et al. 1993).

The objective of this paper is to examine the coupling between relaxation periods after upwelling events off the NW Iberian coast and the deviations from Redfield ratios induced by differential carbohydrate synthesis in the water column.

METHODS

Data were collected during the cruise 'Galicia VIII', which took place between 13 July and 7 August 1984, on board the RV 'García del Cid'. During this survey, a transect perpendicular to the coast off the Ría de Pontevedra (Fig. 1) was sampled every 2 d. This area, south of Cape Finisterre, is characterised by fluctuations of upwelling intensity with a mean period of 14 ± 4 d (Alvarez-Salgado et al. 1993). Further north, adjacent to Cape Finisterre, upwelling appears to be permanent during summer (Fraga 1981, Blanton et al. 1984).

Casts of 7 Niskin bottles of 1.7 l, supplied with 3 thermometers, 2 protected and 1 unprotected, were performed at the hydrographic stations shown in Fig. 1. Samples were taken every 10 m from the surface to the bottom. Salinity was measured with an induction salinometer 'Beckman RS-9'. Nitrate + nitrite and phosphate were determined by colorimetric methods, using a Technicon autoanalyser (Hansen & Grasshoff 1983, Mouriño & Fraga 1985). The technique has a shipboard precision for nitrate of $\pm 0.06 \mu\text{mol kg}^{-1}$ (Castro & Salgado 1996). CO_2 was calculated using equations of the carbonic system (Mehrbach et al. 1973, Weis 1974) from pH and alkalinity determinations made by means of potentiometric techniques (Pérez & Fraga 1987a,b). A 'Metrohm E-510' pH meter with an Orion 81-04 electrode calibrated with 7.413 NBS buffer was used to determine pH. The shipboard precision of the method is ± 0.002 pH (Ríos & Rosón 1996). An accuracy of ± 0.004 has been estimated using samples of Certified Reference Material (CRMs) provided by Dr Dickson at the University of California (Ríos & Rellán 1998). An

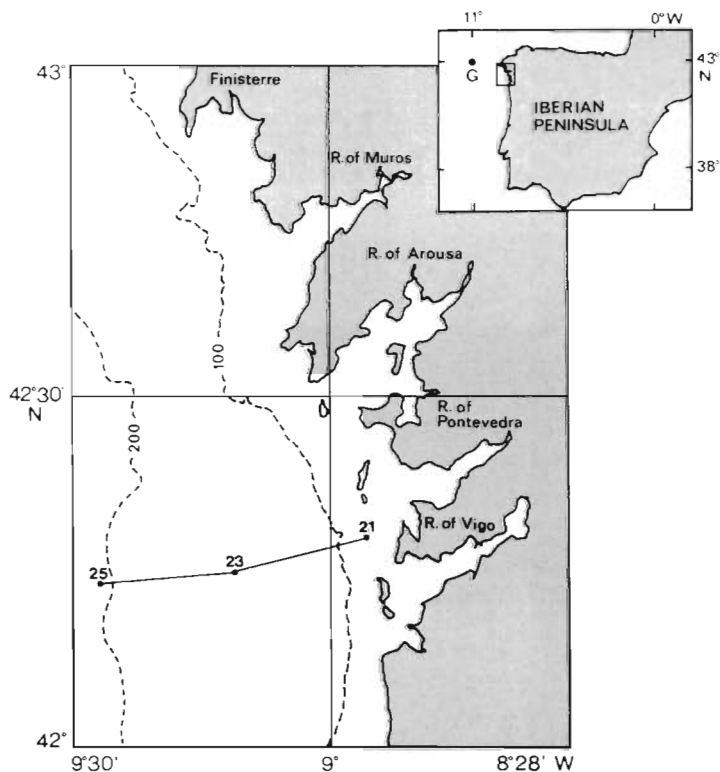


Fig. 1. Position of the stations referred to in this work. Point G in the upper inset indicates the position for which geostrophic wind was calculated

automatic potentiometric titrator 'Metrohm' was used to measure alkalinity with HCl to a final pH of 4.44. This method of alkalinity determination has a precision of 0.1% (Pérez & Fraga 1987b), and the accuracy of $1.4 \mu\text{mol kg}^{-1}$ was estimated from cross-calculation with measured CRMs (Ríos & Rellán 1998). The precision and accuracy of pH and alkalinity translate to $\pm 3 \mu\text{mol kg}^{-1}$ for CO_2 measurements. Dissolved oxygen was analysed by the Winkler method using an automatic titration system 'Metrohm 670' with a platinum electrode. The precision of this method is $0.7 \mu\text{mol kg}^{-1}$. Chlorophyll *a*, retained by a Whatman GF/C filter, was extracted with 90% acetone and the fluorescence of the extract measured using a Turner fluorometer following the technique of Strickland & Parsons (1968). GF/C filters have a larger nominal pore size ($1.2 \mu\text{m}$) than GF/F filters (nominal pore size $0.7 \mu\text{m}$) which are generally used nowadays. However, given the relatively high chlorophyll concentrations found in our study and the probable dominance of large cells, it is unlikely that the use of GF/C filters resulted in any significant chlorophyll underestimation. Recent experiments carried out in the Ría of Vigo (X A Morán pers. comm.) with water of similar chlorophyll concentration did not show any significant differ-

ences between the amount of chlorophyll retained by GF/C or GF/F filters. Chlorophyll concentrations without correction of phaeopigments were calculated according to the method of Yentsch & Menzel (1963). The basic data from the cruise are reported in Mouriño et al. (1985).

Phytoplankton samples were taken between 15 and 27 July, at 10 m intervals between the surface and 30 m depth. Sampling times varied for each station. Subsamples of 120 ml of water were fixed with concentrated Lugol's solution, without acetic acid, and stored in Pyrex bottles. Phytoplankton composition was examined by means of the inverted microscope technique, after sedimentation in composite 100 ml chambers. One transect of the chamber (approximately 1 ml of sample) was observed at $500\times$ to enumerate the smaller organisms and the whole chamber bottom was scanned to enumerate the larger forms. Cells of intermediate size were counted along an additional transect at $125\times$.

Upwelling index values used in this work were taken from Lavín et al. (1990). They were obtained from geostrophic wind calculation (Bakun 1973) for a point G located at 43°N , 11°W , as indicated in the inset of Fig. 1.

In order to represent quantitatively the stoichiometric deviations from the Redfield ratio, Broecker's 'CO' and 'NO' parameters (Broecker 1974) and the 'NCO' parameter proposed by Fraga et al. (1992) were used.

'CO' and 'NO' can be defined as:

$$\begin{aligned} \text{'CO'} &= \text{O}_2 + R_C \cdot \text{CO}_2 & R_C &= -\Delta\text{O}_2/\Delta\text{CO}_2 & R_C &= 1.41 \\ \text{'NO'} &= \text{O}_2 + R_N \cdot \text{NO}_3^- & R_N &= -\Delta\text{O}_2/\Delta\text{NO}_3^- & R_N &= 9.3 \end{aligned}$$

These parameters are related to the preformed nutrients (CO_2° and NO_3°), defined as the nutrient concentrations at the moment of water mass formation in winter, by the expressions:

$$\text{'CO'} = \text{O}_{2\text{sat}} + R_C \cdot \text{CO}_2^\circ \quad \text{and} \quad \text{'NO'} = \text{O}_{2\text{sat}} + R_N \cdot \text{NO}_3^\circ$$

where $\text{O}_{2\text{sat}}$ indicates saturating oxygen concentration. The values of R_C and R_N correspond to the ratios obtained by Fraga et al. (1998).

If biochemical transformations follow Redfield stoichiometry, the parameters 'CO' and 'NO' remain constant during photosynthesis or remineralization of organic matter. However, if there is carbohydrate synthesis in excess of Redfield's stoichiometry, 'NO' increases at the same time that 'CO' decreases, indicating a deviation from Redfield ratios. An alkalinity (A) correction was applied to the 'CO' parameter ($= \text{O}_2 + R_C [\text{CO}_2 - 1/2(\text{A} + \text{NO}_3)]$), in order to make it independent from precipitation or dissolution of CaCO_3 due to biological activity (Broecker & Peng 1982, Takahashi et al. 1985).

The definition of 'NCO' is:

$$'NCO' = O_2 + CO_2 + R_N(1 - 1/R_C) NO_3$$

Fraga et al. (1992), Ríos et al. (1998). This parameter is independent of the fulfilment of Redfield's ratio concerning carbohydrate synthesis; like the other Broecker's parameters, it varies with the exchange of oxygen with the atmosphere. A deviation to lower values at the surface is a quantitative measure of oxygen loss to the atmosphere. During the sampling period, the mean oxygen loss estimated from the 'NCO' profiles was $38 \pm 14 \mu\text{mol kg}^{-1}$. In estimates using gas transfer coefficients given by Kester (1975), surface oxygen concentrations and wind speed gave a mean value of $48 \text{ mmol m}^{-2} \text{ d}^{-1}$, equivalent to $40 \mu\text{mol kg}^{-1}$, for the photic layer. The correlation between estimated oxygen losses to the atmosphere and negative anomalies of 'NCO' was highly significant ($r^2 = 0.72$, $n = 10$). In any case, according to these calculations, mean oxygen losses to the atmosphere amounted to only 6% of the mean value of the oxygen anomaly caused by excess carbohydrate synthesis.

RESULTS

A representative illustration of the thermohaline structure during the studied period corresponding to 19 July is shown in Fig. 2. The upper limit of ENACW (Eastern North Atlantic Central Water) is marked by the salinity maximum (indicated by a broken line in the figure). This limit ranges from 40 m depth during active upwelling to 60 m depth after relaxation periods. The upper water layer is composed of ENACW heated by solar radiation and influenced by fresh water contribution (<2.6%) from the Rías Bajas.

The thermohaline and chemical properties of the upper part of the upwelled ENACW were fairly constant during the observation period (Table 1). The seasonal increase in nutrient concentration due to mineralization of organic matter described by Álvarez-Salgado et al. (1993, 1997) takes place mainly at the end of summer (Fraga 1981).

The beginning of the studied period (Fig. 3) coincided with a phase of upwelling intensification which reached its maximum on 16 July and was followed by a period of relaxation which lasted from 19 to 25 July. A small upwelling event on 27 July was again followed by a strong relaxation (minimum index value on 1 August) and a new upwelling intensification with a peak on 7 August.

Table 1 Characteristics of the upper limit (dotted line in Fig. 2b) of the NACW (North Atlantic Central Water) at Stn 21, from 13 July to 7 August. Number of samples = 13. Oxygen, nutrients and preformed nutrients are in $\mu\text{mol kg}^{-1}$. SD: standard deviation

| | Depth (m) | t (°C) | S | NO ₃ | NO ₃ ^o | O ₂ | O ₂ ^{sat} | CO ₂ | CO ₂ ^o | PO ₄ | PO ₄ ^o |
|------|--------------|-----------|-------|-----------------|------------------------------|----------------|-------------------------------|-----------------|------------------------------|-----------------|------------------------------|
| Mean | 49 | 12.6 | 35.65 | 11 | 1.7 | 177 | 258.6 | 2156 | 2097 | 0.72 | 0.17 |
| ±SD | 9 | 0.1 | 0.02 | 1 | 0.7 | 11 | 0.8 | 10 | 5 | 0.07 | 0.05 |

The temporal evolution of nitrate and chlorophyll a concentrations (Fig. 4) showed a clear association with upwelling intensity. As can be seen in Fig. 4, upwelling intensity maxima on 16 and 27 July were followed by increased nitrate concentrations after a lag of about 2 d. Minimum nitrate concentrations were observed after the relaxation of 1 August. Chlorophyll maxima appeared in the upper water layers with a lag of 2 to 3 d after upwelling events. Chlorophyll maxima became deeper (24 to 27 July and 31 July to 2 August), during relaxation periods, following the deepening of the nitrate isopleths.

The patterns of variability of phytoplankton biomass and composition reflected those of the physico-chemi-

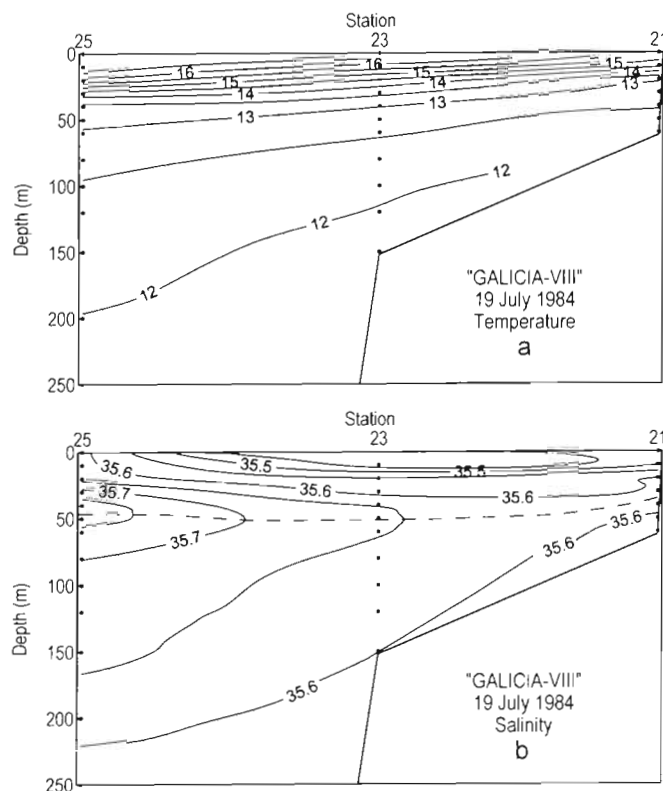


Fig. 2. Vertical profiles of (a) temperature and (b) salinity corresponding to 19 July for the transect between Stns 21 and 23 of Fig. 1. The broken line indicates the upper limit of the ENACW (Eastern North Atlantic Central Water)

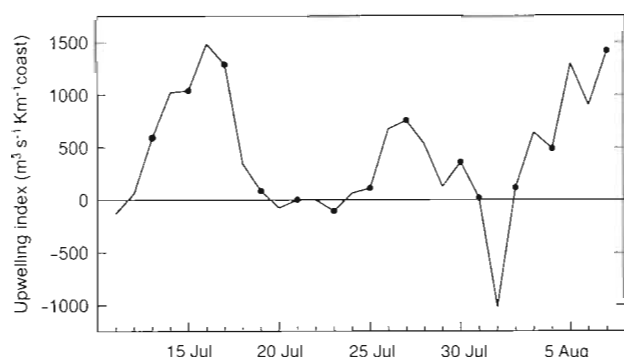


Fig. 3. Daily upwelling index off Cape Finisterre, taken from Lavin et al. (1990) from 11 July to 7 August 1984. •: dates on which Stns 21 to 25 were sampled

cal variables. Diatom abundances (Fig. 5) increased markedly in surface waters following the upwelling event of 16 July and reached a maximum dominated by *Chaetoceros* spp. and *Leptocylinndrus minimus* on 19 July. Their populations decreased during the first relaxation on 21 July, but increased again with a new pulse of upwelling. On 24 July, a diatom maximum dominated by *L. minimus* and small centric diatoms, which appeared to be in a rather senescent state, was present at the surface; however, due to the small cell sizes of these taxa and the probably low pigment content of the senescent diatoms, these high numbers were not strongly reflected in the chlorophyll distribution. The subsurface chlorophyll maximum which appeared during the first relaxation was associated with high population densities of *Mesodinium rubrum*, a photosynthetic ciliate with symbiotic chloroplasts, and several dinoflagellate taxa (Fig. 5). *M. rubrum* and the dinoflagellates are motile organisms and present migratory behaviour (Villarino et al. 1995); therefore, their vertical distribution may be dependent on the time of sampling (see Mouriño et al. 1985) and could have been different at other moments of the diel cycle.

The vertical profiles of O_2 , NO_3 and CO_2 recorded on 17 July and 2 August can be taken as representative of the situations following maximum upwelling intensity on 16 July and strongest downwelling on 1 August (Fig. 6). We have represented the scales of O_2 , CO_2 and NO_3 variables following the classical Redfield ratio (149:106:16). In addition, the preformed values of NO_3^o and CO_2^o (2 and 2097 $\mu\text{mol kg}^{-1}$) have been made to coincide with the saturating oxygen concentration (259 $\mu\text{mol kg}^{-1}$). So, if the Redfield ratio holds, the vertical distributions of NO_3 and CO_2 appear superimposed, and are the mirror image of the vertical distribution of oxygen with respect to the line representing oxygen saturation.

As can be seen in Fig. 6a (17 July), 1 d after maximum upwelling intensity the vertical profiles of O_2 ,

NO_3 and CO_2 followed the pattern of synthesis-rem-ineralisation expected from the Redfield ratio. There was utilisation of CO_2 and NO_3 by photosynthesis from 30 m depth up to the surface, while the remaining excess concentration of NO_3 in surface was 0.46 $\mu\text{mol kg}^{-1}$. On the contrary, on 2 August, after the downwelling event, with the 1% light level at 24 m, NO_3 was completely exhausted between 0 and 20 m, but this coexisted with high O_2 production and CO_2 consumption (Fig. 6b). The vertical profiles of the 3 variables were not symmetrical as in the previous case (17 July), in spite of having taken into account the losses of oxygen to the atmosphere. The observed $\Delta O_2:\Delta CO_2 = 1$ ratio, lower than Redfield's (1.41), was indicative of carbohydrate synthesis (Eq. 1). There was no photosynthesis between 30 and 40 m; however NO_3 was utilised without production of O_2 or the corresponding consumption of CO_2 , which even showed a slight increase at 30 m, as could be expected from Eq. (2). The Redfield ratio did not hold for either the photic or aphotic layers.

The estimated parameters 'NO' and 'CO' showed opposite values indicating a deviation from the Redfield ratio. A 'NO' increase and a 'CO' decrease in the vertical profiles between 0 and 20 m (Fig. 7) indicate carbohydrate synthesis. In the subphotic layer (about 20 to 40 m), a 'NO' decrease and a 'CO' increase reflect nutrient assimilation at the expense of carbohydrate consumption.

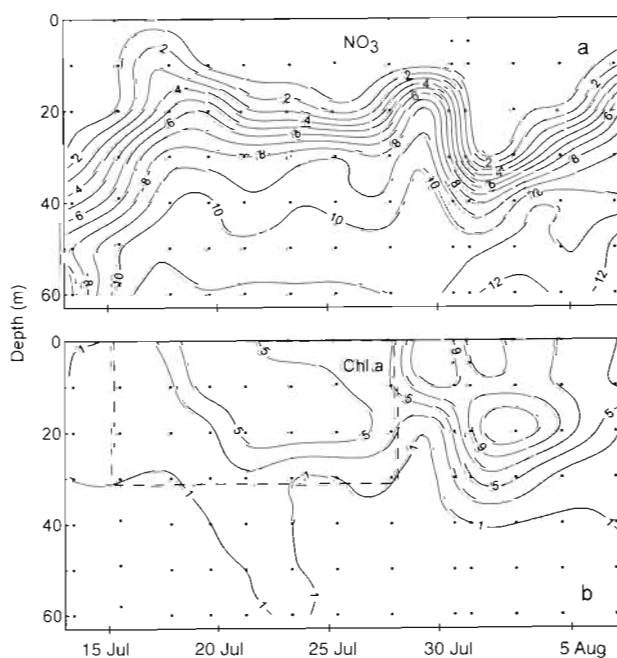


Fig. 4. Vertical distribution of (a) NO_3^- in $\mu\text{mol kg}^{-1}$, (b) chlorophyll a in $\mu\text{g kg}^{-1}$ of sea water, at Stn 21, from 13 July to 7 August. The square in (b) indicates the zone where organisms were identified and phytoplankton cells counted (Fig. 5)

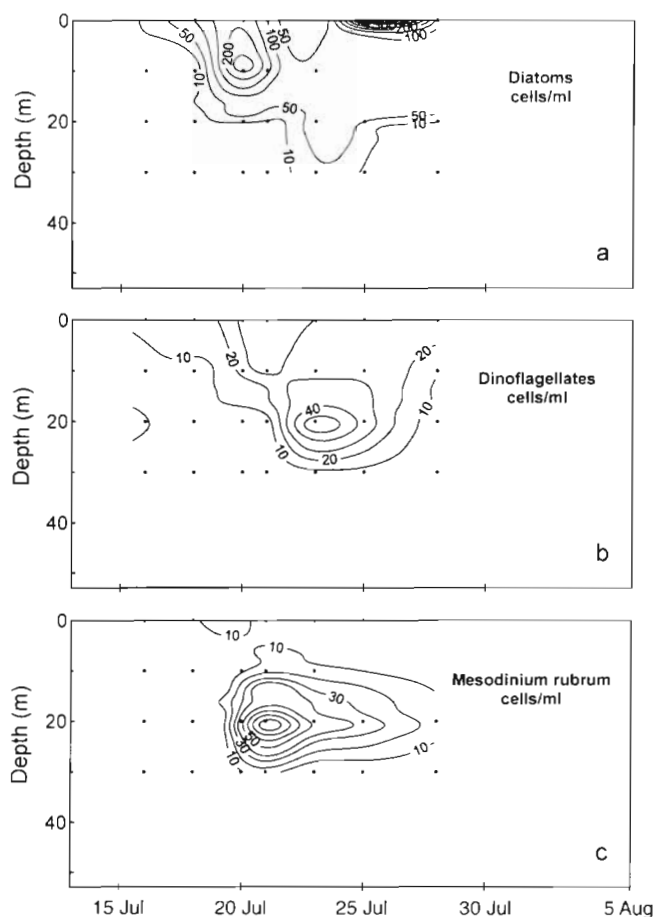


Fig. 5. Vertical distribution of the population density (cells ml^{-1}) of (a) diatoms, (b) dinoflagellates and (c) the photosynthetic ciliate *Mesodinium rubrum*, at Stn 21, from 15 to 27 July

The temporal evolution of 'NO' and 'CO' (Fig. 7) showed a clear relationship with upwelling relaxation, mediated by the lack of nutrient inputs. There were deviations on 13 July, after a relaxation previous to the beginning of our sampling. The subsequent upwelling intensification produced a decrease of the anomalies, which disappeared completely after the upwelling maximum on 17 July. The relaxation period between 20 and 25 July produced an increment of anomalies which was temporarily attenuated by the weak upwelling pulse on 26 to 27 July. The intensification of upwelling after 4 August induced a decrease in anomalies followed by their complete disappearance.

The relationship between vertical nutrient anomalies and upwelling intensity can be studied after quantification of the vertical carbohydrate transport, which may be estimated from the excess carbohydrate synthesised in the euphotic zone and the carbohydrate consumption in the subphotic layers. Excess carbohydrate synthesis can be calculated from the vertical integration of $\Delta'\text{NO}' - \Delta'\text{CO}'$ in the photic layer, while

excess used carbohydrate can be obtained from the vertical integration of $\Delta'\text{NO}' - \Delta'\text{CO}'$ (Fraga et al. 1992) in the subphotic zone. $\Delta'\text{NO}'$ is the difference between the 'NO' value at each depth and a 'NO' reference value, which is considered to be that of the superior level of the North Atlantic Central Water (NACW). $\Delta'\text{CO}'$ is calculated in a similar way. To express carbohydrates (C_{bh}) in carbon units, $\Delta'\text{NO}' - \Delta'\text{CO}'$ is divided by the stoichiometric ratio ($R_C = 1.41$).

Due to the lag between the phytoplankton response and the upwelling and relaxation events, carbohydrate transport was correlated with upwelling intensity (Fig. 8) 2 d before ($r^2 = 0.72$, $n = 13$). During the relaxation periods of 21 to 25 July and 30 to 31 July, carbohydrates increased rapidly. On the contrary, upwelling intensification between 13 to 17 July and 2 to 7 August (Fig. 8) was associated with a decrease in the carbohydrate excess and even negative vertical transport values. These negative transport values corresponded to situations of intense upwelling in which subsurface waters, with a 'NO' deficit due to carbohydrate consumption, reached the surface layers.

The dominant taxa in the subphotic layer during the relaxation period (Fig. 5) were *Mesodinium rubrum* and several dinoflagellates, motile and capable of migrating within the water column. If phytoplankton were responsible for the excess carbohydrate consumption and corresponding differential synthesis of organic matter, a significant correlation would be expected between vertically integrated chlorophyll and excess carbohydrate used in the subphotic layer. This was indeed the case ($r^2 = 0.7$, $n = 11$), as can be seen in Fig. 9, in which the samplings of 15 and 17 July, corresponding to the peak of upwelling intensity, have been excluded. The relationship shown in Fig. 9 provides evidence of the usefulness of the 'NO' and 'CO' parameters to estimate synthesis, transport and utilisation of carbohydrates and the usefulness of 'NCO' to calculate the cumulative O_2 loss to the atmosphere.

DISCUSSION

The results of this study show that during upwelling relaxation, when nutrients become exhausted at the surface, production of carbohydrates by phytoplankton leads to deviations from Redfield stoichiometry. This is a process in which the amount of carbohydrates does not represent the synthesis actually taking place in the photic zone at a particular moment, but the cumulative amount of carbohydrate transported from the photic to the subphotic zone during all the relaxation period. *Mesodinium rubrum* has been shown to be able to take up amino acids and dissolved organic carbon, although the importance of this ability for its overall carbon bud-

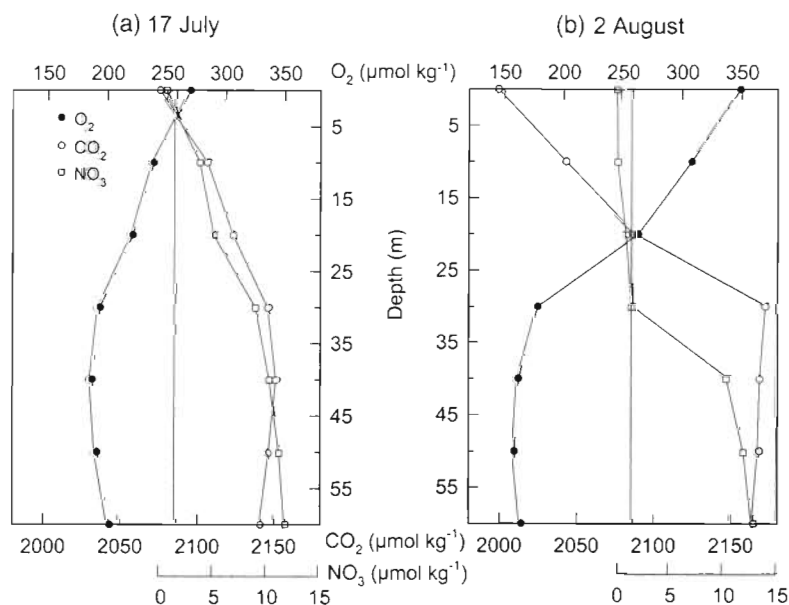


Fig. 6. Vertical distribution of O_2 , CO_2 and NO_3^- at Stn 21, (a) in conditions of intense upwelling on 17 July, and (b) after a relaxation of upwelling on 2 August. The relative magnitude of the unit for each scale is proportional to the inverse of the Redfield ratio. The preformed values of each parameter ($O_{2\text{sat}}$, CO_2^* , and NO_3^* , Table 1) have been made to coincide with the vertical line at the centre of the figure

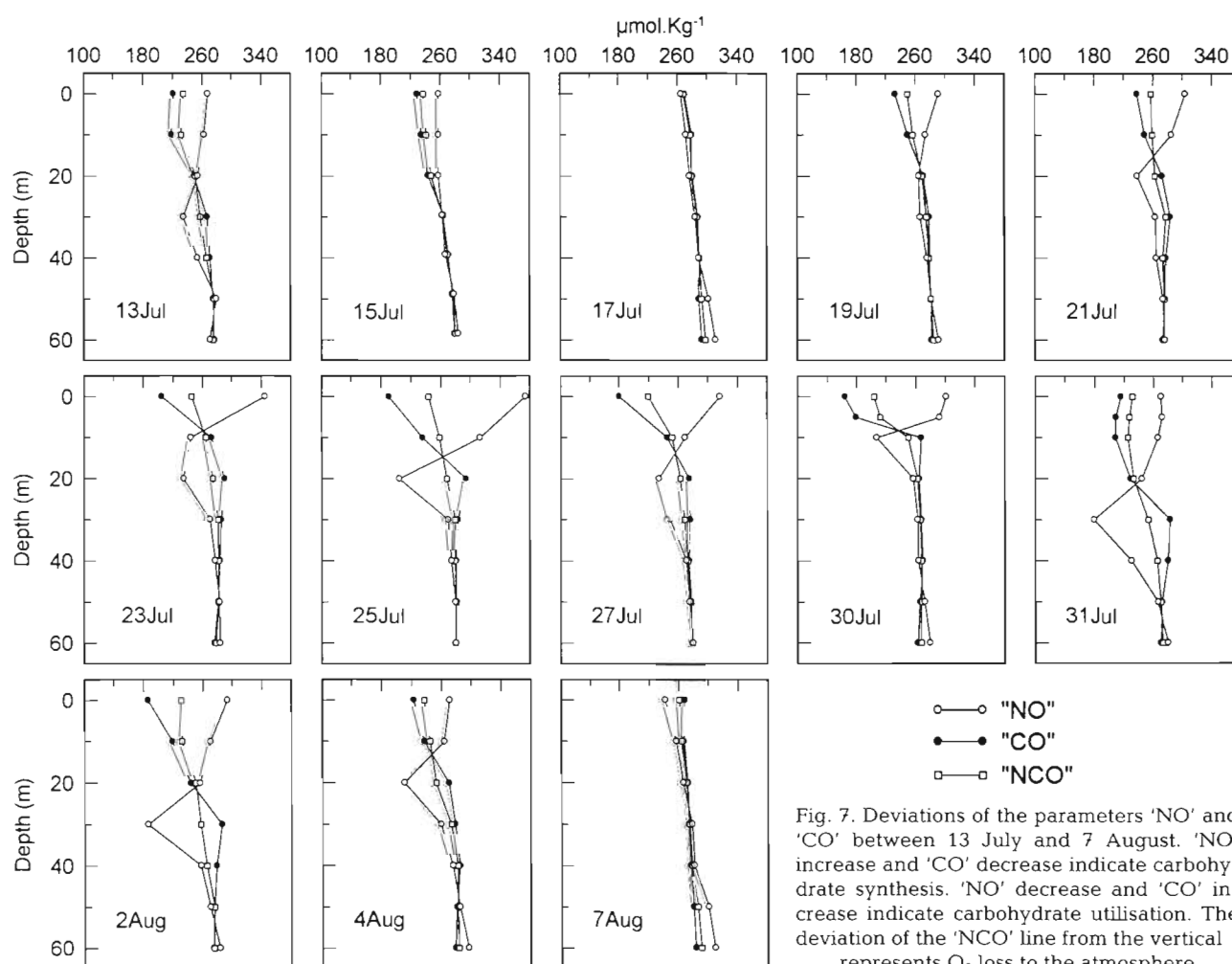


Fig. 7. Deviations of the parameters 'NO' and 'CO' between 13 July and 7 August. 'NO' increase and 'CO' decrease indicate carbohydrate synthesis. 'NO' decrease and 'CO' increase indicate carbohydrate utilisation. The deviation of the 'NCO' line from the vertical represents O_2 loss to the atmosphere

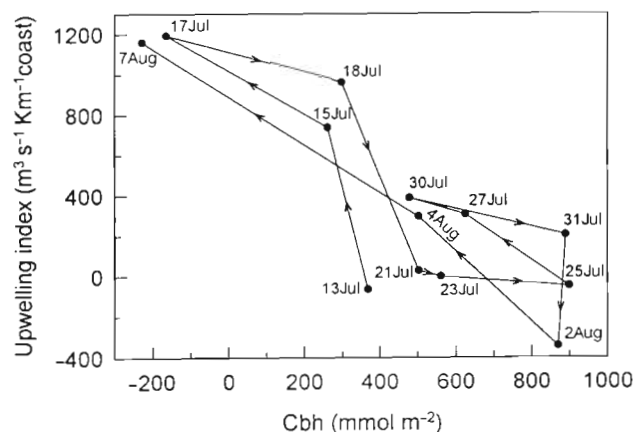


Fig. 8. Carbohydrates (Cbh) transported from the euphotic to the subphotic zone versus upwelling index. Cbh were calculated from 'NO' and 'CO' as explained in the text. The numbers indicate the sampling date and are linked sequentially, from 13 July to 7 August

get was unclear (Smith & Barber 1979). Our interpretation of the data presented in this study has not been affected by this heterotrophic activity, because our calculation of carbohydrate synthesis is based on the loss of inorganic carbon in the photic zone, without nitrate assimilation, a process that can only be attributed to photosynthetic activity.

According to Villareal et al. (1996), N limitation is a key factor in the regulation of the migratory behaviour of phytoplankton through its effect on carbohydrate metabolism. Moore & Villareal (1996) showed that the buoyancy of different *Rhizosolenia* species in culture was inversely proportional to their carbohydrate content. These authors observed that *R. formosa* was able to take up nitrate during the night and that production and consumption of carbohydrates by this diatom was adequate to explain the buoyancy changes. Richardson et al. (1998) presented a numerical model of nutrient uptake and photosynthesis during migrations of *Rhizosolenia* and estimated that new primary production due to *Rhizosolenia* migrations in the tropical ocean represented up to 17% of the new production due to turbulent fluxes of nitrate. According to Villareal et al. (1999), N transport by *Rhizosolenia* mats in the North Pacific central gyre could represent, on average, 20% of the turbulent nitrate flux. Dinoflagellates may use carbohydrates as a reserve of energy to allow nitrate uptake in the dark (Cullen 1985). Carbohydrates have also been shown to support dark protein synthesis in natural phytoplankton populations (Cuhel et al. 1984, Lancelot & Mathot 1985).

Carbohydrate synthesis is affected very rapidly by changes in upwelling intensity, as can be seen in Fig. 8. Intensification of upwelling favourable winds

(Fig. 3) produces vertical advection of deep waters and introduces nutrients into the euphotic zone. In the presence of nutrients, dinoflagellates stop carbohydrate accumulation (Cullen 1985), and nutrient relationships adopt Redfield stoichiometry before the occurrence of any significant change in phytoplankton assemblages. These observations suggest that carbohydrates play an important role in the life strategy of vertical migrators and in the anomalies of the nutrient and oxygen distributions in the water column.

Excess carbohydrate synthesis in the photic layer has also been described in embayments affected by coastal upwelling (Fraga et al. 1992), generating vertical transport of nitrogen and high $\Delta C:\Delta N$ relationships in surface layers. In a tropical upwelling ecosystem, Walsh (1996) described high $\Delta C:\Delta N$ uptake ratios (from 10 to 28.6) when nitrate was exhausted from the surface layers. In this case, N_2 fixation was the proposed mechanism to explain high CO_2 consumption figures. This process can be disregarded on the Galician coast because the distribution of PO_4H^- was similar to that of NO_3^- . The correlation coefficient between both variables was $r^2 = 0.94$ ($n = 81$), and the slope of the regression line of PO_4H^- on NO_3^- was 16.05.

In the subtropical oligotrophic waters of the NE Pacific, layers of negative preformed nitrate appear to occur in the subphotic zone above the nutricline, and have been attributed to the occurrence of respiration without the stoichiometric component of nitrogen remineralisation (Emerson & Hayward 1995). These authors have observed nitrate deficits amounting up to $5 \mu mol kg^{-1}$ associated to the subphotic layer as negative preformed NO_3^- . In this study, the subsuperficial 'NO' anomalies found at times of maximum relaxation reached $60 \mu mol kg^{-1}$ (about $6 \mu mol kg^{-1}$ of nitrate), a value comparable to those found by Emerson & Hayward (1995). Pérez et al. (1986) found negative nitrate anomalies with slightly lower mean values ($2.5 \mu mol kg^{-1}$) in the oligotrophic waters of the NW Mediterranean, just below the deep chlorophyll maximum (DCM), which is typically found during the stratification period and underlies a slightly shallower oxygen maximum (Estrada 1985, Estrada et al. 1993). Lewis et al. (1986), working in oligotrophic Atlantic waters, found that 1/3 of the nitrate consumption took place at depths receiving <1% of surface light. Subsurface chlorophyll maxima are ubiquitous in stratified waters and are due to the combination, in varying proportions, of increased phytoplankton abundances and higher chlorophyll content per cell due to photoacclimation (Cullen 1982, Estrada 1985). In some regions, like the frontal zones of the English Channel (Holligan 1978), the phytoplankton community of the DCM is dominated by 1 or a few species of migratory dinoflagellates. In more oligotrophic areas, like the Mediter-

ranean, the phytoplankton assemblage of the DCM is very diverse, but may contain patches of high phytoplankton biomass dominated by diatom taxa like *Chaetoceros*, *Thalassiosira* and *Rhizosolenia* (Estrada 1991). The occurrence of negative nitrate anomalies in the subphotic zone in different regions and the observation that not only dinoflagellates and photosynthetic ciliates like *Mesodinium*, but also some diatoms like *Rhizosolenia* may vary their position in the water column suggest that the situation described here for the Galician upwelling could be widespread in other marine areas.

A high $\Delta\text{CO}_2:\Delta\text{NO}_3$ uptake ratio was observed by Sambrotto et al. (1993) in the North Atlantic, when exhaustion of nitrate after the spring bloom produced a similar situation to that described in the present study for upwelling relaxation. Sambrotto et al. (1993) proposed the synthesis of dissolved organic matter with a high C:N ratio to explain their findings. However, an alternative mechanism could be the transport of nitrogen due to vertically migrating phytoplankton.

Diel patterns of nitrogen uptake were investigated by Probyn et al. (1993) in the Southern Benguela Upwelling System, by means of ^{15}N uptake experiments. These authors found that NO_3 consumption in the subphotic zone during the night was about 60 % of the total for the whole water column near the coast, and tended to decrease offshore. On the other hand, the night:day nitrate consumption ratio increased with distance from the coast. These findings suggested that the contribution of dark nitrate uptake to new production increased with decreasing nutrient availability in the euphotic zone (Probyn et al. 1993). In the present study, nutrient and carbohydrate anomalies were also calculated at Stns 23 and 25 (Fig. 1) which were sam-

pled on the same dates as Stn 21. As reported by Probyn et al. (1993), the intensity of the anomalies decreased seawards. At Stn 21, the nutricline was located at 15 m depth and carbohydrate utilisation in the subphotic layer was 100 % of the synthesised carbohydrate in the photic layer. At Stn 23, the nutricline depth was 23 m and carbohydrate utilisation was 50 %. Further offshore, at Stn 25, the nutricline level was 38 m and carbohydrate utilisation was only 18 %. A likely explanation of these findings could be a decrease of nutrient utilization by migratory organisms with increasing nutricline depth, due to the longer travel distance for their migration.

This study has used Broecker's (1974) 'NO' and 'CO' parameters to show the biogeochemical implications of vertical carbohydrate transport in an ecosystem subjected to intermittent upwelling pulses. This vertical transport was mediated by migrating organisms with the ability to generate high $\Delta\text{C}:\Delta\text{N}$ ratios due to excess carbohydrate synthesis in the euphotic layer during the day and nitrogen consumption in the subphotic layer during the night. Some of these characteristics have been observed in other aquatic systems, suggesting that vertical migration may play a greater role in the vertical transport of nitrogen and carbon than previously considered.

Some ecological and biogeochemical implications of deviations from Redfield stoichiometry have been outlined by Goldman et al. (1992) and Richardson & Cullen (1995), who carried out culture experiments, and Villareal et al. (1999), who worked in the oligotrophic central North Pacific Ocean. We showed that uncoupling between photosynthesis and nutrient uptake can occur in an upwelling region. In the process described here, carbohydrate synthesis in the euphotic zone represents only a first step in the production of additional biomass. The synthesis of this biomass needs to be completed in the subphotic zone with the incorporation of the necessary nutrients. Thus, there is no deviation from Redfield stoichiometry when both euphotic and subphotic layers are considered as a whole, although the upwards flux of new nitrogen increases, as pointed out by Villareal et al. (1999). In addition, the uncoupling between photosynthesis and nutrient uptake reported here may have important biogeochemical implications due to its effect on the distribution of CO_2 and on its exchanges between the sea surface and the atmosphere.

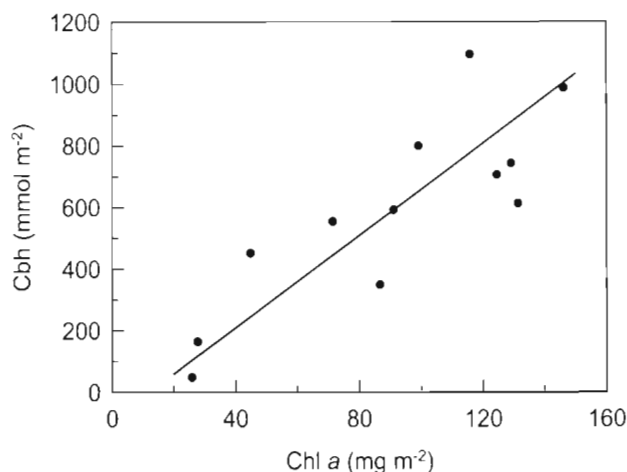


Fig. 9. Carbohydrate utilised in the subphotic layer in mmol m^{-2} of carbon versus chlorophyll a in mg m^{-2} . These are vertically integrated values for the subphotic zone

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