



PERGAMON

Deep-Sea Research II 48 (2001) 3023–3047

---

---

DEEP-SEA RESEARCH  
PART II

---

---

www.elsevier.com/locate/dsr2

# Supply and demand of nutrients and dissolved organic matter at and across the NW European shelf break in relation to hydrography and biogeochemical activity

D.J. Hydes<sup>a,\*</sup>, A.C. Le Gall<sup>a</sup>, A.E.J. Miller<sup>b</sup>, U. Brockmann<sup>c</sup>, T. Raabe<sup>c</sup>,  
S. Holley<sup>a</sup>, X. Alvarez-Salgado<sup>b</sup>, A. Antia<sup>d</sup>, W. Balzer<sup>e</sup>, L. Chou<sup>f</sup>, M. Elskens<sup>g</sup>,  
W. Helder<sup>h</sup>, I. Joint<sup>b</sup>, M. Orren<sup>i</sup>

<sup>a</sup>Southampton Oceanography Centre (SOC), Empress Dock, Southampton SO14 3ZH, UK

<sup>b</sup>Plymouth Marine Laboratory (PML), West Hoe, Plymouth PL1 3DH, UK

<sup>c</sup>Institute for Biogeochemistry and Marine Chemistry, University of Hamburg (UH), Martin Luther King Platz 6, D-20146 Hamburg, Germany

<sup>d</sup>Institut für Meereskunde an der Universität Kiel (IfM), D-24118 Kiel, Germany

<sup>e</sup>Universität Bremen (UB), FB-2 Meereschemie, Postfach 330440, D-28334 Bremen, Germany

<sup>f</sup>Laboratoire d'Océanographie Chimique et Géochimie des Eaux, Université Libre de Bruxelles (ULB), Campus Plaine - CP 208, Bd. du Triomphe, B-1050 Brussels, Belgium

<sup>g</sup>Laboratorium voor Analytische Chemie, Vrije Universiteit Brussel (VUB), Pleinlaan 2, B-1050 Brussels, Belgium

<sup>h</sup>Nederlands Instituut voor Onderzoek der Zee (NIOZ), Postbus 59, NL-1790 AB Den Burg, Texel, The Netherlands

<sup>i</sup>Oceanography Department, University College Galway (UCG), Galway, Ireland

---

## Abstract

As part of the OMEX I project, nutrient determinations were made on 17 cruises in the region of the Goban Spur and La Chapelle Bank between 46 and 51°N, in all seasons of the year, between 1993–1995. Over this period no change was detectable in the structure of the water masses below the deep winter mixed layer. The N:P (dissolved nitrate-to-phosphate) ratio changed from 16 at 100-m depth to less than 15 at 3300-m depth. At intermediate depths nutrient and oxygen data indicate the presence of Mediterranean Outflow water overlying Labrador Sea Water at its most eastern extension. Estimated maximum levels of production in the spring bloom are the total N-limited new primary production equivalent between 24 and 41 gC m<sup>-2</sup>, the equivalent maximum diatom production is 11 gC m<sup>-2</sup>. Measurements during the spring bloom suggest a conversion factor of 1 μM nitrate to 1 μg l<sup>-1</sup> chlorophyll, at the shelf break, which is consistent with other recent measurements in European shelf seawaters. Sediment trap data suggest that 80% (5.4 g m<sup>-2</sup>) of the opal produced in the spring bloom dissolved before reaching the sediment trap at 600 m. A comparison of the winter and summer profiles for dissolved silicon suggests a similar dissolution of 9 ± 3 g opal m<sup>-2</sup> above 300-m depth. Measurements of dissolved organic carbon (DOC) in September

---

\*Corresponding author. Tel.: +44-23-8059-6547; fax: +44-23-8059-6554.

E-mail address: david.j.hydes@soc.soton.ac.uk (D.J. Hydes).

1994 show an enrichment of  $7\ \mu\text{M-C}$  above the seasonal thermocline relative to the winter values ( $52 \pm 4\ \mu\text{M}$ ). In winter dissolved organic nitrogen represents 40% of the pool of total dissolved nitrogen. There is no consistent evidence of an increase in the concentration of DON during summer. Measurements of nitrate in surface waters in January 1994 show that concentrations off-shelf vary with the temperature of the water and are related to the depth of winter mixing. Mixing in surface waters is discontinuous at the shelf break, demonstrating the degree to which exchange across the shelf break is limited even in winter. OMEX winter measurements of nitrate concentrations can be used to estimate the flow of water across the shelf break that would be required to maintain the nitrogen balance in the North Sea at a steady state. The estimate is  $0.6\ \text{Sv}$  ( $1\ \text{Sv} = 10^6\ \text{m}^3\ \text{s}^{-1}$ ), which is similar to an earlier estimate of a total flow of  $1.7\ \text{Sv}$  based on salt budgets (*cf.* Huthnance, *Deutsche Hydrographische Zeitschrift*, 49 (1997) 153). © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Plankton; Biogeochemical cycle; Nutrients; Dissolved organic carbon; Shelf edge dynamics; Northwest European shelf sea; Northeast Atlantic

---

## 1. Introduction

The Ocean Margin EXchange (OMEX) Project is an international project developed to investigate the importance of the European margins in terms of exchange between shelf seas and the oceans. Topics of interest are the examination of the hypotheses that the shelf break is an area of enhanced biological production (see Joint et al., 2001) and that the underlying sediments may act as a depocentre for organic carbon (Walsh et al., 1981; van Weering et al., 1998). The first part of the OMEX project from 1993 to 1996 focused on the Celtic Sea shelf break, including the Goban Spur and La Chapelle Bank areas, approximately between  $46\text{--}51^\circ\text{N}$  and  $5\text{--}15^\circ\text{W}$ . The different sampling programmes overlapped the “Goban Spur Box” around the line of the OMEX sediment trap array (Antia et al., 2001) between  $48.7\text{--}49.3^\circ\text{N}$  and  $14\text{--}12.5^\circ\text{W}$ . Measurements of the “nutrient” compounds, nitrate<sup>1</sup>, phosphate and silicate were made throughout the project in support of a range of OMEX process studies. Additionally on some cruises parallel measurements were made of dissolved organic carbon (DOC) and the dissolved organic fraction of nitrogen and phosphorus (DON and DOP). This paper is an attempt to produce an overview of the large amount of nutrient and nutrient-related data gathered, and it concentrates on an evaluation of the temporal changes in the “Goban Spur Box”.

The recent EU-MAST project NOWESP produced a compilation of the available hydrographic and nutrient data for the North West European shelf region. Even such a comparatively data-rich region of the globe, few data exist for the winter period (Radach et al., 1995). A success of the OMEX project was that two cruises (*M27/1*, *CD84*) were conducted in winter when exchange processes should be most intense. The availability of data from cruises through the year makes possible a quantitative evaluation of nutrient fluxes from the observed changes in concentrations. For this evaluation we have to assume that the water in the “Goban Spur Box” was contained within a volume of the ocean whose properties and internal processes were uniform on a scale

---

<sup>1</sup>Note: Measurements of “nitrate” referred to in this paper are the results of analytical methods, which have determined the combined concentration of both nitrate and nitrite in the sample.

greater than that of the Box, where there is a general northward flow of water at a rate of about  $1 \text{ cm s}^{-1}$  ( $315 \text{ km a}^{-1}$ ) (cf. ; Pingree and Le Cann, 1989).

The seasonal cycle in primary production in the OMEX study area has been investigated by Joint et al. (2001). In primary production, inorganic forms of carbon and nutrients are taken up and fixed by phytoplankton in organic compounds with a varying degree of efficiency (Bronk et al., 1994). Secondary processes, such as grazing by zooplankton, transform the phytoplankton into products that include both particulate debris, which settles out of the surface layers to the ocean floor, and dissolved organic matter (Anderson and Williams, 1998). Dissolved organic matter (DOM) is the largest reservoir of organic carbon in the ocean (Williams, 1995). The ocean margin is a key area for investigating the global impact of dissolved organic carbon (DOC) on the carbon cycle since both the export of terrestrial DOC and the import of oceanic DOC occur at this boundary. The degree to which biogeochemical cycling of carbon, nitrogen and phosphorus overlaps with the cycling of the pool of DOC compounds is becoming appreciated (Banoub and Williams, 1973; Butler et al., 1979; Anderson and Williams, 1998; Hydes et al., 1999), but reliable new data on which this understanding is to be developed are still sparse (Williams, 1995). Sugimura and Suzuki (1988) described their attempt to determine DOC by high-temperature catalytic oxidation (HTCO). Although the findings of the paper were subsequently retracted (Suzuki, 1993), the description of the method and its subsequent detailed scrutiny provided a turning point in the determination of DOC (Hedges et al., 1993). It is currently held that such HTCO methods provide enhanced routine precision (Cauwet, 1999) and accuracy (Sharp, 1997) over other methods of oxidation, as well as an increased rate of sample throughput. Three laboratories (UH, UB and PML) participating in the OMEX project successfully used this method to process samples collected on OMEX cruises. Here, we present the analytical

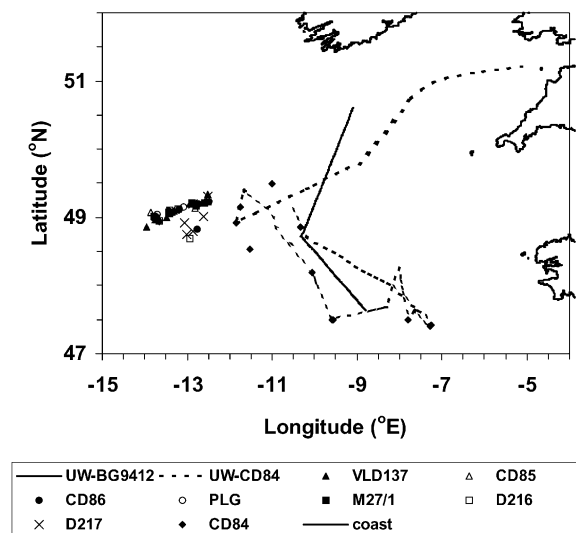


Fig. 1. Map showing underway sampling track cruises *CD84* and *BG9412*, stations sampled along the shelf break during cruise *CD84*, and the positions of the stations sampled within the OMEX Goban Spur Box between  $14^{\circ}\text{W}$  and  $12.5^{\circ}\text{W}$  and  $48.3^{\circ}\text{N}$  and  $49.7^{\circ}\text{N}$ .

background to the measurements and review observations made as a result of cruises *M27/1*, *CD84*, *CD94* and *M30/1* in the Goban Spur Box. These cruises in January and February 1994, June 1995 and September 1994 allowed the evaluation of changes in concentrations through an annual cycle. In addition to measurements of DOC, DON and DOP measurements are also discussed.

The range of physical processes occurring at the shelf break have been described (Huthnance, 1995), but the actual volumes of water exchanging across the shelf break resulting from the sum of these processes are poorly known (Huthnance, 1997). The North Sea appears to be rapidly flushed by ocean waters crossing the shelf break in winter, and it has tended to be assumed that riverine inputs of nutrients would give rise to a net export of nutrients from the shelf to the ocean (Brockmann et al., 1988; Nelissen and Stefels, 1988; Wollast, 1992). The idea that the northwest European shelf is a net exporter of nitrate has been challenged by the recent estimates of likely rates of denitrification in shelf seas made by Seitzinger and Giblin (1996). The new data available from the OMEX project enable us to evaluate the estimates of Seitzinger and Giblin (1996) in comparison to known concentrations and possible exchange volumes.

## 2. Methods

### 2.1. Sampling area and cruises and OMEX data products

The region of study is the shelf break of the Celtic Sea, between 48.7–49.3°N and 14–12.5°W. A total of 944 samples for the determination of nutrients were collected between April 1993 and October 1995. This area corresponds to the two boxes “OMEX 1” and “OMEX 2” considered by Joint et al. (2001). The box includes the sites of the two OMEX sediment trap moorings, which were located at 49.187°N, 12.820°W and at 49.083°N, 13.430°W (Antia et al., 2001). The data were collected on 10 of the 18 OMEX-related cruises between 1993 and 1995. Details of all the stations occupied and the samples collected and analysed from these cruises can be found in the OMEX Project Data Set (Lowry et al., 1997). The cruises considered are listed in Table 7, and the positions of the stations considered in this paper are shown in the map in Fig. 1. In addition, data are discussed from surface water samples collected underway during two cruises—*CD84* (February 1994) and *BG9412* (April 1994). The area of the underway observations extends along the shelf break from Goban Spur to La Chapelle Bank (Fig. 1). An atlas of the maps of the OMEX hydrographic data (temperature, salinity, dissolved oxygen, nitrate, phosphate and silicon) has been compiled and is part of the OMEX CD-ROM, which includes the full OMEX dataset (Osborne et al., 1997; Lowry et al., 1997). The Atlas contains: (i) A description of the water masses of the northeast Atlantic that occur in the OMEX study area; (ii) Presentations of temperature and salinity diagrams for each cruise along the Goban Spur section and of time series at the individual sediment trap stations and at one station on La Chapelle Bank; (iii) Maps of nutrient sections and time series; (iv) An index of the data used. The Atlas contents are detailed in Table 8. Details of all the sampling and analytical procedures used are included as meta-data in the OMEX CD-ROM. The meta-data also include details of any known problems with specific data sets, and all suspect data are flagged in the data files (Lowry et al., 1997). The variations

between cruises are not considered. The methods used by the different groups are summarised below.

## 2.2. Measurement—nutrients

**NIOZ:** Samples were taken from water bottles deployed on a CTD rosette and analysed at sea using a TRAACS 800 autoanalyser, usually within 4 h of collection. The samples were stored in cool and dark conditions between collection and analysis. On cruise *PLG93*, the samples from the CTD rosette were analysed unfiltered. On *CD86* and *PLG95*, the samples were filtered through a 0.45- $\mu\text{m}$  Acrodisc filter to improve the quality of the ammonium results. The following chemistries were used: Phosphate: Ammonium molybdate/ascorbic acid method (Murphy and Riley, 1962), Nitrate/nitrite: Sulphanilamide/naphthylethylenediamine method using a Cu/Cd coil (efficiency >98%) for reduction (Armstrong et al., 1967). Silicate: Ammonium molybdate/ascorbic acid method (Grasshoff et al., 1983). Samples were always analysed from the surface to the bottom to minimise the risk of cross-sample contamination. Working standards were prepared fresh each day by diluting stock standards to the required concentration with natural, aged, low-nutrient seawater. The nutrient concentrations in these standards were determined by manual colorimetric analysis. The low-nutrient seawater also was used as a wash between samples. A second mixed nutrient stock, poisoned with 0.2% chloroform or  $20\text{ mg l}^{-1}\text{ HgCl}_2$ , was used as an independent check. Pipettes and volumetric flasks were calibrated before each cruise, and batches of standard solutions were inter-calibrated. The accuracy of analyses is reported as about 1% of the full-scale value for nitrate, nitrite and silicate, and 2% of the full scale for phosphate. The data were reported as nitrate and nitrite, the nitrate values having been computed by subtracting nitrite from nitrate *plus* nitrite. BODC practice is to store nitrate *plus* nitrite, and the values in the database have been determined by summing the nitrate and nitrite values supplied. In the cases where multiple bottles were fired at a single depth, nutrient values were reported from each bottle. These have been averaged, excluding any bottles flagged as leaking, to give a single nutrient value for each depth.

**SOC:** Samples were collected from bottles on the CTD rosette (*CD84* and *D216*) and from the continuously pumped surface seawater supply (*CD84*). The samples were analysed unfiltered using a Chemlab AA-II type autoanalyser, using the same chemistries as NIOZ. During cruise *D216* a quality control sample was collected in bulk at the first deep station worked on the cruise. It was taken from the two deepest Niskin bottles and divided into 50 sample vials, which were stored in a refrigerator at 4°C. One or more of these vials were then analysed each time ( $n = 22$ ) a group of measurements was made. The precision of the data for this quality control sample was for Si mean =  $40.8\ \mu\text{M}$ , %rsd = 0.53 ( $n = 68$ ),  $\text{NO}_3$  mean =  $21.58\ \mu\text{M}$ , %rsd = 1.23,  $\text{PO}_4$  mean =  $1.41\ \mu\text{M}$ , %rsd = 1.01 ( $n = 67$ ). During cruise *D216*, 288 samples were determined in duplicate. The mean differences and ( $\pm$  one standard deviation) between duplicates were  $0.09 \pm 0.09\ \mu\text{M-Si}$ ,  $0.06 \pm 0.1\ \mu\text{M-NO}_3$ ,  $0.008 \pm 0.009\ \mu\text{M-PO}_4$ .

**UH:** Water samples were taken from bottles deployed on a CTD rosette and analysed immediately on board during cruises *V137*, *M27/1*, *D217*; a full set of samples from *CD94* was analysed on shore. The samples were analysed unfiltered, provided the particulate content was not considered too high, in which case the samples were GF/C filtered. Parameter coding in the BODC database has assumed the analysis of unfiltered samples. Samples were analysed using a

Technicon AA-II type autoanalyser system using the same basic methods as NIOZ; the phosphate method followed the modification of Eberlein and Kattner (1987).

VUB: Water samples were taken from water bottles deployed on a CTD rosette. On two cruises (*BG9322* and *BG9412*) continuous underway measurements were made by drawing discrete samples at frequent intervals from the continuous seawater supply. Nutrient determinations were carried out on board, immediately after sampling. Nitrate *plus* nitrite and phosphate were determined using a Technicon AA-II autoanalyser as described by Elskens and Elskens (1989).

PML: Standard autoanalyser methods were used as described in Rees et al. (1995). Nitrite-corrected nitrate data were supplied to BODC. The nitrite corrections were removed and the data was stored as nitrate + nitrite in the database.

### 2.2.1. Data quality

The quality of data from different cruises and groups contributing to OMEX was compared in a region with uniform hydrography (cf. Saunders, 1986). The results for the measurements of temperature and salinity from waters below 2000-m depth suggest that these waters had a constant composition from cruise to cruise. Samples in this deep water in the Goban Spur Box were collected on 8 cruises. In Fig. 2, all the results for the determination of dissolved silicon below a depth of 3000 m reported by NIOZ, UH and SOC made on board the ship are plotted against the CTD-derived potential temperature at the depth of the sampling. A 5% error bar is drawn on the NIOZ data. A comparison of the data in the plot suggests some erroneous data are present in the OMEX database. The SOC data particularly appear to contain a high proportion of outliers. However, the general agreement of the data is within the 5% error bar. The UH data shows a high degree of consistency between the two cruises. The level of agreement achieved between the NIOZ, SOC and UH results does not reach the 3% level that the WOCE group of experts consider should be achievable in the determination of silicon (WOCE, 1991). Within water masses, nitrate and phosphate concentrations tend to co-vary linearly. In Table 1, we consider the co-variation of determinations of nitrate and phosphate against one another in water below 2000-m depth. The data for these variables have the same source, and should be free from extra errors introduced when nutrient data are compared to derived data such as temperature (the derivation of which assumes that bottles have closed at the nominal depth and not leaked). The N:P ratio

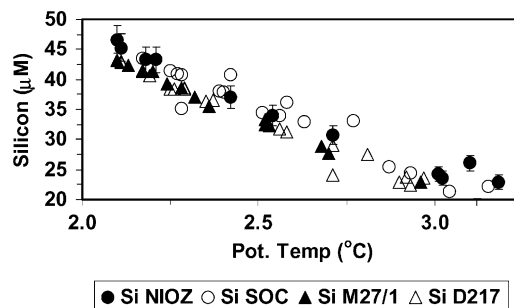


Fig. 2. Plot of all data in samples below 3000-m water depth for dissolved silicon collected on board ship by NIOZ (cruises *CD86*, *PLG93*, *PLG95*) SOC (*D216*) UH (*M27/1*, *D217*) plotted against the potential temperature calculated from CTD data. (Error bar = 5%).

Table 1  
Summary of N:P ratio data in samples collected at depths below 2000 m

Cruise	Originator	N:P ratio	$R^2$	$n$
<i>M27/1</i>	UH	14.89	0.98	17
<i>D217</i>	UH	14.00	0.71	24
<i>D216</i>	SOC	15.11	0.99	20
<i>PLG, CD86</i>	NIOZ	14.89	0.95	17

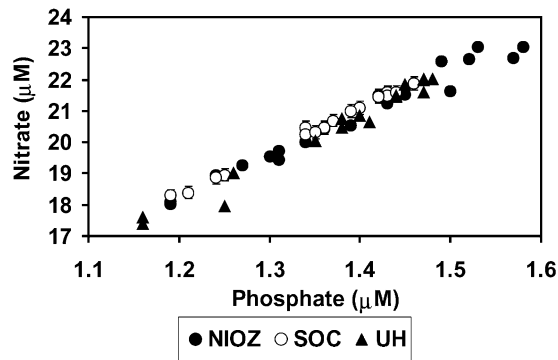


Fig. 3. Plot of all data in samples below 2000-m water depth for nitrate collected on board ship by NIOZ (cruises *CD86*, *PLG93*, *PLG95*) SOC (*D216*) UH (*M27/1*, *D217*) plotted against phosphate. (Error bar = 1%).

calculated by fitting a linear regression line with a zero intercept through the data sets gives ratios for the NIOZ and UH (*M27/1*) data, which agree to the second decimal place while that calculated from the SOC data is different by 1.5% (Table 1). A 1% error bar drawn on the SOC data in Fig. 3, indicates that the offset is consistent between the data sets. The level of agreement achieved between the NIOZ, SOC and UH results in these OMEX data sets attains that considered achievable in the determination of nitrate and phosphate (WOCE, 1991).

### 2.3. Measurements—dissolved and colloidal organic carbon, nitrogen and phosphorus

PML: Samples were taken from the CTD rosette and generally filtered through GF/F filters, although some samples in low particulate waters were analysed unfiltered to assess filtration as a source of contamination. Ultra-clean handling techniques were used throughout. The analytical technique involves the direct injection of acidified and decarbonated seawater onto a platinised alumina catalyst at a high temperature (680–900°C) under an atmosphere of oxygen or high purity air. The quantitative production of CO<sub>2</sub> gas allows DOC concentrations to be determined using a CO<sub>2</sub>-specific infrared gas analyser (IRGA). Analyses were undertaken at sea using a Shimadzu TOC-5000 HTCO analyser fitted with a Li-Cor Li6252 IRGA. This overcame the problems associated with using the standard TOC-5000 IRGA on an unstable platform. The total nitrogen analytical technique is based on the above method. The quantitative production of the nitric oxide

radical allows total dissolved nitrogen concentrations to be determined using a nitrogen-specific chemiluminescence detector. Analyses were undertaken at sea using a Shimadzu TOC-5000 HTCO analyser fitted with an Antek 705-D chemiluminescence detector. The combustion products travelled through a Drierite trap (97% CaSO<sub>4</sub>, 3% CoCl<sub>3</sub>) and a membrane (permeation tube) drier to remove any trace of water. The dried nitric acid radical was then reacted with ozone to produce the excited chemiluminescent nitrogen species and passed to the detector. Each sample was injected four times, with each injection cycle taking 5.5 min. Great care was taken to quantify blank signals generated at all stages of both the analytical procedures and to correct the data for them.

UH: Water samples were taken from the CTD rosette and filtered through Whatman GF/C filters. The filtrate was poisoned with mercuric chloride and stored in glass and polyethylene bottles in a cooling chamber until it was analysed. The samples were analysed by high-temperature catalytic oxidation using a nickel catalyst. The water samples for DON and DOP were oxidised by peroxodisulphate in an autoclave (Eberlein and Kattner, 1987) followed by nitrate and phosphate determinations.

UB: Water samples were taken from the CTD rosette and filtered under ultra-clean conditions through pre-combusted GF/F filters. The filtrate was then acidified, sealed in brown glass ampoules and stored at 4°C until it was analysed. The samples were analysed in triplicate using the HTCO method seen above.

### 2.3.1. Data quality

The current routine precision of the HTCO method is considered to be about  $\pm 1$ –2% of concentration over the 40–80  $\mu\text{M-C}$  range, and about 1% at higher concentrations (Sharp et al., 1995). Work on the OMEX project using the Shimadzu TOC-5000, total organic carbon analyser, gave a precision of 1.5%, i.e., around  $\pm 1$   $\mu\text{M-C}$  at seawater concentrations (Alvarez-Salgado and Miller, 1998).

High and variable blanks are a major problem with HTCO techniques (Cauwet, 1994; Sharp et al., 1995), and may be the main reason for the large discrepancies between techniques (Hedges et al., 1993). Blanks vary between different types and between batches of the same catalyst, but are generally around 15–22  $\mu\text{M-C}$  for the platinised alumina used in the Shimadzu TOC-5000 (Cauwet, 1999). However, for thoroughly conditioned batches of catalyst, blanks several times lower than this have been observed (Alvarez-Salgado and Miller, 1998). Catalyst conditioning consists of running the “blank check” programme of the Shimadzu TOC-5000 several times to wash the catalyst with *Milli-Q* water thoroughly. The subsequent injection of pre-pyrolised water (50 injections, of 200  $\mu\text{l}$ ) from the pyrowater trap obtains the system blank. During the OMEX campaign, blanks were  $7.5 \pm 0.3$   $\mu\text{M-C}$  and  $6.5 \pm 2.1$   $\mu\text{M-C}$  during 1994 and 1995, respectively.

As a check on the accuracy of the analytical systems, the analysts participated in the international DOC inter-comparison exercises, under the auspices of the US NSF (Sharp, 1997). Comparisons have shown that a carefully prepared open ocean “reference sample” remains stable for many months under controlled conditions (Sharp et al., 1995). Concentrations of the “reference” materials determined by OMEX analysts were consistent with the limits ( $\pm 10\%$ ) of the predetermined concentrations (Jonathan Sharp, pers. com.). A further check on the reliability of the instruments involved concerns of the consistency of the analytical performance. It is possible to demonstrate the consistency in part by referencing to the calibration data for the

analytical system. During the OMEX cruises, the analytical systems were standardised daily in the range 0–200  $\mu\text{M-C}$  with potassium hydrogen phthalate in *Milli-Q* water. This calibration routine is suitable for accurate analyses of seawater samples, as significant differences have not been found between the slopes of the calibration curves for *Milli-Q* and natural sea water (Alvarez-Salgado and Miller, 1998). The Calibration using *Milli-Q* is preferred for routine analysis because of its low organic carbon and nitrogen content and lower risk of biological degradation and contamination (seawater must be previously filtered and decarbonated). In 1994, the coefficient of variation for the slopes of the five-point calibration curves was around 15%. Fluctuations of this order were a likely function of gas flow variation induced by “salting” of the catalyst column. However, this phenomenon does not compromise the determination of DOC concentration for a particular day. Throughout the surveys, the five-point calibration curves were characterised by correlation coefficients ( $r^2$ ) greater than 0.99, and the analyses of standards and samples were all performed closely in time. During 1995, calibration curves were similarly defined by correlation coefficients greater than 0.99, and the coefficient of variation for the slopes of the five-point calibration curves was less than 2%.

### 3. Water masses in OMEX area

The water masses of the northeast Atlantic have been well described on the basis of temperature, salinity and nutrient information (e.g., Tsuchiya et al., 1992; Schmitz and McCartney, 1993; Perez et al., 1993). For the “Goban Spur Box”, the temperature, salinity and nutrient relationships from cruise to cruise appear to show that the water masses below the seasonal thermocline were essentially in a steady state through the period of the OMEX cruises. Above the seasonal thermocline, analysis of the data also suggests that processes in this region are uniform on a scale that makes quantitative assessment possible. Of hydrographic interest is the extent of Labrador Sea Water (LSW) in the OMEX box. LSW is formed by winter convection in the Labrador Sea. It is characterised by low salinity and a high concentration of dissolved oxygen. It is advected through the North Atlantic at depths between 500 and 2000 m, occurring as far south as 40°N in the northeast Atlantic (Talley and McCartney, 1982). The extent of LSW is thought to vary with the intensity of the North Atlantic Oscillation (Paillet et al., 1998; Koltermann et al., 1999). In the OMEX data it is characterised by a minimum salinity (34.93) and higher oxygen concentrations between 1800 and 2000-m depth (Osborne et al., 1997). This water mass was present during all cruises from January 1994 to September 1995. The oxygen measurements indicate that a smaller fraction of LSW is present at La Chapelle Bank than at the Goban Spur. This appears to confirm the suggestion of Tsuchiya et al. (1992) that one limit of the extent of LSW is a line between the Azores and Biscay.

Above LSW in the northeast Atlantic two water masses dominate. These are Sub Arctic Intermediate Water (SAIW) (Arhan, 1990) and Mediterranean Sea Water (MSW). MSW is the dominant water at these depths in the OMEX area (Harvey, 1982), present at depths of around 1000 m. It is detectable as water with salinities approaching 35.7, temperatures close to 9°C, and relatively low oxygen concentrations (Osborne et al., 1997). For OMEX, the most significant water masses are the surface waters with the potential to exchange across the shelf break. The “Mode” water above the MSW is more variable between stations than the deeper water masses. In

the North Atlantic waters, the top 600 m of the water column tend to be characterised by relatively high temperature and high salinity. Two water masses have been described: Sub Polar Mode Waters (SPMW, McCartney and Talley, 1982) and the Eastern North Atlantic Water (ENAW, Pollard et al., 1996). ENAW is formed by deep winter mixing in the Bay of Biscay. It contributes to the water in the slope current that flows along the continental slope from the Bay of Biscay to the Norwegian Sea (Pingree and Le Cann, 1990; Ellett, 1995). In the water column below 300-m depth, concentrations of nutrients and oxygen were similar on all cruises. In the upper 300 m of the water column, concentrations were altered from cruise to cruise by a cycle of processes associated with deep winter mixing followed by seasonal biological production, respiration and regeneration.

## 4. Results and discussion

### 4.1. Inorganic nutrient distributions in the region of the Celtic Sea shelf break

In Table 2, results are summarised for determinations of nutrients in the upper 25 m of the water column for all OMEX cruises that were sampled in the Goban Spur box. The variation in concentration with time of year (Fig. 4) suggests that the OMEX cruises returned a data set that presents an internally consistent picture of variations in concentrations. During the two winter cruises (*M27/1* and *CD84*) the temperature and salinity data suggest that the base of the deep winter mixed layer was at 300 m in the Goban Spur Box. Concentrations of nitrate were well

Table 2

Summary of results for determinations of nutrients in the upper 25 m of the water column for all OMEX cruises that were sampled in the Goban Spur box

Cruise	<i>M27/1</i>	<i>CD 85</i>	<i>CD 86</i>	<i>CD 94</i>	<i>VLD 317</i>	<i>D 216</i>	<i>PLG 95B</i>	<i>M 30/1</i>	<i>BG 9322A</i>	<i>D 217</i>	<i>PLG 93</i>	<i>D216 (ULB)</i>
Month	1	4	5	6	7	8/9	9	9	9	9	10	
Nitrate												
Count	6	13	18	19	44	8	9	4	5	44	6	
Mean ( $\mu\text{M}$ )	7.87	7.89	4.87	0.75	0.08	0.22	0.04	0.81	0.18	0.24	1.83	
Stdev	0.32	0.22	0.39	0.62	0.04	0.40	0.02	0.06	0.09	0.17	0.10	
Phosphate												
Count	6	13	18	6	44	8	9	4	5	43	6	15
Mean ( $\mu\text{M}$ )	0.51	0.39	0.31	0.06	0.08	0.02	0.06	0.14	0.03	0.09	0.17	0.03
Stdev	0.05	0.05	0.03	0.04	0.01	0.02	0.01	0.03	0.00	0.03	0.03	0.02
Silicon												
Count	6	4	18	6	44	8	9	4	3	43	6	
Mean ( $\mu\text{M}$ )	2.78	2.78	0.86	0.47	0.48	0.27	0.41	0.60	1.13	0.51	0.87	
Stdev	0.14	0.01	0.25	0.17	0.08	0.11	0.18	0.03	1.12	0.06	0.12	

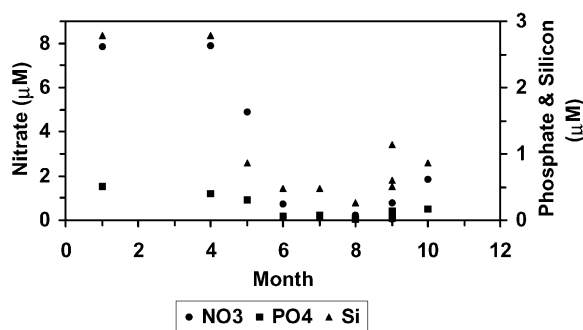


Fig. 4. Variation of concentration of nutrients in top 25 m of water column through out the year in the Goban Spur Box.

mixed down to the bottom of the winter mixed layer. The observations made on *M27/1* show a consistent value of  $7.9 \pm 0.3 \mu\text{M}$  ( $n = 19$ ) at the five Goban Spur stations sampled. On cruise *CD84*, similar results for nitrate were obtained in the deep winter mixed layer at a depth between 47 and 300 m. The mean concentration was  $8.5 \pm 0.5 \mu\text{M}$  ( $n = 13$ ). At the stations sampled along the shelf break during cruise *CD84* between Goban Spur and La Chapelle Bank concentrations ranged from 6.5 to 8.5  $\mu\text{M}$ . In April 1994, in early spring, during cruise *CD85*, concentrations of nutrients in the mixed layer were the same as for the winter cruises ( $8.0 \pm 0.7 \mu\text{M}$ ,  $n = 31$ ). This suggests that the depth of deep winter mixing did not increase after the end of cruise *M27/1*. There is no evidence that the cooling of surface waters after that time of cruise *M27/1* induced an increase in the mixed layer depth. Cruise *CD86* (May/June 1994) coincided with the onset of spring primary production. The limited number of samples collected show that the concentrations of nitrate were reduced to 4.8  $\mu\text{M}$  and a nutricline was developing at a 50-m water depth. In summer and autumn, the concentrations of nitrate were close to zero (less than 0.05  $\mu\text{M}$ ) within the upper 50 m of the water column. Compared to the winter situation higher concentrations were found in summer and autumn at 100 to 300-m depth. At 200-m depth, concentrations of nitrate were 3  $\mu\text{M}$  higher in summer than in winter. Below the depth of the deep winter mixed layer concentrations increase rapidly to about 17  $\mu\text{M}$  at 1000-m depth.

In January 1994, the concentration of phosphate in surface waters was  $0.5 \pm 0.1 \mu\text{M}$ . Concentrations of phosphate fell to less than 0.1  $\mu\text{M}$  in water above the nutricline in summer and autumn. As with the concentrations of nitrate, an increase in comparison to the winter values was observed between 100 and 300 m. At 200-m depth, concentrations were 0.15  $\mu\text{M}$  higher in summer than winter. Concentrations of phosphate increased with the depth, reaching 1.6  $\mu\text{M}$  in the deepest samples below 4000 m. At a depth above 1000 m, the ratio of concentrations of nitrate to phosphate (N:P) is approximately 16 and decreases to less than 15 with increasing depth down through the LSW. At deeper below LSW in the North Atlantic Deep Water, the ratio remains constant. Similar changes in the N:P ratio have been reported by Perez et al. (1993).

The winter concentration of silicate in surface waters was  $2.8 \pm 0.2 \mu\text{M}$ . In summer (*D216* and *D217*) the concentrations ranged from 0.1 to 0.5  $\mu\text{M}$ . The gradient of the summer nutricline was less sharp than that observed in changes of concentration of nitrate and phosphate—an enrichment from 3 to 4  $\mu\text{M}$  was observed at 200 m.

#### 4.2. Dissolved organic carbon, nitrogen and phosphorus

For samples collected below a depth of 1000 m the measurements of DOC by UH plot are over  $50\ \mu\text{M}$  higher than both the UB and PML measurements in samples from similar depths. The cause for this discrepancy remains unresolved—possibly the result of an error in blank correction—and therefore we do not discuss the UH-DOC measurements further. The UB and PML measurements of DOC on all the four cruises are plotted in Fig. 5. The mean and standard deviation concentrations of DOC in samples collected in the winter mixed layer (Table 3) are internally consistent between the two laboratories—showing little seasonal variation at the respective sampling locations between winter and spring (PML) and between winter and summer (UB) for the mean water column distributions. In order to distinguish the broadest seasonal signal in the productive upper water column, a subset of data (UB, upper 300 m) is plotted in Fig. 6. These data suggest an enrichment of DOC, in the order of  $7\ \mu\text{M-C}$ , above the seasonal thermocline at the end of summer (September 1994, *M30/I*) relative to the winter values (January 1994, *M27/I*). The corresponding difference in the concentration of nitrate is a decrease of  $7.0 \pm 0.4\ \mu\text{M-N}$ .

Measurements of total dissolved nitrogen and phosphorus were made on samples collected from five cruises in the Goban Spur Box by the UH group (*VLD137*, *M27/I*, *M30/I*, *CD94* and *D217*). Nitrogen and phosphorus were determined in these samples by a chemical oxidation with peroxodisulphate in an autoclave followed by the determination of the inorganic nitrogen and phosphorus produced using autoanalyser based methods (Eberlein and Kattner, 1987). On cruise *CD94*, tests of a new method for the determination of total nitrogen based on HTCO technology (Alvarez-Salgado and Miller, 1998) was tested. The total dissolved nitrogen was determined in nine samples by both methods. The results and a regression analysis shown in (Fig. 7) suggest that there was no significant difference between the results of the two procedures.

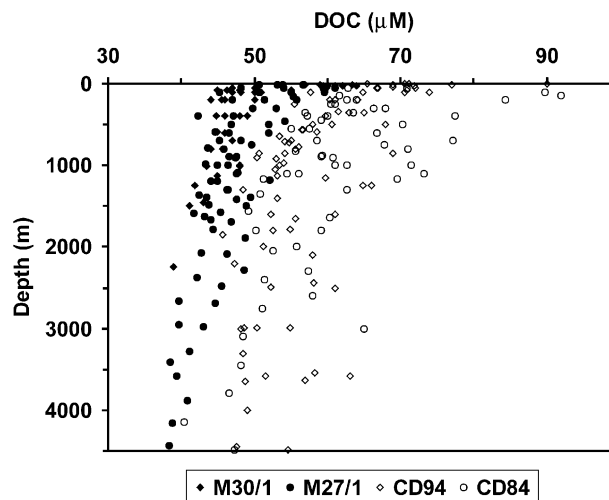


Fig. 5. Data for DOC determined by UB for cruises *M27/I*, *M30/I*, and by PML for cruises *CD84*, *CD94* with HTCO methods.

Table 3

Statistics for measurements of DOC  $\mu\text{M}$ . Winter values (*M27/1*, *CD84*) compared to spring (*CD94*) and summer (*M30/1*) values

	<i>M27/1</i> (300 m)	<i>M30/1</i> (300 m)	<i>M30/1</i> (50 m)	<i>M30/1</i> (50–300 m)
Count	17	25	9	16
Mean	52.87	53.55	58.27	50.90
Stdev	4.04	6.79	5.75	5.95
	<i>CD84</i> (300 m)	<i>CD94</i> (300 m)		
Count	14	20		
Mean	68.90	68.41		
Stdev	11.29	7.49		

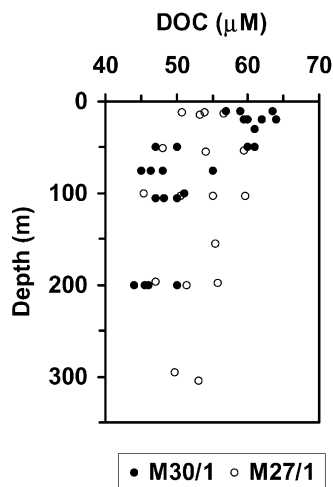


Fig. 6. Data for DOC for the top 300 m of the water column determined by UB on samples collected on cruises *M27/1* and *M30/1*.

For samples from the *M27/1* cruise, the UH group determined the total dissolved and inorganic nitrogen and phosphorus in 19 samples through the deep winter mixed layer down to a depth of 300 m. These results are summarised in Table 4. DON is 39% of the total dissolved nitrogen pool in winter. Comparing the results for DOC and DON (shown in Tables 3 and 4) suggests that in winter the dissolved organic matter in this region has a C/N ratio of 9.7 (on the basis of UB, DOC data), about one and a half times the Redfield ratio. Both DON and DOP are determined as the difference between a measurement of the total nutrient present after oxidation and the amount of inorganic nutrient. When the organic fraction is small compared to the inorganic fraction errors in the two measurements it can give rise to negative estimates of the dissolved organic fraction (Table 4). DOP was not detectable ( $-0.02 \pm 0.05 \mu\text{M}$ ) in surface waters sampled on cruise *M27/1*. Assuming that the concentrations of DOP greater than twice the standard deviation of the method ( $0.05 \mu\text{M}$ ) would have been detected, the winter ratio of DON : DOP present in the DOM pool must have been greater than 50.

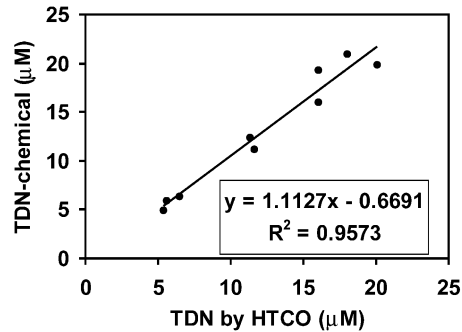


Fig. 7. Plot of data for determinations of dissolved organic nitrogen (DON) obtained by a new HTCO method compared to from a standard chemical oxidation method on portions of the same samples collected on cruise *CD94*.

Table 4

Aggregated results for determinations of dissolved nitrogen and phosphorus compounds in the winter mixed layer (0–300 m) during cruise *M27/1* (19 samples)

	Depth (m)	TDN (μM)	NH <sub>4</sub> (μM)	NO <sub>3</sub> + NO <sub>2</sub> (μM)	DON (μM)	TDP (μM)	PO <sub>4</sub> (μM)	DOP (μM)
Mean	87.52	13.99	0.64	7.91	5.44	0.48	0.50	– 0.02
Stdev		1.13	0.15	0.28	1.10	0.03	0.04	0.05
%TDN			5	57	39			

The aggregated data for the samples collected in the seasonal thermocline above 25-m depth are shown in Table 5. Through the year, concentrations of dissolved inorganic nitrogen change by a factor of about 20 fold. Concentrations of total dissolved nitrogen change only by a factor of 2. An annual cycle in DON concentrations begins and ends with deep winter mixing, creating a uniform concentration in the top few hundred meters of the water column. In the intervening period, the concentration of total DON or the molecular composition of the DON will be changed by processes, that may include: (i) an increase in DON during the spring bloom due to a leakage of DON from plankton production, (ii) inputs due to the degradation of planktonic detritus, (iii) losses due to the bacterially mediated conversion of DON to dissolved inorganic nitrogen compounds– (DIN), and (iv) diffusive losses across the nutricline when the concentration in the surface layer is greater than that in subsurface waters. After the spring bloom, during cruise *CD94*, concentrations of DIN are low, with little change in the concentration of DON, relative to the winter results. The change in the concentration of DOC between winter and late summer (cruises *M27/1* and *M30/1*) was 7 μM. The C:N ratio estimated above was 9.7. If the C:N ratio had remained constant through the year, this would suggest that the increase in DON between *M27/1* and *M30/1* should have been about 0.7 μM. Such a change is of a similar magnitude to the errors in the data shown in Table 5. A change in the concentration of DON is not detectable within the OMEX data set. Similarly, the fraction of phosphorus in the DOM pool remains insignificant throughout the year.

Table 5

Aggregated results for determinations of dissolved nitrogen and phosphorus compounds in the top 25 m of the water column. Results for cruise *D217* sampled in Oct. 1995 are plotted before the results for cruise *M30/1* (Sept. 1994), as the condition in autumn 1995 were exceptionally calm so that the results from cruise *D217* represent earlier conditions in a “normal year” than do the results from *M30/1*. DON is shown as a percentage of the total dissolved nitrogen (TDN) for each cruise and as a percentage of the TDN in winter DON% (W N) (cruise *M27/1* data). (Concentrations in  $\mu\text{M}$ )

	Month		NH <sub>4</sub>	NO <sub>3</sub>	TDN	DON	DON (% TDN)	DON (%W N)	TDP	PO <sub>4</sub>	DOP
<i>M27/1</i> <i>n</i> = 6	Jan-94	mean	0.7	7.9	13.8	5.2	38	38	0.5	0.5	0
		stdev	0.18	0.32	0.67	0.73			0.04	0.05	0.06
<i>CD94</i> <i>n</i> = 3	Jun-95	mean	0.7	1.2	7	5.1	73	37	0.2	0.3	0.1
		stdev	0.08	1.15	1.96	0.81			0.06	0.04	0.08
<i>VLD137</i> <i>n</i> = 40	Jul-93	mean	0.6	0.1	11.1	10.4	94	75	0.2	0.1	0.1
		stdev	0.07	0.04	5.01	5.01			0.05	0.01	0.05
<i>D217</i> <i>n</i> = 27	Oct-95	mean	0.2	0.2	6.9	6.5	94	47	0.1	0.2	0.2
		stdev	0.12	0.18	2.39	2.37			0.03	0.22	0.22
<i>M30/1</i> <i>n</i> = 5	Sep-94	mean	0.7	1.7	6.9	4.6	67	33	0.2	0.2	0.1
		stdev	0.02	1.92	2.19	0.68			0.1	0.08	0.07

#### 4.3. Changes in nutrient distributions resulting from biological production

The observed winter concentrations can be used to set a maximum limit on the new production that can occur during the spring bloom. An inspection of the OMEX hydrographic data sets suggests that the depth of the seasonal thermocline formed at the time of the spring bloom ranged from 40 to 60 m. As noted above, along the shelf break between the Goban Spur and La Chapelle Bank winter concentrations of nitrate ranged between 6.5 and 8.5  $\mu\text{M}$  (*CD84*). Therefore, at a Redfield C:N ratio of 106:16, the N-limited organic carbon production during the spring bloom might have ranged from 23  $\text{gC m}^{-2}$  in regions of lower nitrate with a shallower thermocline to 41  $\text{gC m}^{-2}$  in regions of high nitrate with a deeper thermocline. At a N:Si ratio of 1.0, the likely total of diatom production would have been between 6.7 and 10.1  $\text{g opal (SiO}_2\text{) m}^{-2}$  assuming that complete utilisation of 2.8  $\mu\text{M}$  silicon had occurred. That actual diatom production is likely to be lower than this, is indicated by the presence of a residual concentration of silicon through out spring and summer (Table 2). The relatively low concentrations of silicon present in these waters may effectively limit the uptake of silicon. The initial nitrate concentration is above the half-saturation constant for nitrate uptake (1.28  $\mu\text{M}$ ; Tett and Droop, 1988). The observed silicon concentrations are of similar magnitude to the limited number of available measurements of the saturation rate constant for silicon uptake (Paasche, 1973; Goerring et al., 1973), hence the uptake of silicon will not be as complete as that of nitrate. This suggests that the significant levels of dissolved silicon detected during the summer cruises may be residual rather than regenerated silicon. If this is the case then the initial spring bloom utilised only about 2.3  $\mu\text{M-Si}$ . This is equivalent to a production of 6.9  $\text{g opal m}^{-2}$  in the surface layer 50-m deep.

Table 6

Aggregated results for determinations of particulate carbon (determined before and after the digestion of carbonate carbon with acid) nitrogen, phosphorus and silicon in the top 50 m of the water column, in the Goban Spur Box (number of samples in brackets).

Cruise	Date	PC (acid.) ( $\mu\text{M}$ )	PC (unacid.) ( $\mu\text{M}$ )	PN ( $\mu\text{M}$ )	PP ( $\mu\text{M}$ )	PSi ( $\mu\text{M}$ )
<i>M27/1</i>	Jan-94		5 (3)	0.0 (2)	0.02 (7)	
<i>CD85</i>	Apr-94	8 (9)				0.7 (9)
<i>CD94</i>	Jun-95		16 (6)	2.0 (6)	0.09 (6)	
<i>VLD317</i>	Jul-93		12 (67)	1.7 (67)	0.09 (32)	
<i>BG9322A</i>	Sep-93	7 (6)		0.9 (6)		
<i>M30/1</i>	Sep-94		5 (7)	0.8 (7)	0.04 (7)	
<i>D217</i>	Oct-95	3 (3)	8 (45)	0.9 (45)	0.05 (27)	

The aggregated results for determinations of particulate carbon (determined before and after digestion of carbonate-carbon with acid), nitrogen, phosphorus and silicon in the top 50 m of the water column in the Goban Spur Box are listed in Table 6. The results in this table are consistent with the measurements of chlorophyll in cruises following the spring bloom, which suggest that little of the material formed by primary production is retained in the surface layer after the bloom. Antia et al. (2001) have estimated the quantity of material exported from the surface layer and collected in the OMEX sediment traps. About  $1.5 \text{ g opal m}^{-2} \text{ a}^{-1}$  reaches the sediment trap at 600 m. The biogenic siliceous material reaching the traps is dominated by diatom remains. The time series data from the sediment traps show that it tends to reach the traps in a single pulse following the spring bloom. Approximately  $5.4 \text{ g opal m}^{-2}$  return to solution between the nutricline at 50-m depth and the sediment trap at 600 m. A comparison of the winter and summer profiles for dissolved silicon (Fig. 8) suggests that they become coincident at the depth of the deep winter mixed layer 300 m. Above this depth and below the nutricline, summer concentrations of nutrients are higher than in winter. The regeneration of the biological detritus sinking from the surface layer into solution is detectable in these profiles. A simple integration based on the average concentrations in 50-m depth boxes of the summer (*D216* and *D217*) compared to the winter (*M27/1*) data suggests a dissolution of  $9 \pm 3 \text{ g opal m}^{-2}$ . Given the uncertainty in both the estimates, the pattern of change in water column concentrations is consistent with the change in surface layer concentrations and the load reaching the sediment trap.

Plankton blooms tend to be transient features. Their immediate product—plankton biomass—is notoriously difficult to observe on oceanographic cruises. It may (i) be grazed by zooplankton, (ii) coalesce and sink rapidly to the sea bed (Billett et al., 1983), or (iii) be dispersed horizontally. However, in an area that had a uniform concentration of nitrate before the start of a bloom, an inverse relationship between the concentrations of nitrate and chlorophyll would be expected to develop if nitrate uptake is fast relative to loss of bio-mass due to sinking and grazing. Within the Goban Spur Box the concentration of nitrate remained relatively constant from January (cruises *M27/1* and *CD84*) to April 1994 (cruise *CD85*) at a concentration of  $8 \mu\text{M}$ . At the same time the average chlorophyll concentration in the top 50 m of the water column was  $0.4 \mu\text{g l}^{-1}$ . Inspection of the data suggests that in 1994 two OMEX cruises sampled while the

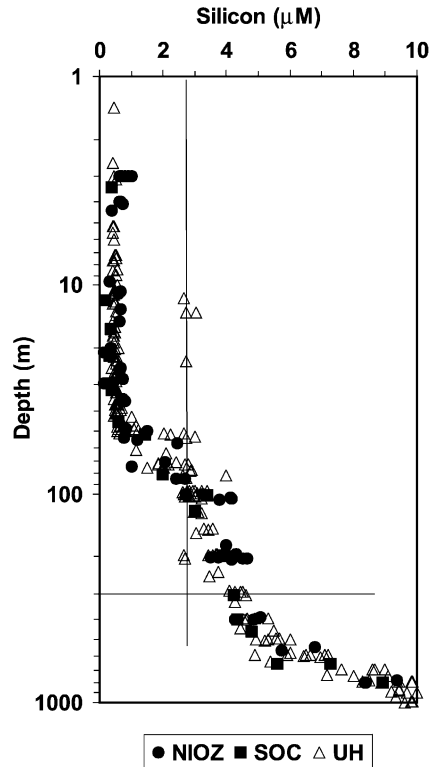


Fig. 8. Dissolved silicon data plotted against  $\log_{10}$  depth. Guidelines are drawn at the depth of deep winter mixing 300 m and at the concentration of the winter deep mixed layer  $2.8 \mu\text{M-Si}$ .

spring bloom was in progress (*CD85*, *BG9412*). The highest chlorophyll levels (approx.  $12 \mu\text{g l}^{-1}$ ) reported in the OMEX data set were observed in underway samples collected during cruise *BG9412*, along the 200-m depth contour of the shelf break. Nitrate measurements were not being made at the time the highest reported chlorophyll values were detected. Measurements of both chlorophyll and nitrate were made on the 24 and 25 April 1994 when the ship was between  $47$  and  $49^\circ\text{N}$ . These data are plotted in Fig. 9. Cruise *CD85* worked stations on a line from approximately  $13.3^\circ\text{W}$  extending to  $10.9^\circ\text{W}$  to the east of the Goban Spur Box. A high concentration of  $3.1 \mu\text{g l}^{-1}$  of chlorophyll was detected at  $11.4^\circ\text{W}$  on 1 May 1994. The concentration of nitrate in this sample was  $6.2 \mu\text{M}$ . Data for the concentrations of nitrate and chlorophyll in the top 50 m of the water column during cruise *CD85* show a similar trend to the data plotted in Fig. 9. Both sets of data show an inverse relationship between nitrate and chlorophyll concentrations, with the bulk of points plotted close to or below a line consistent with a conversion factor of  $1 \mu\text{M}$  of nitrate to  $1 \mu\text{g l}^{-1}$  of chlorophyll. Points below the line correspond to less chlorophyll in the sample than predicted by the apparent decrease in the concentration of nitrate. This may be explained by loss of material by diffusion along the concentration gradients in a patchy bloom, or grazing, or sinking of the organisms. The variations on short time and space scales in the data from cruise *BG9412* suggest that a rapid sinking of the bloom (cf Billett et al., 1983) is more likely

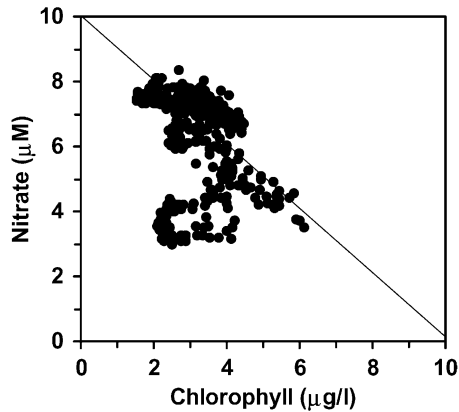


Fig. 9. The data for chlorophyll and nitrate in surface water samples collected underway during cruise *BG9412* on 24/25 April 1994 at shelf break between 47 and 49°N. Guideline indicates 1:1 conversion of nitrate to chlorophyll.

to occur than grazing. Points higher than the line may reflect different nitrate-to-chlorophyll conversion factors. This conversion factor will vary with the mix of plankton species in the bloom and the state of development of the bloom. It is interesting to note that the conversion factor of  $1 \mu\text{M}$  of nitrate to  $1 \mu\text{g l}^{-1}$  of chlorophyll may be a common one for the European shelf. Aminot et al. (1998) proposed this conversion ratio after analysing detailed observation from boats in the Baie de Seine. Tett et al. (1993) estimated the same ratio from observations in the southern North Sea when the peak of a bloom was measured by a calibrated fluorometer on a moored instrument array.

#### 4.4. Shelf break exchange

The state of knowledge of the volumes of water, which exchange across the northwest European shelf break and the continuity, with which the process occurs, is poor (Huthnance, 1995). Flows at the shelf edge are predominantly along the slope rather than across it. This makes it difficult to measure the relatively small amount of cross-shelf-break transport (Huthnance, 1997). Existing estimates of exchange have been made on the basis of the salt balance (Otto et al., 1990). Recently Burrows and Thorpe (1999) and Burrows et al. (1999) have established by tracking floats that exchange tends to be limited to those areas of the shelf break where the bottom topography of the shelf slope is less steep. Their float releases were to the north of the OMEX area 56.25°N on the Hebridean shelf slope, so they do not provide direct evidence about exchange in the Goban Spur region but suggest that it would be small. The tracking of floats on the shelf in the Celtic Sea suggests that the residence time of water is of the order of a year, again suggesting that there are no large flows of water across the shelf which flush the Celtic Sea rapidly (Pingree et al., 1999).

The OMEX cruises that took place in winter (*M27/1* and *CD84*) provide nutrient data that gives first-hand evidence that the severe winter of January 1994 did not lead directly to the large scale transport of water across the shelf break. Cruise *M27/1* in particular was badly affected by severe storms. The sampling that was possible during *M27/1* was restricted to five stations along a line from 13.7 to 11.2°W where the water depth was 300 m. At all stations along this line the water

was mixed at 300 m, and the concentration of nutrients in the surface layer was uniform. During cruise *CD84*, samples were collected from a wider area over-lapping with the *M27/1* sampling. Samples were collected both from CTD rosette bottles and using a pumped water supply while underway. These samples were collected along the shelf break from La Chapelle Bank (47.5°N, 7°W) to the Goban Spur (49.5°N, 12°W) and then across the Celtic Sea to 51.2°N, 5°W, on the way back to the port (Fig. 1). The temperature and salinity of the underway samples (Fig. 10) show a mixing relationship, made of three identifiable areas. Most of the oceanic samples are plotted on the right-hand side of the graph (group C). There is a small change in the slope of the lines of groups C and B about a salinity of 35.4, which corresponds to the start of sampling in water depths shallower than 200 m, at about 10°W. The slope of the line changes significantly below a salinity of 35.2. The last five samples collected (group A) form a distinct mixing series clearly influenced by the dispersion of freshwater from the Bristol Channel. In comparison to the measurements made during cruise *M27/1* in the small area of the Goban Spur Box, where the waters of the deep winter layer are uniform in concentrations, the data in Fig. 10 show that over the wider area from the Goban Spur to La Chapelle Bank, the waters are not well mixed. In Fig. 11, the data of the concentration of nitrate in the underway samples are plotted against the salinity data. Ninety-nine of the 126 underway samples, in which nitrate was determined, have salinities greater than 35.52. All but four of these samples plot as a well-defined group (A) in Fig. 11. In Fig. 12, the relationship between nitrate and temperature in these higher salinity surface samples is plotted in comparison to the results from the water bottle samples collected from the mixed layer at all the sites sampled during cruise *CD84*. Both sets of data display a similar relationship between the temperature and concentration of nitrate. This suggests that variations seen in the surface waters are probably related to a variation in the depth of mixing along the shelf break. The similarity of the values suggests that no major modification of the surface temperature by cooling or reduction in nitrate concentration by winter production (Joint et al., 2001) had occurred since mixing took place. The data in Figs. 11 and 12 indicate the variability in the extent of deep winter mixing at the shelf break in January 1994.

In Fig. 11, a discontinuity in the composition of the sampled water is evident between samples collected off shelf and in waters shallower than 200 m. Waters across the Celtic Sea (mixing line B)

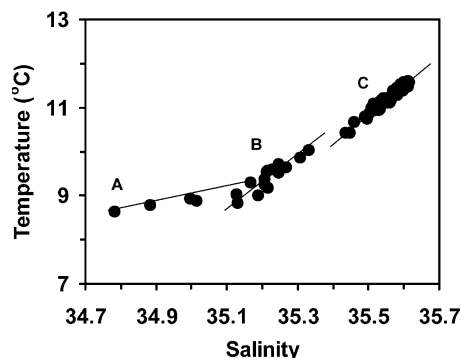


Fig. 10. Underway data from cruise *CD84*, for temperature and salinity. Lines are sketched on the plot to indicate the 3 mixing series that appear to be identifiable in the data set: (A) river influenced data close to the Bristol Channel; (B) mixing on the open shelf; (C) mixing at the shelf break.

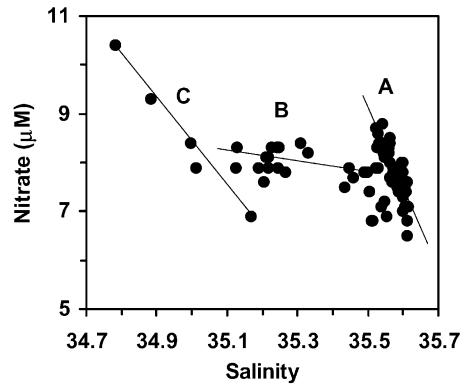


Fig. 11. Underway data from cruise *CD84*, for nitrate and salinity, corresponding to the data in Fig. 10.

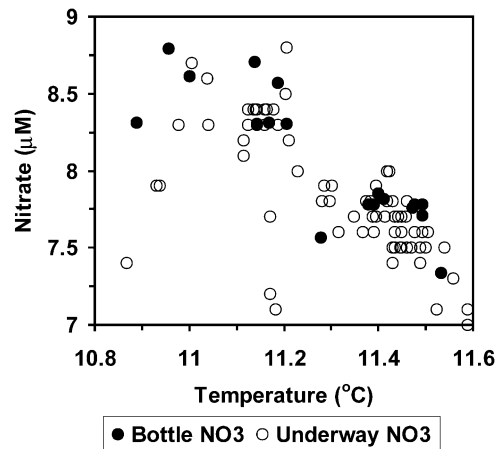


Fig. 12. Data from cruise *CD84* a comparison of results of measurements of temperature and salinity in underway samples and in bottle samples collected in the top 50 m of the water column.

contain a relatively uniform concentration of nitrate with respect to the changes with salinity demonstrated in the groups of data A and C. The steeper gradients (A and C) are the result of mixing processes taking place over relatively small scales—vertical mixing off shelf in group A and horizontal dispersion of river water in group C. The discontinuity in the nitrate salinity plot at low salinities is explicable in terms of the finite amount of time required in winter for the input of nitrate from rivers to disperse out into waters that were depleted in nitrate by biological production, burial, transport of detrital material and denitrification during spring and summer (Hydes et al., 1999; Le Gall et al., 2000). Similarly, the discontinuity between data groups A and B (Fig. 11) indicates the limited degree of penetration of the winter deep mixed waters across shelf

break once they have formed. The nitrate data reveal this shelf break front more clearly than do the temperature and salinity data. It confirms the impression again from float tracking studies (Pingree et al., 1999; Burrows and Thorpe, 1999) that the exchange of surface waters in the Goban Spur region is limited. The residence time of waters in shelf seas is sufficiently long that there is no direct export of dissolved nitrogen to the ocean in this region. The discontinuity in the distribution of nitrate is consistent with extensive removal of nitrate-nitrogen from the system predicted for this region by Seitzinger and Giblin (1996). Hydes et al. (1999) estimated that if the bulk of the transport of water across the shelf break does take place in winter at the winter concentration of nitrate of  $8 \mu\text{M}$  determined during the OMEX cruises, a flow averaged over a year of  $0.6 \text{ Sv}$  ( $1 \text{ Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$ ) would balance the estimated loss of nitrate-nitrogen calculated by Seitzinger and Giblin (1996). The comparable estimate from salt budgets is  $1.7 \text{ Sv}$  (Otto et al., 1990).

### Acknowledgements

This work was partly supported by the EU through the MAST programme, contract MAS3-CT96-0056 (Ocean Margin EXchange—OMEX). John Huthnance is thanked for his help with an earlier version of this manuscript.

### Appendix

OMEX associated cruises (see Table 7) and atlas contents (see Table 8).

Table 7

List of OMEX associated cruises, from which data has been examined in the preparation of this paper

PSO	Country	Began	Ended	Area	Ship	Cruise
Wollast	B	4/19/93	5/6/93	2°E–11°W 42–52°N	RV <i>Belgica</i>	BG9309
Raabe	D	6/23/93	7/16/93	5–15°W 45–50°N	FS <i>Valdivia</i>	VLD137
Wollast	B	9/21/93	9/29/93	5–15°W 45–50°N	RV <i>Belgica</i>	BG9322A
Wollast	B	10/3/93	10/6/93	5–15°W 45–50°N	RV <i>Belgica</i>	BG9322B
Helder	N	10/11/93	10/31/93	5–15°W 45–50°N	RV <i>Pelagia</i>	PLG93
Balzer	D	12/29/93	1/17/94	5–15°W 45–50°N	FS <i>Meteor</i>	M27/1
Statham	UK	1/18/94	2/2/94	5–15°W 45–50°N	RRS <i>Charles Darwin</i>	CD84
Pugh	UK	4/11/94	5/7/94	5–15°W 45–50°N	RRS <i>Charles Darwin</i>	CD85
Wollast	B	4/20/94	5/5/94	5–15°W 45–50°N	RV <i>Belgica</i>	BG9412
Van Weering	N	5/18/94	6/13/94	5–15°W 45–50°N	RRS <i>Charles Darwin</i>	CD86
Pfannkuche	D	9/6/94	9/20/94	11–16°W 38–50°N	FS <i>Meteor</i>	M30/1
Wollast	B	3/3/95	3/17/95	5–15°W 45–50°N	RV <i>Belgica</i>	BG9506
Statham	UK	6/3/95	6/20/95	5–15°W 45–50°N	RRS <i>Charles Darwin</i>	CD94
Statham	UK	8/26/95	9/12/95	5–15°W 45–50°N	RRS <i>Discovery</i>	D216
Van Weering	N	9/5/95	9/24/95	5–15°W 45–50°N	RV <i>Pelagia</i>	PLG95B
Frankignoulle	B	9/11/95	9/20/95	5–15°W 45–50°N	RV <i>Belgica</i>	BG9521
Lampitt	UK	9/27/95	10/22/95	5–15°W 45–50°N	RRS <i>Discovery</i>	D217

Table 8  
Maps and plots in OMEX Hydrographic Atlas (Osborne et al., 1997)

Individual cruise maps			
Cruise	Vessel	Month/Year	Graphs available
VLD137	<i>Valdivia</i>	Jun/Jul 93	N PO4 DOxy Si4 Temp Salin
BG93/22A	<i>Belgica</i>	Sep 93	N PO4 DOxy Si4 Osat Temp Salin
PLG93	<i>Pelagia</i>	Oct 93	N PO4 DOxy Si4 Osat Temp Salin Chl
M27/1	<i>Meteor</i>	Jan 94	N PO4 DOxy Si4 Temp Salin
CD84	<i>Charles Darwin</i>	Jan 94	N DOxy Sat Temp Salin
CD86	<i>Charles Darwin</i>	May/June 94	N PO4 DOxy Si4 OSat Temp Salin Chl
M30/1	<i>Meteor</i>	Sep 94	N PO4 DOxy Si4 Temp Salin Chl
CD94	<i>Charles Darwin</i>	Jun 95	N PO4 DOxy Si4
DI216	<i>Discovery</i>	Aug/Sep 95	N PO4 DOxy Si4 OSat Temp Salin Chl
DI217	<i>Discovery</i>	Oct 95	N PO4 DOxy Si4 Temp Salin Chl
Time series			
Site	Area		Graphs available
OMEX2	49.2°N 12.8°W		N PO4 DOxy Si4 Temp Salin
OMEX8	48.9°N 13.7°W		N DOxy
Belgica	47.5°N 7.3°W		N PO4 DOxy Temp Salin
Difference Plots			
Site	Area		Graphs available
Goban Spur	13.8°–11.2°W		N Temp

## References

- Alvarez-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 precise shipboard measurements. *Marine Chemistry* 62, 325–334.
- Aminot, A., Guillaud, J-F., Andrieux-Loyer, F., Kerouel, R., Cann, P., 1998. Apports de nutriments et développement phytoplanctonique en baie de Seine. *Oceanologica Acta*. 21, 923–935.
- Anderson, T.R., Williams, P.J.LeB., 1998. Modelling the seasonal cycle of dissolved organic carbon at station E in the English Channel. *Estuarine and Coastal Shelf Science*. 46, 93–109.
- Antia, A.N., Maaßen, J., Herman, P., Voß, M., Scholten, J., Groom, S., Miller, P., 2001. Spatial and temporal variability of particle flux at the N.W. European continental margin. *Deep-Sea Research II* 48, 3083–3106.
- Arhan, M., 1990. The north Atlantic current and subarctic intermediate water. *Journal of Marine Research* 48, 109–144.
- Armstrong, F.A.J., Stearns, C.R., Strickland, J.D.H., 1967. The measurement of upwelling and subsequent biological processes by means of the technicon autoanalyser and associated equipment. *Deep-Sea Research II* 14, 381–389.
- Banoub, M.W., Williams, P.J.LeB., 1973. Seasonal changes in the organic forms of carbon, nitrogen and phosphorous in seawater at E1, in the English Channel during 1966. *Journal of the Marine Biological Association of the United Kingdom*, Plymouth 53, 695–703.

- Billett, D.S.M., Lampitt, R.S., Rice, A.L., Mantoura, R.F.C., 1983. Seasonal sedimentation of phytoplankton to the deep-sea benthos. *Nature (London)* 302, 520–522.
- Brockmann, U., Billen, G., Gieskes, W.W.C., 1988. North Sea nutrients and eutrophication. In: Solomons, W., Bayne, B.L., Duursma, E.K., Forster, U. (Eds.), *North Sea Pollution*. Springer, Berlin, pp. 348–389.
- Bronk, D.A., Glibert, P.M., Ward, B.B., 1994. Nitrogen uptake, dissolved organic nitrogen release, and new production. *Science* 265, 1843–1846.
- Burrows, M., Thorpe, S.A., 1999. Drifter observations of the Hebrides slope current and nearby circulation patterns. *Annales Geophysicae* 17, 280–302.
- Burrows, M., Thorpe, S.A., Meldrum, D.T., 1999. Dispersion over the Hebridean and Shetland shelves and slopes. *Continental Shelf Research* 19, 49–55.
- Butler, E.I., Knox, S., Liddicoat, M.I., 1979. The relationship between inorganic and organic nutrients in sea water. *Journal of the Marine Biological Association of United Kingdom*, Plymouth 59, 239–250.
- Cauwet, G., 1994. HCO<sub>3</sub><sup>-</sup> method for dissolved organic carbon analysis in seawater: influence of catalyst on blank estimation. *Marine Chemistry* 47, 55–64.
- Cauwet, G., 1999. Determination of dissolved organic carbon and nitrogen by high temperature combustion. In: Grasshoff, K., Kremling, K., Ehrhardt, E. (Eds.), *Methods of seawater Analysis*. Wiley-VCH, Weinheim, pp. 407–420.
- Eberlein, K., Kattner, G., 1987. Automatic method for the determination of ortho-phosphate and total dissolved phosphorus in the marine environment. *Fresenius Zeitschrift analytische Chemistry* 326, 354–357.
- Ellett, D., 1995. Physical oceanography of the Rockall Trough. *Ocean Challenge* 6, 18–23.
- Elskens, I., Elskens, M., 1989. Handling Voor de Bepaling van Nutrienten in Zeewater Met an Autoanalyser II Systeem. Vrije Universiteit, Brussel, 50p.
- Goerring, J.J., Nelson, D.M., Carter, J.A., 1973. Silicic acid uptake by natural populations of marine phytoplankton. *Deep-Sea Research* 20, 777–789.
- Grasshoff, K., Ehrhardt, M., Kremling, K. (Eds.), 1983. *Methods of Seawater Analysis*, 2nd Edition. Verlag Chemie, Weinheim, 419 p.
- Harvey, J., 1982. Theta-S relationships and water masses in the Eastern North Atlantic. *Deep-Sea Research* 29, 1021–1033.
- Hedges, J.I., Bergamaschi, B.A., Benner, R., 1993. Comparative analyses of DOC and DON in natural waters. *Marine Chemistry* 41, 121–134.
- Huthnance, J.M., 1995. Circulation, exchange and water masses at the ocean margin: the role of physical processes at the shelf edge. *Progress in Oceanography* 35, 353–431.
- Huthnance, J.M., 1997. North Sea interaction with the North Atlantic Ocean. *Deutsche Hydrographische Zeitschrift* 49, 153–162.
- Hydes, D.J., Kelly-Gerreyn, B.A., Le Gall, A.C., Proctor, R., 1999. Supply of nutrients balanced with the demands of biological production and denitrification in a temperate latitude shelf sea - a treatment of the southern North Sea as an extended estuary. *Marine Chemistry* 68, 117–131.
- Joint, I, Wollast, R., Chou, L., Batten, S., Elskens, M., Edwards, E., Hirst, A., Burkill, P., Groom, S., Gibb, S., Miller, A., Hydes, D.J., Dehairs, F., Antia, A., Barlow, R., Rees, A., Pomroy, A., Brockmann, U., Cummings, D., Lampitt, R., Loijens, M., Mantoura, R., Miller, P., Raabe, T., Alvarez-Salgado, X., Stelfox, C., Woolfenden, J., 2001. Pelagic production at the Celtic Sea shelf break. *Deep-Sea Research II* 48, 3049–3081.
- Koltermann, K.P., Sokov, A.V., Tereschenkova, V.P., Dobroliubov, S.A., Lorbacher, K., Sy, A., 1999. Decadal changes in the thermohaline circulation of the North Atlantic. *Deep-Sea Research II* 46, 109–138.
- Le Gall, A.C., Hydes, D.J., Kelly-Gerreyn, B.A., Slinn D.J., 2000. Development of a 2D horizontal biogeochemical model for the Irish Sea DYMONIS. *ICES Journal of Marine Science* 57, 1050–1059.
- Lowry, R.K., Downer, R.M., Loncar, Z., Cramer, R.N., 1997. Ocean Margin EXchange OMEX I data set users' guide. In: *OMEX I Data Set*, CD-ROM electronic publication, British Oceanographic Data Centre, Birkenhead, UK.
- McCartney, M.S., Talley, L.D., 1982. The subpolar mode water of the North Atlantic Ocean. *Journal of Physical Oceanography* 12, 1169–1188.
- Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* 27, 31–36.

- Nelissen, P.H.M., Stefels, J., 1988. Eutrophication in the North Sea. Nederlands Instituut voor Onderzoek der Zee, Report 1988-4, 100p.
- Osborne, L., Hughes, M., Callow, M., Hydes, D.J., Le Gall, A.C., 1997. OMEX hydrographic and nutrient atlas. In: OMEX I Data Set, CD-ROM electronic publication, British Oceanographic Data Centre, Birkenhead, UK.
- Otto, L., Zimmermann, J.T.F., Furnes, G.K., Mork, M., Saetre, R., Becker, G., 1990. Review of physical oceanography of the North Sea. *Netherlands Journal of Sea Research* 26, 161–238.
- Paasche, E., 1973. Silicon and the ecology of marine plankton diatoms. II. Silicate-uptake kinetics in five diatom species. *Marine Biology* 19, 262–269.
- Paillet, J., Arhan, M., McCartney, M.S., 1998. Spreading of Labrador Sea Water in the eastern North Atlantic. *Journal of Geophysical Research C* 103, 10223–10239.
- Perez, F.F., Mourino, C., Fraga, F., Rios, A.F., 1993. Displacement of water masses and remineralisation rates off the Iberian Peninsula by nutrient anomalies. *Journal of Marine Research* 51, 869–892.
- Pingree, R.D., Le Cann, B., 1989. Celtic and Armorican slope and shelf residual currents. *Progress in Oceanography* 23, 303–338.
- Pingree, R.D., Le Cann, B., 1990. Structure, strength and seasonality of the slope currents in the Bay of Biscay region. *Journal of the Marine Biological Association of the United Kingdom*, Plymouth 70, 857–885.
- Pingree, R.D., Sinha, B., Griffiths, C.R., 1999. Seasonality of the European slope current (Goban Spur) and ocean margin exchange. *Continental Shelf Research* 19, 929–975.
- Pollard, R.T., Griffiths, M.J., Cunningham, S.A., Read, J.F., Perez, F.F., Rios, A.F., 1996. Vivaldi 1991—a study of the formation, circulation and ventilation of eastern North Atlantic Central Water. *Progress in Oceanography* 37, 167–192.
- Radach, G., Paetsch, J., Gekeler, J., Herbig, K., 1995. Annual cycles of nutrients and chlorophyll in the North Sea. *Berichte aus dem zentrum für Meeres und Klimaforschung der Universität Hamburg*. No. 20, 172pp.
- Rees, A.P., Owens, N.J.P., Woodward, E.M.S., 1995. Phytoplankton nitrogen assimilation at low nutrient concentrations in the NW Mediterranean Sea. In: Martin, J.-M., Barth, H. (Eds.), *Water Pollution Research Report 32 in EROS 2000*, European Commission, Brussels, pp. 141–148.
- Saunders, P.M., 1986. The accuracy of measurement of salinity, oxygen and temperature in the deep ocean. *Journal of Physical Oceanography* 16, 189–195.
- Schmitz Jr., W.J., McCartney, M.S., 1993. On the North Atlantic circulation. *Reviews of Geophysics* 31, 29–49.
- Seitzinger, S.P., Giblin, A.E., 1996. Estimating denitrification in the North Atlantic continental shelf sediments. *Biogeochemistry* 35, 235–260.
- Sharp, J.H., 1997. Marine dissolved organic carbon: Are the older values correct? *Marine Chemistry* 56, 265–277.
- Sharp, J.H., Benner, R., Bennett, L., Carlson, C.A., Fitzwater, S.E., Peltzer, E.T., Tupas, L.M., 1995. Analyses of dissolved organic carbon in seawater: the JGOFS EqPac methods comparison. *Marine Chemistry* 48, 91–108.
- Sugimura, Y., Suzuki, Y., 1988. A high temperature catalytic oxidation method for the determination of non-volatile dissolved organic carbon in seawater by direct injection of a liquid sample. *Marine Chemistry* 24, 105–131.
- Suzuki, Y., 1993. On the measurement of DOC and DON in seawater. *Marine Chemistry* 41, 287–288.
- Talley, L.D., McCartney, M.S., 1982. Distribution and circulation of Labrador Sea Water. *Journal of Physical Oceanography* 12, 1189–1205.
- Tett, P., Droop, M.R., 1988. Cell quota models and planktonic primary production. In: Wimpenny, J.W.T. (Ed.), *Handbook of Laboratory Model Systems for Microbial Ecosystem*, Vol. 2. CRC Press, Boca Raton, pp. 177–233.
- Tett, P.B., Joint, I.R., Purdie, D.A., Baars, M., Oosterhuis, S.N., Daneri, G., Hannah, F., Mills, D.K., Plummer, D., Pomroy, A.J., Walne, A.W., Whitte, H.J., 1993. Biological consequences of tidal stirring gradients in the North Sea. *Philosophical Transactions of the Royal Society: A* 343, 493–508.
- Tsuchiya, M., Talley, L.D., McCartney, M.S., 1992. An eastern Atlantic section from Iceland southward across the equator. *Deep-Sea Research I* 39, 1885–1917.
- van Weering, T.C.E., Hall, I.R., de Stigter, H.C., McCave, I.N., Thomsen, L., 1998. Recent sediments, sediment accumulation and carbon burial at Goban Spur, NW European continental margin (47–50°N). *Progress in Oceanography* 42, 5–35.
- Walsh, J.J., Rowe, G.T., Iverson, R.L., McRoy, C.P., 1981. Biological export of shelf carbon is a sink of the global CO<sub>2</sub> cycle. *Nature (London)*. 291, 196–201.

- Williams, P.J.LeB., 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. *Marine Chemistry* 51, 17–29.
- WOCE, 1991. WOCE Operations Manual WHP Office Report WHPO 91-1. WHP Office, Woods Hole, MA, USA.
- Wollast, R., 1992. Interactions of carbon and nitrogen cycles in the coastal zone. In: Wollast, R., Mackenzie, F.T., Chou, L. (Eds.), *Interactions of C, N, P and S Biogeochemical Cycles and Global Change*. NATO ASI Series. Springer, Berlin, pp. 195–210.