The carbonic system distribution and fluxes in the NE Atlantic during Spring 1991

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1. INTRODUCTION

The role of the oceans in fixing and sequestering anthropogenic CO₂ emissions is a topical issue (e.g. Takahashi, 1989; Fraga and Pérez, 1990). In order to study the oceanic carbon cycle it is necessary to examine the factors which influence the rate of carbon uptake from the atmosphere, and how carbon is then exported from the upper ocean and then regenerated at depth. The air-sea exchange of carbon has been extensively researched in different areas and seasons to provide information on the importance of the ocean in climate change (Andrié et al., 1986; Oudot et al., 1987; Anderson et al., 1990; Garçon et al., 1989; Murphy et al., 1991). The North Atlantic Ocean has been proposed as a major sink for atmospheric CO₂ (Brewer, 1978; Roos and Gravenhorst, 1984; Takahashi, 1989; Merlivat et al., 1991).

The exchange of carbon between atmosphere and ocean depends on the CO₂ partial pressure (pCO₂) difference and the exchange coefficient (k). The oceanic pCO₂ depends on physical factors such as temperature, and, very importantly, the marine phytoplankton which use CO₂ for growth, lowering the partial pressure. The greatest reduction in pCO₂ occurs during the spring bloom. Watson et al. (1991) related pCO₂ with physical (temperature) and biological (chlorophyll) variables, finding that in the region 47-60°N, 20°W the air-sea flux is strongly modulated by biological activity and is variable on short spatial scales, during the spring of 1989. Modelling studies (e.g. Taylor et al., 1991) have also been used to study the progression of the spring bloom and how it affects pCO₂ in surface waters. Wind speed is the main factor which influences the exchange coefficient, although sea state is also important (Liss and Merlivat, 1986). Its value has been determined using wind tunnel experiments (Broecker et al., 1978; Merlivat and Memery, 1983) and *in situ* in the ocean using the radon method (Peng et al., 1979; Smithie et al., 1985).

If the ocean is to be an effective sink for CO₂, then carbon must be transported away from the surface and sequestered at depth. This transport occurs via the gravitational settling of biogenic debris produced in the photic zone, a process known as the "biological carbon pump" (Takahashi, 1989). The biogenic debris consists of "soft" organic compounds and hard skeletal material. The latter could be calcareous (e.g. Foraminifera) or siliceous (e.g. frustules of diatoms). Most of the soft material regenerates in the upper waters of the oceans, whereas the dissolution of calcareous skeletons takes place predominantly in deeper waters (Takahashi, 1989). Studies of remineralisation of organic matter have been made by means of direct observations of the increase of CO₂ in the water column (Brewer, 1978) or by establishing models to obtain stoichiometric equations between inorganic carbon and nitrate, phosphate and dissolved oxygen (Papaud and Poisson, 1986).

This study aims to investigate the potential of the North Atlantic as a sink for atmospheric CO₂ by examining the carbonic system, using data collected in the spring of 1991 on cruise "Darwin-58". The distribution of pCO₂ and chlorophyll is studied, and the flux of CO₂ between atmosphere and ocean calculated. The remineralisation of organic matter and redissolution of calcareous skeletal matter is examined in vertical sections representative of the study area.

2. MATERIALS AND METHODS

The "Darwin-58" cruise was carried out in the NE Atlantic as part of the UK VIVALDI project which is a component of UK World Ocean Circulation Experiment (WOCE). The cruise track is illustrated in Fig. 1, showing a total of four latitudinal and five meridional sections. Nineteen stations were studied between 48°37.1'N, 9°20.7'W and 39°10.2'N, 26°43.3'W.

At each station a CTD cast with a General Oceanics, 24 by 10 litre bottle rosette, a Chelsea Instruments fluorometer, and a Sea Tech 1 m path transmissometer were deployed. Samples from the water bottles were taken to measure chlorofluorocarbons, oxygen, nutrients (silicate, phosphate and nitrate), salinity, pH, alkalinity and chlorophyll. The methodology is described in Pollard et al. (1991), Smythe-Wright et al (1992, 1993); data can be found in Griffiths et al. (1992).

Discrete samples were taken from the non-toxic supply every 30 minutes to determine pH at approximately hourly intervals, which coincided with the Seasoar at the surface. Chlorophyll was determined using continuous readings from a wet lab fluorometer. The temperature and salinity of non-toxic supply of sea-water was measured by the Seabird thermosalinograph every 30 seconds.

A Metrohm 654 pH meter with a Ross (Orion 8104) combination glass electrode was used to determine pH. The temperature of the samples was measured using a platinum resistance thermometer to correct for the effect of temperature on pH (Pérez and Fraga, 1987a). All of the pH values were corrected to a standard temperature of 15°C.

Alkalinity was measured using a Metrohm E-410 pH meter with a separate glass electrode and a reference electrode connected to an automatic burette and an impulsomat. Potentiometric titrations were carried out with HCl to a final pH of 4.44. The electrodes were standardised using an NBS buffer of pH 7.413 and checked using an NBS buffer of 4.008. This method of determining alkalinity has a precision of 0.1% (Pérez and Fraga, 1987b).

Total inorganic carbon and $p\text{CO}_2$ were calculated from alkalinity and pH using published equations for the oceanic carbon system (Mehrbach et al, 1973; Weiss, 1974). The alkalinity of surface seawater was calculated fitting the specific alkalinity data of casts against pressure ($r^2=0.93$) with 65.4 specific alkalinity at zero metres.

The wind stress was measured on board using a Multimet for mean meteorology located in the main mast.

A zooplankton net was lowered to 100 m immediately after the CTD was brought back on board at each station. Samples were emptied into jars with 10% formalin for identification back on land.

3. RESULTS

3.1 Distributions in vertical sections

Distributions of temperature, salinity, carbonic system parameters and nutrients are shown for two representative sections, along 42°N and 20°W, in Figs. 2 and 3. Examination of the thermohaline structure between the surface and 4000 metres highlights the different water masses in the sampled zone. The surface layer is 100 to 200 metres deep. Below this layer there is Eastern North Atlantic Central Water (ENAW) which extends up to a further 750 metres. Although not obvious from Figs. 2 and 3, ENAW has two components: subtropical and subpolar (Ríos et al, 1992). The most saline water is Mediterranean Water (MW), which is centred mainly at a depth of about 1000 metres, and was observed to spread from the southeast to the northwest, reaching 43°N. The tongue of MW restricts the penetration of ENAW of polar origin (Fig. 3), as was seen by Ríos et al. (1992) in the North Atlantic Ocean. Labrador Sea Water (LW), characterised by salinities lower than 34.9, is located between 1800 and 2000 metres. Its influence is evident in the 42°N section between

28°W and 16°W, and in the 20°W section north of 42°N. Below 2500 metres North Atlantic Deep Water (NADW) occurs, distinguishable by its uniform temperature and salinity.

3.1.1 Regeneration of carbon

The vertical distribution of inorganic carbon with depth throughout the study area is shown in Fig. 4a. This distribution reflects the uptake of CO₂ by phytoplankton for photosynthesis in surface waters and its subsequent regeneration deeper in the water column. Two phases can be distinguished: a rapid increase of ΣCO₂ near the surface tapering to almost no increase below 1000 m, and a second increase, occurring at a slower rate, commencing at approx. 2300 m. To help interpret these observations, ΣCO₂ is plotted against alkalinity (Fig. 4b). When skeletal carbon (CaCO₃) dissolves, alkalinity increases by two equivalents for each mole increase in carbon. On the other hand, when soft tissue remineralises a decrease of one equivalent of alkalinity occurs for each mole of nitrate formed (Ríos et al., 1989). The expected slope of an alkalinity/ΣCO₂ plot is then (Broecker and Peng, 1982):

$$\frac{\Delta A}{\Delta \Sigma \text{CO}_2} = 2 \frac{\Delta C_{\text{org}}}{\Delta C_{\text{CaCO}_3} + \Delta C_{\text{org}}} - \frac{\Delta C_{\text{CaCO}_3}}{R \cdot \Delta C_{\text{CaCO}_3} + \Delta C_{\text{org}}} \quad (1)$$

where A is alkalinity, C_{CaCO₃} is hard (skeletal) carbon, C_{org} is soft tissue carbon, and R is the ratio of carbon to nitrogen in soft tissue. Rearrangement of Eq. 1 permits the fractions of soft and hard material in biogenic material to be predicted:

$$\frac{\Delta C_{\text{CaCO}_3}}{\Delta C_{\text{org}}} = \frac{\Delta A / \Delta \Sigma \text{CO}_2 + 1/R}{2 - \Delta A / \Delta \Sigma \text{CO}_2} \quad (2)$$

Calculated slopes for the A/ΣCO₂ relationships shown in Fig. 4b are 0.141 and 0.952 for data in depth ranges 0-2300 m and >2300 m respectively. Despite the involvement of different water masses and the variation in the composition of organic matter with depth (Tanoue, 1985), we used the classic Redfield C:N ratio of 6.625 (Redfield et al., 1963) to estimate values of the ΔC_{CaCO₃}/ΔC_{org} ratio for the two depth ranges of 0.16 (<2300 m) and 1.05 (>2300 m). In other words, 14% of regenerated carbon in the upper depth range derives from hard skeletal matter, whereas this increases to 51% for the deeper range. The upper ocean is supersaturated with calcium carbonate (Broecker and Peng, 1982), and therefore the regeneration of inorganic carbon is dominated by soft tissue remineralisation. Most soft tissue carbon is remineralised within the top 1000 m of the water column, as shown by plots of pH and nitrate in Figs. 2 and 3. Below about 2300 m calcium carbonate starts to dissolve more readily

(because of the increased pressure and decreased temperature), and the regeneration of carbon is dominated by skeletal dissolution. This is reflected by a marked increase in alkalinity (Figs. 2 and 3).

Silicon is also exported as opaline compounds in biogenic matter (mostly in diatom frustules) and redissolved in the deep ocean. As for carbonate, most opaline silica dissolution occurs below about 2300 m (Figs 2 and 3).

3.1.2 Covariance between CO_2 and nutrients

Here, we develop a model to predict ΣCO_2 from nutrients (nitrate and silicate) in the water column. Because of the regeneration pattern of carbon described above, one would expect good correlations between pH and nitrate, and alkalinity and silicate (Figs. 2 and 3). Once pH and alkalinity have been calculated, then a theoretical value for ΣCO_2 ($\Sigma\text{CO}_{2\text{pred}}$) can be predicted using standard equations (Mehrbach et al., 1973, and Weiss, 1974). Note that the model only predicts ΣCO_2 variations resulting from the regeneration of carbon, and not those caused by different water masses mixing within the study area. In other words, predicted ΣCO_2 must be compared with observed values which have been normalised to salinity.

Normalised alkalinity shows a high correlation with silicate (Fig. 5):

$$A_{(\text{norm})} = (2286 \pm 3) + (1.52 \pm 0.02) * \text{SiO}_{4(\text{norm})} \quad r^2 = 0.96 \quad (3)$$

Similarly, pH (corrected to 15°C) shows a high correlation with nitrate (Fig. 6):

$$\text{pH}_{15} = (8.258 \pm 0.016) - (0.01432 \pm 0.0001) * \text{NO}_{3(\text{norm})} \quad r^2 = 0.96 \quad (4)$$

The success of the model at reproducing observed ΣCO_2 ($\Sigma\text{CO}_{2\text{real}}$) is shown in Fig. 7. The error in the prediction is typically less than 1 $\mu\text{mol C kg}^{-1}$.

Previous studies (Broecker and Peng, 1982; Poisson and Cheng, 1987) have provided models to predict ΣCO_2 from nitrate. We have also derived this model from our data:

$$\Sigma\text{CO}_{2(\text{norm})} = (2001 \pm 9) + (8.79 \pm 0.08) * \text{NO}_{3(\text{norm})} \quad r^2 = 0.97 \quad (5)$$

The covariance ($r^2=0.97$) is only slightly lower than that of the model described above ($r^2=0.98$): Eqs. 3 and 4.

3.2 Surface distributions

The temperature-salinity (T-S) properties of surface water, measured every half hour throughout the cruise, are shown in Fig. 8. Reference curves for WNAW and ENAW according to Iselin (1936) and Fiuza (1984) respectively are superimposed. Two separate sets of data points can be distinguished: one above the WNAW curve and the second more or less on the ENAW curve. The observations positioned above the WNAW represent mixing between surface water and WNAW over winter. This water is situated to the west of 21°W. The other group of observations reflects winter mixing between surface water and ENAW, and is situated between 12°W and 21°W. The surface distributions of variables of interest to this study are shown in Fig. 9. The temperature distribution shows the boundary between eastern surface water (ESW) and western surface water (WSW) at 13.5°C. The divide between the two groups of observations shown in Fig. 8 is located at 21°W.

3.2.1 Distributions of chlorophyll and pCO₂.

The distribution of chlorophyll (Fig. 9) shows high values (with a maximum of 8.98 mg m⁻³) in ESW (i.e. to the east of 21°W), and much lower values (less than 1.5 mg m⁻³) in the west (WSW). It is not surprising that biological dynamics are not the same between the two water masses, because of their differing properties. In the cooler waters to the east of 21°W, the phytoplankton spring bloom was occurring during the observational period. To the west of 21°W, the lower chlorophyll concentrations indicate that the bloom had already occurred, or had not yet been initiated. The distribution of surface nitrate throughout the study area (Fig. 9) shows that nitrate values in the WSW were still quite high, suggesting that the phytoplankton bloom had not yet got underway. Zooplankton samples taken during the cruise were dominated by copepods in the ESW, with a very marked transition to salps in WSW (Fig. 10). Copepods are generally thought to be the dominant large grazers on phytoplankton (e.g. Parsons and Lalli, 1988). Salps, however, are important suspension feeders (Alldredge and Madin, 1982), and we are of the opinion that they were feeding on the decaying remains of a post-bloom scenario. The relatively high nitrate concentrations in the WSW might then be explained by zooplankton grazing preventing phytoplankton from fully exploiting nitrate during the bloom.

In some areas, pCO₂ shows a distribution that coincides roughly with chlorophyll (Fig. 9). The minimum values observed were about 300 ppm, located between 43° and 45°N at 16°W. They correspond with a nucleus of chlorophyll at the zone where the planktonic bloom is most evident. The best correlation between pCO₂

and chlorophyll for any of the latitudinal sections was found along 16°W (Fig. 11). The two variables show a distinct negative correlation ($r^2 = 0.46$):

$$pCO_2 = (353 \pm 12) - (8.9 \pm 1.3)[Chl] \quad r^2 = 0.46 \quad (6)$$

When chlorophyll is zero, the pCO_2 of the surface water is in equilibrium with the atmosphere. This value of 353 ppm compares favourably with Takahashi's (1989) figure of 350 ppm, which he estimated assuming an annual increase of 0.35% in atmospheric CO_2 .

If all five latitudinal sections are examined, however, correlations between chlorophyll and pCO_2 are less obvious. The correlations (r^2) for the 12°, 16°, 20°, 24° and 28°W sections are 0.003, 0.46, 0.05, 0.10 and 0.02 respectively. The r^2 value for all the data put together is 0.02. Two sets of factors may contribute to weak correlations between chlorophyll and pCO_2 : environmental (chemical and physical) and biological. The physical and chemical environment, and in particular temperature and wind, affects pCO_2 . An *in situ* temperature increase of 1°C causes an *in situ* pH decrease of 0.0127, resulting in a pCO_2 increase of about 15 ppm (4.3%). The wide variation in temperature (12° to 17°C) throughout the study area (Fig. 9) therefore causes large variations in pCO_2 in surface waters (once the pCO_2 of these waters has equilibrated with the atmosphere), independently of biological processes. The carbon flux between atmosphere and ocean increases with wind speed (see below), and thus in windy areas a poor correlation between pCO_2 and chlorophyll might be expected. Another contributory factor may be biological processes. If the phytoplankton bloom has been grazed down by zooplankton (i.e. a post-bloom situation is reached), and the grazed material is not immediately recycled to ΣCO_2 in surface waters (e.g. it is exported via particulate matter or maintained in zooplankton biomass), then a close correlation between pCO_2 and chlorophyll would not be expected. In the western part of the study area (WSW) all these factors may be important: wind (in the northwest), temperature and biological effects. The situation is less clear further east (ESW). In addition to the factors described above, the upwelling of water (REF) with high ΣCO_2 may be causing the relatively high pCO_2 values observed there (particularly at 12°W). Over the study area as a whole, it is not surprising that a poor correlation is found between chlorophyll and pCO_2 because of all these interacting factors.

3.2.2 CO_2 flux between atmosphere and ocean.

The exchange of carbon between the atmosphere and ocean, F ($mmol\ m^{-2}\ d^{-1}$), can be calculated using the following equation:

$$F = 0.24kS(p\text{CO}_2_{\text{oc}} - p\text{CO}_2_{\text{atm}}) \quad (7)$$

where k (cm h^{-1}) is the exchange coefficient or "piston velocity", S ($\text{mol l}^{-1} \text{atm}^{-1}$) is the solubility of CO_2 in seawater, $p\text{CO}_{2\text{oc}}$ is $p\text{CO}_2$ in the ocean, and $p\text{CO}_{2\text{atm}}$ is the partial pressure of CO_2 in air (both in μatm). The factor 0.24 converts between units. The seasonal and inter-annual variations in the atmospheric $p\text{CO}_2$ are small when compared to $p\text{CO}_2$ variations in the surface ocean (Andri et al., 1986). We therefore assumed a constant atmospheric CO_2 partial pressure of 352 ppm (Fraga and Prez, 1990; Chipman et al., 1993; Robertson et al., 1993). The value is similar to that obtained in Eq. 6 when the chlorophyll concentration is zero and the partial pressures of CO_2 in the sea and atmosphere are in equilibrium.

The impact of wind speed on the exchange coefficient, k , must be taken into account. This relationship has been studied using a wind tunnel experiments (Broecker et al., 1978; Merlivat and Memery, 1983), and in the ocean *in situ* using radon (Peng et al., 1979; Smithie et al., 1985). Liss and Merlivat (1986) reviewed both these types of study, and proposed equations for 20°C (Schmidt number 600) which have also been used by Andri et al., 1986 and Oudot et al., 1987. However, given that the range of temperature in our data lies between 12 and 17°C , the equations used by Woolf and Thorpe (1991) were used:

$$k = 0.17U_{10}(600/Sc)^{2/3} \quad U < U_1: \text{smooth water regime} \quad (8)$$

$$k = (2.85U_{10} - 9.65)(600/Sc)^{1/2} \quad U > U_1: \text{rough water regime} \quad (9)$$

$$U_1 = 9.65[2.85 - 0.17(600/Sc)^{1/6}]^{-1} \quad (10)$$

where Sc is Schmidt number, and U_{10} is the wind speed 10 m above the ocean surface (m s^{-1}). We obtain $U_1 = 3.6 \text{ m s}^{-1}$ for our temperature range. We have derived the following equation relating Schmidt number to temperature, using data tabulated by Andri et al. (1986: table 1):

$$\log(600/Sc) = -1.0687 + 0.05127T \quad r^2 = 0.995 \quad (11)$$

Positive fluxes indicate exchange from ocean to atmosphere. Calculated fluxes are shown in Fig. 12, showing uptake of carbon by the ocean. The highest rates of uptake occur in two zones. The first, located at $45^\circ13'\text{N}$, $16^\circ04'\text{W}$ ($F = -6.4 \text{ mmol C m}^{-2} \text{ d}^{-1}$) is where the highest primary production was occurring, and coincides with water of subpolar origin (ENAW_p). This zone was also observed by Pollard and Pu (1985). The second zone is at $47^\circ57'\text{N}$, $28^\circ19'\text{W}$ ($F = -7.8 \text{ mmol C m}^{-2} \text{ d}^{-1}$), and

coincides with the highest wind speeds (Fig. 9). Fluxes of CO_2 from the ocean to the atmosphere occur in areas centred around 45°N , 12°W and $44^\circ 21'\text{N}$, $27^\circ 30'\text{W}$.

4. DISCUSSION

In order to validate our results we compared our data (D58) with those collected ten years ago in the TTO (Transient Tracers in the Ocean) program, which are summarised in Tables 1 and 2. Only stations with similar geographical positions are compared (Fig. 1). At depths greater than 2000 m both thermohaline characteristics, alkalinity and total inorganic carbon are very similar (Table 1). Data for depths less than 2000 m for the TTO and D58 cruises are compared in Table 2. Differences in normalised alkalinity are only about two per thousand. Variations in normalised ΣCO_2 are double those of alkalinity. This variation is due to a different degree of ageing (oxidation) of water masses, as can be seen from the oxygen values. On the other hand, Labrador Sea Water, which is situated at about 2000 m, has similar values of alkalinity and ΣCO_2 for both cruises (Table 1). However, Labrador Water sometimes shows the same ageing patterns (i.e. variations in alkalinity and ΣCO_2 as the surface waters (Table 2). Although the methodologies for measuring ΣCO_2 used by TTO and D58 are different, the similarity in the results shows the effectiveness of the simple and rapid method used in this study, which was developed by Pérez and Fraga (1987a, b).

Examination of the vertical sections showed that the regeneration of carbon takes place in two principal stages: 0-1000 m, and >2300 m. Nearly all of the soft tissue carbon remineralised in the upper 1000 m: oxidation of organic debris takes place preferentially in this zone (Takahashi, 1989). Similarly, Pérez et al. (in press) found high remineralisation rates in a mixing layer between 400 and 1000 m depth, when working off the Iberian peninsula (NE Atlantic). We calculated that 86% of regenerated carbon in the upper 1000 m was derived from soft tissue, by examining a plot of normalised ΣCO_2 versus alkalinity. Despite the carbonate supersaturation of the upper ocean, we nevertheless calculated that 14% of regenerated carbon in this zone was skeletal (CaCO₃) in origin. Broecker and Peng (1982) found this fraction to be as high as 20% in temperate surface waters. The second phase of carbon regeneration starts at approx. 2300 m. Below this depth the regenerated carbon originating from carbonate skeletons is more important than in the upper ocean because of the effects of increased pressure and decreased temperature on carbonate dissolution. Moreover, in deep waters the residence time of hard skeletons is higher because of the small size and slow settling velocities of particles. The fraction of

regenerated carbon arising from carbonate skeletons therefore increases to 54%. This compares favourably with a fraction of 50% for deep waters in various oceans which Broecker and Peng (1982) derived using GEOSECS data. As for carbonate, most opaline silica dissolution occurs below about 2300 m, below which a marked increase in silicate is seen. A simple model is developed to predict ΣCO_2 from nutrients (nitrate and silicate) in the water column. This model reproduces the observed pattern of ΣCO_2 , showing an error typically less than $1 \mu\text{mol C kg}^{-1}$.

A good correlation between pCO_2 and chlorophyll was found along 16°W in this study ($r^2=0.46$; Eq. 6). Watson et al. (1991) also found good linear relationships between these variables in the NE Atlantic ($47\text{--}60^\circ\text{N}$, 20°W). The y-intercept of our relationship of 353 ppm agrees well with the pCO_2 in the atmosphere (Fraga and Pérez, 1990; Robertson et al., 1992; Chipman et al., 1993). The increase of pCO_2 with latitude observed by Watson et al. (1991) was also found in this study. Throughout much of the study area, however, poor correlations were found between pCO_2 and chlorophyll. Various factors may explain this: (i) different water masses (which have different ΣCO_2 , salinities and temperatures) were present (ii) high wind speeds (particularly in the northwest and east of the study area) cause a large atmosphere-ocean carbon flux and (iii) biological processes (particularly grazing) which impact on the chlorophyll biomass.

The exchange of carbon between atmosphere and ocean is largely controlled by the product kS (Eq. 7), where k is piston velocity and S is the solubility of CO_2 in seawater. Merlivat et al. (1991) defined an exchange coefficient K as $K=kS$, and calculated K to be $0.028 \text{ mmol m}^{-2} \text{ y}^{-1} \mu\text{atm}^{-1}$ to the north of 40°N in the North Atlantic. We calculated a similar mean value over the study area for K from S and k (Eqs. 8-11) as $0.021 \text{ mmol m}^{-2} \text{ y}^{-1} \mu\text{atm}^{-1}$.

The calculated mean CO_2 flux from atmosphere to ocean for the period and zone sampled was $0.50 \text{ mmol m}^{-2} \text{ d}^{-1}$. This value confirms the role of the North Atlantic as a sink for atmospheric CO_2 (Brewer et al., 1989; Takahashi et al., 1989). This mean value is, however, slightly lower than values found by other authors (Table 3), although these other values are not specific to the spring bloom period, and cover different geographical ranges. Our mean value is closest to Merlivat et al's (1991) value of $0.68 \text{ mmol m}^{-2} \text{ d}^{-1}$, which they estimated from data of Maier-Reimer and Hasselman (1987). Schlitzer (1989) developed a model of carbon exchange between atmosphere and ocean in the North Atlantic ($10^\circ\text{--}50^\circ\text{N}$) using annually averaged data (Levitus, 1982) and calculated fluxes to the ocean of 0.39 to $1.48 \text{ mmol m}^{-2} \text{ d}^{-1}$. Our mean value is within these limits.

The 1989 spring bloom in the North Atlantic ($47^\circ\text{--}60^\circ\text{N}$, 20°W) was modelled by Taylor et al. (1992). Predicted oceanic carbon uptake from the atmosphere was 9

mmol m⁻² d⁻¹. This is higher than a value of 4.9 mmol m⁻² d⁻¹ which we calculated in this study for the area where the bloom was most evident (45°N, 16°W). Our value is closer to the mean flux of 5.9 mmol m⁻² d⁻¹ found by Chipman et al. (1993) at 47°N 20°W in spring 1989.

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REFERENCES

- ALLDREDGE, A.L. and L.P. MADIN (1982). Pelagic tunicates: unique herbivores in the marine plankton. *BioSci.*, **32**, 655-663.
- ANDERSON, L.G., D. DYRSSEN and E.P. JONES (1990). An Assessment of the Transport of Atmospheric CO₂ into the Arctic Ocean. *J. Geophys. Res.*, **95**, 1703-1711
- ANDRIÉ, C., C. OUDOT, C. GENTHON and L. MERLIVAT (1986). CO₂ fluxes in the Tropical Atlantic during FOCAL cruises. *J. Geophys. Res.*, **91**, 11741-11755.
- BREWER, P.G. (1978). Direct observations of the oceanic CO₂ increase. *Geophysical Research Letters*, **5**, 997-1000.
- BREWER, P.G. and J.C. GOLDMAN (1976). Alkalinity changes generated by phytoplankton growth. *Limnol. Oceanogr.*, **21**, 108-117.
- BREWER, P.G., C. GOYET and D. DYRSSEN (1989). Carbon dioxide transport by ocean currents at 25°N Latitude in the Atlantic Ocean. *Science*, **247**, 477-479.

- BROECKER, H.C., J. PETERMANN and W. SIEMS (1978). The influence of wind-wave tunnel including the effects of monolayers. *J. Mar. Res.*, **36**, 595-610.
- BROECKER, W.S. and T.H. PENG (1982). *Tracers in the sea*. Eldigio Press, Palisades, New York, 690 pp.
- CHIPMAN, D.W., J. MARRA and T. TAKAHASHI (1993). Primary production at 47°N and 20°W in the North Atlantic Ocean: a comparison between the ^{14}C incubation method and the mixed layer carbon budget. *Deep-Sea Res.*, **40**, 151-169.
- ESTRADA, M. (1989). Phytoplankton - Inorganic Carbon uptake and respiratory ETS activity. In "The expedition Antarktis VII/3 (EPOS LEG 2) of RV 'Polarstern' in 1988/89" Ed. Hempel, Schalk and Smetacker. *Berichtezur Polarforschung*, **65**, 88-91.
- FIUZA, A.F.G. (1984). Hidrologia e dinamica das aguas costeiras de Portugal. These Doctoral Science. University Lisbonne. Portugal, 294 pp.
- FRAGA, F. and F.F.PÉREZ (1990). El agua de mar como sumidero del exceso de carbono atmosférico. *Boletín Academia Galega de Ciencias*, **9**, 5-13.
- GARÇON, V.C., L. MARTINON, C. ANDRIÉ, P. ANDRICH and J.F. MINSTER (1989). Kinematics of CO_2 fluxes in the Tropical Atlantic Ocean during the 1983 Northern summer. *J. Geophys. Res.*, **94**, 855-870.
- GRIFFITHS, G., S. CUNNINGHAM, M. GRIFFITHS, R.T. POLLARD, H. LEACH, S. HOLLEY, R. PAYLOR, T.W.N. HAINE, A.F. RIOS, S.G. ALDERSON, R.K. LOWRY, P. SMITH, M. PRESTON, T.J.P. GWILLIAM, J. SMITHERS, S. KEENE, J. HEMMINGS and T.R. ANDERSON (1992). CTD oxygen, tracer and nutrient data from RRS *Charles Darwin* cruises 58/59 in the NE Atlantic as part of Vivaldi '91. *IOSDL Report*, **296**, 51 pp.
- HARVEY, J. 1982. O-S relationship and water masses in the eastern North Atlantic. *Deep-Sea Research.*, **29**, 1021-1033.
- ISELIN, C.O'D. 1936. A study of the circulation of the western North Atlantic. *Papers in Physical Oceanography and Meteorology*, **4**, 101 pp.

- KEELING, C.D., R.B. BACASTOW, A.E. BAINBRIDGE, C.A. EKDAHL, P.R. GUENTHER and L.S. WATERMAN (1976). Atmospheric carbon dioxide variations at Mauna Loa Observatory, Hawaii. *Tellus*, **28**, 438-551.
- KIRCHMAN, D.L., Y. SUZUKI, C. GARSIDE and H.W. DUCKLOW (1991). High turnover rates of dissolved organic carbon during a spring phytoplankton boom. *Nature*, **352**, 612-614.
- LISS, P. and MERLIVAT (1986). Air-sea gas exchange rates: Introduction and synthesis, in *The Role of Air-Sea Exchange in Geochemical Cycling*, *Adv. Sci. Inst. Ser.*, edited by P. Buat-Ménard, D. Reidel Pub. Co., Dordrecht, Holland, 113-127.
- MEHRBACH, C., C.H. CULBERSON, J.E. HAWLEY and R.M. PYTKOWICZ (1973). Measurements of the apparent dissociation constant of carbonic acid in seawater at atmospheric pressure. *Limnology and Oceanography*, **18**, 897-907.
- MERLIVAT, L., J. ETCHETO and J. BOUTIN (1991). CO₂ exchange at the air-sea interface: time and space variability. *Adv. Space. Res.*, **11**, 77-85
- MERLIVAT, L. and L. MEMERY (1983). Gas exchange an air-water interface: Experimental results and modeling of bubble contribution to transfer. *J. Geophys. Res.*, **88**, 707-724.
- MURPHY, P.P., R.A. FEELY, R.H. GAMMON, D.E. HARRISON, K.C. KELLY and L.S. WATERMAN (1991). Assessment of the air-sea exchange of CO₂ in the South Pacific during Austral autumn. *J. Geophys. Res.*, **96**, 20455-20465.
- OUDOT, C., C. ANDRIÉ and Y. MONTEL (1987). Evolution du CO₂ océanique et atmosphérique sur la période 1982-1984 dans l'Atlantique tropical. *Deep-Sea Research*, **34**, 1107-1137
- PAPAUD, A and A. POISSON (1986). Distribution of dissolved CO₂ in the Red Sea and correlations with other geochemical tracers. *J. Mar. Res.*, **44**, 385-402.

- PARSONS, T.R., and C.M. LALLI (1988). Comparative oceanic ecology of the plankton communities of the subarctic Atlantic and Pacific oceans. *Oceanogr. Mar. Biol. Annu. Rev.*, **26**, 317-359.
- PENG, T.H., W.S. BROECKER, G.G. MATHIEU and Y.H. LI (1979). Radon evasion rates in the Atlantic and Pacific oceans as determined during GEOSECS Program. *J. Geophys. Res.*, **84**, 2471-2486.
- PÉREZ, F.F., C. MOURIÑO, F. FRAGA and A.F. RÍOS. Displacement of water masses and remineralization rates off the Iberian peninsula by nutrient anomalies. *J. Mar. Res.* (submitted)
- PÉREZ, F.F. and F. FRAGA. 1987a. The pH measurements in seawater on the NBS scale. *Marine Chemistry*, **21**, 315-327.
- PÉREZ, F.F. and F. FRAGA. 1987b. A precise and rapid analytical procedure for alkalinity determination. *Marine Chemistry*, **21**, 169-182.
- POLLARD, R.T., H. LEACH and G. GRIFFITHS. 1991. RRS Charles Darwin cruises 58 & 59, 25 Apr - 16 May; 18 May - 10 Jun 1991. *IOSDL, Cruise Report*, **228**, 49 pp.
- REDFIELD, A.C., KETCHUM, B.H. and RICHARDS, F.A. (1963). The influence of organisms on the composition of sea-water. pp. 26-77 in M.N. Hill (ed.), *The Sea*, Vol. 2, Interscience.
- RÍOS, A.F., FRAGA, F. and PÉREZ, F. (1989). Estimation of coefficients for the calculation of "NO", "PO", and "CO", starting from the elemental composition of natural phytoplankton. *Scient. Mar.* **53**, 779-784.
- RÍOS, A.F., F.F. PÉREZ and F. FRAGA. 1992. Water masses in the upper and middle North Atlantic Ocean east of the Azores. *Deep-Sea Research*, **39**, 645-658.
- ROBERTSON, J.E., A.J. WATSON, C. LANGDON, R.D. LING and J.W. WOOD (1993). Diurnal variation in surface pCO₂ and O₂ at 60°N, 20°W in the North Atlantic. *Deep-Sea Res.*, **40**, 409-422.

- ROOS, M. and G.GRAVENHORST (1984). The increase in oceanic carbon dioxide and the net CO₂ flux into the North Atlantic. *J. Geophys. Res.*, **89**, 8181-8193.
- SCHLITZER, R. (1989). Modeling the nutrient and carbon cycles of the North Atlantic 2. New production, particle fluxes, CO₂ exchange, and the role of organic nutrients. *J. Geophys. Res.*, **94**, 12781-12794.
- SMITHIE, W.M., T. TAKAHASHI and D.W. CHIPMAN (1985). Gas exchange and CO₂ flux in the Tropical Atlantic ocean determined from ²²²Rn and pCO₂ measurements. *J. Geophys. Res.*, **90**, 7005-7022.
- SMYTHE-WRIGHT, D., PAYLOR, R. and HOLLEY, S.E. (1992). Chemical tracer studies at IOSDL - 3. IOSDL Rep. **302**, 73 pp.
- SMYTHE-WRIGHT, D., PAYLOR, R. and HOLLEY, S.E. (1993). Chemical tracer studies at IOSDL - 4. IOSDL Rep. **303**, 47 pp.
- TAKAHASHI, T. (1989). Only half as much CO₂ as expected from industrial emissions is accumulating in the atmosphere. Could the oceans be the storehouse for the missing gas?. *Oceanus*, **32**, 22-29.
- TANOUE, E. (1985). Distribution and chemical composition of particulate matter in the Pacific sector of the Antarctic Ocean. *Trans. Tokyo Univ. Fish.*, **6**, 43-57.
- TAYLOR, A.H., A.J. WATSON, M. AINSWORTH, J.E. ROBERTSON and D.R. TURNER (1991). A modelling investigation of the role of phytoplankton in the balance of carbon at the surface of the North Atlantic. *Global Biogeochemical cycles*, **5**, 151-171.
- TAYLOR, A.H., A.J. WATSON and J.E. ROBERTSON (1992). The influence of the spring phytoplankton bloom on carbon dioxide and oxygen concentrations in the surface waters of the northeast Atlantic during 1989. *Deep-Sea Res.*, **39**, 137-152.
- Transient Tracers in the Oceans North Atlantic Study. Shipboard Physical and Chemical data report 1 April-19 October (1981). Scripps Institution of Oceanography. University of California. San Diego. 2

- WATSON, A.J., C. ROBINSON, J.E. ROBINSON, P.J. LE B. WILLIAMS and M.J.R. FASHAM (1991). Spatial variability in the sink for atmospheric carbon dioxide in the North Atlantic. *Nature*, **350**, 50-53.
- WEISS, R.F. (1974). Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.*, **2**, 203-215.
- WOOLF, D.K. and S.A. THORPE (1991). Bubbles and the air-sea exchange of gases in near-saturation conditions. *J. Mar. Res.*, **49**, 435-466.

FIGURE CAPTIONS

Fig. 1 - Cruise track for cruise "Darwin-58", showing positions of CTD stations (circles). TTO (1981) stations are also shown (squares). The vertical sections represented in Figs. 2 and 3 are depicted as solid lines.

Fig. 2 - Distributions of temperature, salinity, carbonic system variables and nutrients in a vertical section along 42°N.

Fig. 3 - Distributions of temperature, salinity, carbonic system variables and nutrients in a vertical section along 20°W.

Fig. 4 - Distribution of normalised ΣCO_2 throughout the study area: a) variation with depth b) plotted against normalised alkalinity.

Fig. 5 - Relationship between alkalinity and salinity. Regression line is Eq. 3.

Fig. 6 - Relationship between pH at 15°C and nitrate. Regression line is Eq. 4.

Fig. 7 - Comparison of predicted ΣCO_2 ($\Sigma\text{CO}_{2\text{pred}}$) using the model and observed ΣCO_2 ($\Sigma\text{CO}_{2\text{real}}$).

Fig. 8 - Temperature-salinity properties of surface water throughout the study area. Crosses are data to the west of 21°W and squares correspond to data to the east of this longitude. Curves for WNAW and ENAW according to Iselin (1936) and Fiuza (1984) are superimposed.

Fig. 9 - Surface-water distributions of temperature, salinity, chlorophyll, nitrate and factors affecting the air-sea carbon flux, throughout the study area.

Fig. 10 - Major constituents of zooplankton samples collected at each CTD station. Symbols are: circles - copepods, stars - salps and jellies, squares - chaetognaths, triangles - euphausiids.

Fig. 11 - Latitudinal variation of pCO_2 and chlorophyll along 16°W.

Fig. 12 - Calculated atmosphere-ocean carbon fluxes during the cruise in $\text{mmol m}^{-2} \text{d}^{-1}$. Negative values represent uptake by the ocean.

Table 1

Comparison of termohaline characteristics and carbonic system between Darwin-58 cruise (D58) and Transient Traces in Ocean (TTO) in deep waters (>2000 m)

Lat. N	Long. W	Cruise	Year	Sta.n°	Depth	Salinity	Tpot	Gamma-pot	A _{norm}	CO _{2norm}
37°52.6'	17°27.8'	TTO	1981	111	2453	34.986	3.13	27.86	2321	2165
39°00.2'	17°27.8'	D58	1991	Z39	2423	34.982	3.16	27.86	2321	2170
37°52.6'	17°27.8'	TTO	1981	111	3714	34.920	2.28	27.88	2349	2205
39°00.2'	17°27.8'	D58	1991	Z39	3647	34.918	2.29	27.88	2350	2204
42°08.2'	10°20.2'	TTO	1981	114	2418	35.001	3.23	27.86	2323	2170
42°00.0'	12°44.9'	D58	1991	B42	2429	34.988	3.18	27.86	2323	2175
46°04.1'	11°00.8'	TTO	1981	115	2023 [*]	35.014	3.79	27.82	2308	2161
47°30.0'	11°59.6'	D58	1991	B48	2030 [*]	34.956	3.47	27.81	2313	2165
46°04.1'	11°00.8'	TTO	1981	115	3239	34.932	2.42	27.88	2341	2188
47°30.0'	11°59.6'	D58	1991	B48	3255	34.929	2.40	27.88	2338	2190

^{*} LW (Labrador Sea Water)

A_{norm} Alkalinity normalized at salinity 35

CO_{2norm} CO₂ normalized at salinity 35

Table 2

Comparison of termohaline characteristics, carbonic system and oxygen between Darwin-58 cruise (D58) and Transient Traces in Ocean (TTO) at depths less than 2000 m.

Lat. N	Long. W	Cruise	Year	Sta.n ^o	Depth	Salinity	Tpot	Gamma-pot	A _{norm}	CO _{2norm}	O ₂
37°52.6'	17°27.8'	TTO	1981	111	342	35.622	11.96	27.08	2293	2084	223
39°00.2'	17°27.8'	D58	1991	Z39	402	35.642	11.96	27.10	2291	2094	217
37°52.6'	17°27.8'	TTO	1981	111	569	35.532	10.80	27.23	2299	2114	203
39°00.2'	17°27.8'	D58	1991	Z39	604	35.527	10.84	27.22	2293	2113	203
42°08.2'	10°20.2'	TTO	1981	114	992	36.061	10.77	27.64	2309	2123	185
42°00.0'	12°44.9'	D58	1991	B42	1008	36.086	10.93	27.63	2312	2131	181
42°08.2'	10°20.2'	TTO	1981	114	1996 [*]	35.060	3.98	27.84	2312	2158	255
42°00.0'	12°44.9'	D58	1991	B42	2023 [*]	35.075	4.09	27.84	2316	2165	250

* LW (Labrador Sea Water)

A_{norm} Alkalinity normalized at salinity 35

CO_{2norm} CO₂ normalized at salinity 35

Table 3

Mean fluxes of CO₂ between atmosphere and ocean in the North Atlantic

Year	Location	Mean net Flux mmol.m ⁻² .d ⁻¹	Autor
1903-1973	North Atlantic (0°-40°N)	-1.20	Roos & Gravenhorst, 1984
" "	North Atlantic (0°-80°N)	-2.93	
1986	North Atantic (0°-80°N)	-1.56 ⁽¹⁾	Merlivat et al 1991
1987	North Atantic (0°-80°N)	-0.68 ⁽²⁾	
Spring 1991	North Atantic (39°-48°N)	-0.65	This paper

⁽¹⁾ data derived of Broecker et al. (1986)⁽²⁾ data derived of Maier-Reimer and Hasselmann (1987)⁽¹⁾ and ⁽²⁾ The units have been transformed from gC.y⁻¹ taking into account the surfaces (areas) given by Roos and Gravenhorts (1984).

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

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