
Aida F. Ríos*, Fiz F. Pérez, F. Fraga

Instituto de Investigaciones Marinas (CSIC), Eduardo Cabello 6, 36208-Vigo, Spain

Abstract

From 1977 to 1997 CO₂ parameters were measured in the Eastern North Atlantic Ocean. A data set of 12 cruises carried out between 37°N and 47°N, 20°W and the Iberian Peninsula coast, were used to estimate the anthropogenic carbon (C_{ANT}) based on a back-calculation technique, with the aim of evaluating its temporal evolution in that 20-year period. The rate of change of the integrated C_{ANT} down to 2000 m was 0.95 mol m⁻² yr⁻¹. Half of this input corresponds to a direct uptake of atmospheric CO₂ (0.48 mol m⁻² yr⁻¹), while the other half enters by advection. The C_{ANT} advected by the Mediterranean Water (MW) is the most important contributor to the total C_{ANT} advected into the area, representing 59% (0.27 ± 0.09 mol m⁻² yr⁻¹), whereas the Labrador Sea Water contributes only 15% (0.07 ± 0.04 mol m⁻² yr⁻¹). The particular formation mechanism of MW explains its high content of advected C_{ANT}. When MW is formed in the Gulf of Cádiz, 85% of Central Water is entrained by sinking of the Mediterranean Overflow Water. Central Waters have about 50 μmol kg⁻¹ of C_{ANT}; thus this entrainment represents 0.07 GtC yr⁻¹, which is about 26% of the C_{ANT} transported by the thermohaline circulation in the North Atlantic. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

About one-third to one-half of the anthropogenic CO₂ emitted to the atmosphere is taken up by the oceans (Siegenthaler and Sarmiento, 1993); among them, the Atlantic Ocean is considered as the most important CO₂ sink (Sarmiento et al., 1995). Therefore, it is important to improve the knowledge of the uptake of carbon in different provinces to understand and evaluate the global carbon cycle. Several estimates of the anthropogenic carbon uptake have been performed in the North Atlantic using historical data sets such as GEOSECS or TTO (Chen and Millero, 1979;...
Chen, 1982; Gruber, 1998). Recently, other estimates have been made from cruises that took place in the 1990s (Körtzinger et al., 1998; Wanninkhof et al., 1999). Here, we use a set of 12 cruises from the eastern North Atlantic between 1977 and 1997, with the aim of evaluating the temporal evolution during these 20 years of the anthropogenic CO₂ input in the eastern North Atlantic.

### 2. Database

Temperature, salinity, oxygen, nutrients, alkalinity and dissolved inorganic carbon data from different cruises were used to estimate the anthropogenic carbon based on a back-calculation technique. Table 1 shows the characteristics of the 12 cruises; station locations of the cruises are shown in the map (Fig. 1). The dissolved inorganic carbon (Cᵦ) was estimated from measured pH and alkalinity (TA) using the thermodynamic equations of the carbonate system (Dickson, 1981), with the dissociation constants of Mehrbach et al. (1973), in all cruises, except for the TTO and OACES cruises. TTO Cᵦ data were calculated from potentiometric Cᵦ and alkalinity. For the OACES cruise, the Cᵦ measurements were performed using coulometric detection with a single operator multi-parameter metabolic analyzer (SOMMA) inlet system (Johnson et al., 1993).

TA was determined by potentiometric titration methods as described in Pérez and Fraga (1987a). Likewise, pH was measured potentiometrically in NBS scale (Pérez and Fraga, 1987b) in “Galicia’s”, VIVALDI, Bord-Est 3 and MORENA I cruises, while pH was determined spectrophotometrically in the OACES and FOUREX cruises (Clayton and Byrne, 1993). A comprehensive description of the cruise, the sampling procedures, and the analytical techniques have been discussed in Manríquez et al. (1978), Fraga et al. (1978), Mourino et al. (1984), Pérez et al. (1985), Fraga et al. (1985), Mourino et al. (1985), Fraga et al. (1987), Griffiths et al. (1992), Castle et al. (1998) and Bacon (1998).

#### Table 1
Characteristics of the 12 cruises. The different stations sampled in each cruise are represented by the same symbols in Fig. 1

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Year</th>
<th>Month</th>
<th>Cruise</th>
<th>pH</th>
<th>TA</th>
<th>Cᵦ</th>
</tr>
</thead>
<tbody>
<tr>
<td>◆</td>
<td>1977</td>
<td>October</td>
<td>Galicia IV</td>
<td>P</td>
<td>P</td>
<td>Cal</td>
</tr>
<tr>
<td>▲</td>
<td>1981</td>
<td>November</td>
<td>TTO</td>
<td>—</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>▼</td>
<td>1982</td>
<td>November</td>
<td>Galicia V</td>
<td>P</td>
<td>P</td>
<td>Cal</td>
</tr>
<tr>
<td>△</td>
<td>1983</td>
<td>December</td>
<td>Galicia VI</td>
<td>P</td>
<td>P</td>
<td>Cal</td>
</tr>
<tr>
<td>●</td>
<td>1984</td>
<td>February</td>
<td>Galicia VII</td>
<td>P</td>
<td>P</td>
<td>Cal</td>
</tr>
<tr>
<td>□</td>
<td>1984</td>
<td>July</td>
<td>Galicia VIII</td>
<td>P</td>
<td>P</td>
<td>Cal</td>
</tr>
<tr>
<td>○</td>
<td>1986</td>
<td>September</td>
<td>Galicia IX</td>
<td>P</td>
<td>P</td>
<td>Cal</td>
</tr>
<tr>
<td>■</td>
<td>1989</td>
<td>May</td>
<td>Bordest 3</td>
<td>P</td>
<td>P</td>
<td>Cal</td>
</tr>
<tr>
<td>♦</td>
<td>1991</td>
<td>April–May</td>
<td>Vivaldi</td>
<td>P</td>
<td>P</td>
<td>Cal</td>
</tr>
<tr>
<td>♦</td>
<td>1993</td>
<td>May</td>
<td>Morena I</td>
<td>P</td>
<td>P</td>
<td>Cal</td>
</tr>
<tr>
<td>+</td>
<td>1993</td>
<td>July</td>
<td>OACES</td>
<td>S</td>
<td>P</td>
<td>Coul</td>
</tr>
<tr>
<td>×</td>
<td>1997</td>
<td>August</td>
<td>Fourex</td>
<td>S</td>
<td>P</td>
<td>Cal</td>
</tr>
</tbody>
</table>

*TA is total alkalinity, Cᵦ is total inorganic carbon, P means Potentiometric, S spectrophotometric, Coul coulometric, M measured, and Cal calculated.*
The previous potentiometric methodologies were validated in the WOCE sections A17 and A14 in the South Atlantic where a comparative experiment was performed (Ríos and Pérez, 1999). Analytical errors were $\pm 0.003$ in pH and $\pm 1.1 \mu\text{mol kg}^{-1}$ in TA based on 61 replicates. The average difference between calculated and measured $C_T$ was as low as $0.2 \pm 3.0 \mu\text{mol kg}^{-1}$ for 964 couples. Calculated $C_T$ for 76 certified reference materials (CRMs) also agreed very well with certified concentrations. Finally, the average difference of the 10 $C_T$ samples measured at the Scripps Institution of Oceanography calculated from pH and TA was only $0.9 \pm 2.6 \mu\text{mol kg}^{-1}$. For the cruises performed before 1994, substandard seawater was used to ensure the internal consistency in each cruise. This substandard seawater, similar to CRM, is “quasi-steady” surface seawater, which was filtered and stored in 25-l plastic containers. To avoid the long-term bias, a quality control based on a steady state for deep waters in the relationship pH versus nitrate, and TA normalized to salinity 35 versus silicate was made (Ríos and Pérez, 1999).

3. Method

The initial concentrations of the CO$_2$ in source regions of different water masses are modified by the oxidation of organic materials and the dissolution of carbonaceous skeletons (Broecker and Peng, 1982; Takahashi et al., 1985; Anderson and Sarmiento, 1994). In addition, the initial CO$_2$ of any water mass depends on the CO$_2$ levels in the overlying atmosphere, which have increased from
the pre-industrial reference value of 278 ppm. The total amount of anthropogenic CO$_2$ dissolved in the ocean can be estimated assuming that: (1) dissolved oxygen and CO$_2$ are close to equilibrium (or with the same disequilibrium) with the atmosphere during water-mass formation; and (2) alkalinity is not significantly affected by the CO$_2$ increase (e.g. Chen and Millero, 1979; Poisson and Chen, 1987; Gruber et al., 1996). The anthropogenic CO$_2$ ($C_{\text{ANT}}$) was calculated from $C_T$, TA and dissolved oxygen measured at the sea:

$$C_{\text{ANT}} = C_T - \text{AOU}/R_C - 1/2(TA - TA^0 + \text{AOU}/R_N) - C_T^{278},$$

where AOU$/R_C$ is the $C_T$ increase by organic matter oxidation. Apparent oxygen utilisation (AOU), is calculated with the oxygen saturation equation of Benson and Krause (UNESCO, 1986). $R_C$ is a stoichiometric coefficient ($= -\Delta O_2/\Delta C$). In addition, $1/2(\Delta TA + \text{AOU}/R_N)$ is the $C_T$ change due to CaCO$_3$ dissolution in deep-ocean waters (Broecker and Peng, 1982), where $\Delta TA$ is the total alkalinity change from the initial value during water mass formation ($TA^0$), and $R_N$ is a second stoichiometric coefficient ($= -\Delta O_2/\Delta N$). For open-ocean waters below 400 m, $R_C = 1.45$ and $R_N = 10.6$ (Anderson and Sarmiento, 1994). $TA^0$ stands for preformed alkalinity and was calculated from salinity and ‘PO’ using the empirical equation of Gruber et al. (1996):

$$TA^0 = 367.5 + 54.9S + 0.074\cdot PO,$$

where ‘PO’ = $O_2 + R_pPO_4$. $R_p$ is a stoichiometric coefficient ($= -\Delta O_2/\Delta P$), with a constant value of 170 molO$_2$/molP$^{-1}$ (Anderson and Sarmiento, 1994). $C_T^{278}$ is the initial $C_T$ of any water mass in the pre-industrial era, which can be calculated from time-independent TA$^0$ and the atmospheric pCO$_2$ level at that time and water vapour pressure (Pérez et al., submitted), where $pCO_2 = xCO_2^0 \cdot (P_{\text{atm-vapor pressure}})$ according to DOE (1994). The mole fraction of CO$_2$ in the pre-industrial atmosphere ($xCO_2^0$) was 278.2 ppm (Neftel et al., 1994; Sarmiento et al., 1995).

Previous approaches have been used by other authors to calculate $C_{\text{ANT}}$ (Chen and Pytkowicz, 1979; Chen, 1982, 1993; Poisson and Chen, 1987; Gruber et al., 1996; Körtzinger et al., 1998). Gruber et al. (1996) introduced the disequilibrium term, which includes the CO$_2$ disequilibrium at the time the water lost contact with the atmosphere plus any residual effects due to their choice of oxygen and alkalinity end-members and data uncertainties. Available CFC data for thermocline waters of two cruises enabled the estimation of the disequilibrium term. The calculated values ($3.8 \pm 4.8 \, \text{mmol kg}^{-1}$) notably differed from those reported by Gruber et al. (1996) for the North Atlantic (between $-12$ and $-24 \, \text{mmol kg}^{-1}$), but agreed with the estimations obtained by Pérez et al. (submitted). Furthermore, considering the assumptions made by Gruber et al. (1996) that the ocean has been operating in a steady state, the effective disequilibrium would have been practically constant, and therefore would not effectively affect our results, since we are dealing with temporal changes of $C_{\text{ANT}}$.

The method to estimate $C_{\text{ANT}}$ is subject to a number of uncertainties. The maximum errors estimated by other authors range between $\pm 6 \, \text{mmol kg}^{-1}$ (Sabine et al., 1999) and $\pm 10 \, \text{umol kg}^{-1}$ (Gruber et al., 1996; Körtzinger et al., 1998). We have performed the same error analysis, obtaining $\pm 10.3 \, \text{umol kg}^{-1}$. But as our study is based on an average $C_{\text{ANT}}$ profile for each cruise, the terms and variables involved in the calculations are so many that the averaging effect acting on the independent errors becomes large enough to decrease considerably the real errors (Matsukawa and Suzuki, 1985). Deep waters below 3000 db are expected to have no $C_{\text{ANT}}$ due to their old age (Körtzinger et al., 1998). Below 3000 db the $C_{\text{ANT}}$ average value and standard deviation obtained for the whole data set was $0.7 \pm 2.5 \, \text{mmol kg}^{-1}$ ($n = 274$). Given that the
data population has no $C_{\text{ANT}}$ (the shift 0.7 is not significative), the standard deviation of $C_{\text{ANT}}$ below 3000 db equivalent to the error estimate of $C_{\text{ANT}}$. Therefore, the error of the $C_{\text{ANT}}$ estimates is $\pm 2.5 \mu\text{mol/kg}$.

4. Results

The $C_{\text{ANT}}$ was calculated for the entire temporal set of stations. Then, in order to obtain a vertical profile for each cruise, individual station values were linearly interpolated to fixed depth levels, then for each cruise an average $C_{\text{ANT}}$ profile was obtained (Fig. 2). The highest $C_{\text{ANT}}$ values appear in the main thermocline down to about 600 db, with a range between 33 and 50 $\mu\text{mol kg}^{-1}$. Below this level the $C_{\text{ANT}}$ values decrease slowly down to 1200 db, exhibiting values varying from 25 to 38 $\mu\text{mol kg}^{-1}$. Beneath 1200 db, $C_{\text{ANT}}$ values decrease quickly, reaching values lower than 5 $\mu\text{mol kg}^{-1}$ at 3000 db. The deep waters show the lowest $C_{\text{ANT}}$ concentrations ($-3$ to $3 \mu\text{mol kg}^{-1}$). Down to 2000 db, the slopes of the $C_{\text{ANT}}$ profiles differ in relation with the surveyed area. The cruises performed westward from 15°W, such as VIVALDI, OACES and FOUREX, present slopes higher than cruises carried out farther east and south. Therefore, it seems to be a spatial component in the variability of the average $C_{\text{ANT}}$ profiles.

![Fig. 2. Average vertical profile of $C_{\text{ANT}}$ for each cruise. The same set of symbols is used in Table 1 and Fig. 1. Each profile is displaced 5 $\mu\text{mol kg}^{-1}$. The error bar represents the SDM (standard deviation weighted by the number of individual determinations). The year the cruise was performed is detailed at the extreme of each profile. When two cruises were performed in the same year, the month is indicated next to the year separated by one point. The inset shows the average profiles represented with the same scale.](image-url)
Even taking into consideration this variability due to the average position of each cruise, the gradual temporal increase of C\textsubscript{ANT} concentrations over the main thermocline is evident. Starting from 30 \( \mu \text{mol kg}^{-1} \) in 1977 (Galicia IV), going through 40 \( \mu \text{mol kg}^{-1} \) in 1981 (TTO), reaching concentrations between 40 and 45 \( \mu \text{mol kg}^{-1} \) in the 1980s, and finally rising from 46 to 50 \( \mu \text{mol kg}^{-1} \) in the 1990s. Conversely, in deep layers (below 2000 db), although C\textsubscript{ANT} seems to increase with time (Fig. 2), the average C\textsubscript{ANT} values (2 \(+\) 3 \( \mu \text{mol kg}^{-1} \)) are rather constant and within the error of the model.

The entire set of cruises did not have the same spatial coverage. Thus, the average thermohaline profiles of each cruise differ spatially, and therefore the percentage of water masses is also different, introducing variations in the C\textsubscript{ANT} inventory. To remove this effect on the average C\textsubscript{ANT} profiles, we have obtained average vertical profiles of C\textsubscript{ANT} for four locations North at 46°N, South at 38°N, East at 10°W, and West at 20°W. The C\textsubscript{ANT} average vertical profiles at the northern and southern positions (Fig. 3a) were obtained from the Galicia VI, VII and Bord-Est 3 data. In the upper 700 db, the C\textsubscript{ANT} values are slightly higher at the northern than at the southern position. This layer belongs to the Central Water domain. Thereby, the differences found in C\textsubscript{ANT} and salinity depend on the origin of the Eastern North Atlantic Central Water, subpolar or subtropical (Rios et al., 1992). Between 700 and 1400 db the influence of the Mediterranean Water (MW) is higher at the southern position, whereas the northern profile is more influenced by Labrador Sea Water (LSW). Similarly, we have calculated the mean vertical C\textsubscript{ANT} profiles for the W–E positions from the FOUREX data (Fig. 3b). Within the upper 700 db, the Central Waters domain, the C\textsubscript{ANT} concentrations are higher at the western than at the eastern position. Between 1000 and 2000 db the MW influence predominates towards the east, while the LSW influence is higher towards the west. Along the N–S
Fig. 4. Temporal evolution of the integrated $C_{\text{ANT}}$ within the four depth intervals: Note that $C_{\text{ANT}}$ concentrations were previously normalised to the average position, $42^\circ \text{N}, 15^\circ \text{W}$. The annual rate of $C_{\text{ANT}}$ increase (µmol kg$^{-1}$ yr$^{-1}$) along with its determination coefficient is given for each later. The dashed line is the surface annual rate assuming equilibration with the atmospheric $pCO_2$ increase in the zone. The error bar represents the SDM (standard deviation weighted by the number of individual determinations).

and W–E axes, the anomalies of $C_{\text{ANT}}$ concentrations are remarkably related with the salinity anomalies, which indicate the spreading of MW and LSW.

In order to obtain a spatially normalised average profile of $C_{\text{ANT}}$ for every cruise, we have calculated the average profile of salinity for the central position of the study area ($42^\circ \text{N}, 15^\circ \text{W}$) using data from the FOUREX cruise. Then, we have normalised the $C_{\text{ANT}}$ average profile of each cruise by the ratio between salinity and $C_{\text{ANT}}$ anomalies, in such a way that every $C_{\text{ANT}}$ profile is representative of the same position ($42^\circ \text{N}, 15^\circ \text{W}$) (see Appendix A).

We have divided the water column into four layers according to the spreading domain of the different water masses of the study region. Central Waters occupy the upper layer. MW spreads from 700 to 1400 db. The third layer between 1400 and 2000 db comprises the core of LSW. Deep and bottom waters occupy the layer up to 2000 db. Using the $C_{\text{ANT}}$ profiles normalised to the centre of the study area, we have averaged $C_{\text{ANT}}$ values within the previous depth layers, searching for any temporal evolution in the $C_{\text{ANT}}$ inventory in the Eastern North Atlantic.

Fig. 4 shows the annual rates of $C_{\text{ANT}}$ invasion within each layer, as well as the determination coefficient for every trend line. The upper layer shows an annual $C_{\text{ANT}}$ uptake rate of 0.83 µmol kg$^{-1}$ yr$^{-1}$ in agreement with the surface annual rate of 0.92 µmol kg$^{-1}$ yr$^{-1}$. This later value was estimated assuming equilibrium between the upper mixed layer ( < 150 db) and the atmospheric $pCO_2$ increase in the zone, reported by the monitoring station for atmospheric $pCO_2$ of Izaña (Tenerife, Spain). Note the gradual but remarkable decrease of the $C_{\text{ANT}}$ annual rates between the domain of MW and LSW, 0.30 and 0.23 µmol kg$^{-1}$ yr$^{-1}$, respectively. The deep-water layer does not present any discernible $C_{\text{ANT}}$ annual rate; the average $C_{\text{ANT}}$ content is $1.9 \pm 2.0$ µmol kg$^{-1}$.

The average $C_{\text{ANT}}$ inventory for the upper 2000 m is 0.95 mol m$^{-2}$ yr$^{-1}$. Considering an average upper mixed layer of 500 m in the study zone (Paillet and Arhan, 1996; Pollard et al., 1996) and the
Table 2
Mass transport, in Sverdrup (1 Sv = 10⁶ m³ s⁻¹), through the three walls of the box comprised within 37°N–47°N, 20°W and the Iberian Peninsula coast. Transports, with an error estimate ± 30%, were taken from Saunders (1982). Positive transport values indicate fluxes into the box, conversely negative values indicate outflows. 1990-referred concentrations of CANT for the different layers were calculated according to the annual rates of CANT increase given in Fig. 4. Advec ted CANT rates were calculated by multiplying the transports by the previous CANT concentrations. The errors of the advected CANT and total CANT storage rates were calculated from an error propagation analysis, including the transport and the CANT estimation errors.

<table>
<thead>
<tr>
<th>Box layers</th>
<th>Transport (Sv) (Saunders, 1982)</th>
<th>CANT (µmol kg⁻¹) for 1990</th>
<th>Advec ted CANT rates</th>
<th>Total CANT storage rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (db)</td>
<td>N</td>
<td>S</td>
<td>W</td>
<td>N</td>
</tr>
<tr>
<td>0–700</td>
<td>− 1</td>
<td>− 4.5</td>
<td>+ 5.5</td>
<td>44</td>
</tr>
<tr>
<td>700–1400</td>
<td>− 2.5</td>
<td>+ 2</td>
<td>+ 0.5</td>
<td>31</td>
</tr>
<tr>
<td>1400–2000</td>
<td>+ 6</td>
<td>− 2</td>
<td>− 4</td>
<td>16</td>
</tr>
</tbody>
</table>

input of CO₂ across the surface layer (0.92 µmol kg⁻¹ yr⁻¹), the atmospheric input of CANT is 0.47 mol m⁻² yr⁻¹, which represents a 49% of the estimated inventory. The likely mechanism responsible for this accumulation is an advection of CANT-loaded water driven by the thermohaline circulation.

To investigate the portion of CANT advected into the study zone, we have defined a box comprised within 37°N, 47°N, 20°W and the coast. This box has three layers, coinciding with the Central Waters, MW and LSW domains as defined previously (see Table 2). The volume transports across the box walls and within each layer were taken from Saunders (1982). The corresponding CANT concentrations are referred to the year 1990 according to the annual rates of CANT increase given in Fig. 4. Then, as these values represent an average spatial mean for the central position (42°N, 15°W), we have applied the corresponding geographical water masses correction, using salinity, to obtain values referred to the actual position of the walls. The CANT-advected rates at each layer were obtained by subtracting the inflows by the outflows into the box.

Table 2 shows the advected and storage rates of CANT. In the Central Water layer, the advection rate (0.18 mmol m⁻³ yr⁻¹) only contributes with a 21% to the storage rate of CANT (0.85 mmol m⁻³ yr⁻¹). Thus, the remaining 79% is the atmospheric CANT (0.67 mmol m⁻³ yr⁻¹) that penetrates through the air-sea interface into the box. In the layer dominated by MW, all the CANT is advected into the box. Moreover, the CANT storage rate (0.31 mmol m⁻³ yr⁻¹) is even 0.08 mmol m⁻³ yr⁻¹ lower than the advected CANT rate, suggesting that MW is losing CANT, probably by mixing with LSW. In the LSW domain the CANT advected (0.12 mmol m⁻³ yr⁻¹) by this water mass is half of the storage rate. Therefore, the remaining CANT (0.11 mmol m⁻³ yr⁻¹) must come from the above MW layer by mixing.

5. Discussion

Both the average vertical profiles (Fig. 2) and the depth-averaged values geographically normalised (Fig. 4) point to a temporal increase in the CANT content in the eastern North Atlantic. In
the upper 700 db layer, the Central Water domain, the annual rate of $C_{\text{ANT}}$-uptake (0.83 $\mu$mol kg$^{-1}$ yr$^{-1}$) agrees with the surface annual rate (0.92 $\mu$mol kg$^{-1}$ yr$^{-1}$), calculated from the atmospheric $p$CO$_2$ increase in the study zone assuming atmospheric equilibrium within the upper 150 m. The annual rates of $C_{\text{ANT}}$-uptake decrease with depth in the layers dominated by MW and LSW (0.30 and 0.23 $\mu$mol kg$^{-1}$ yr$^{-1}$, respectively). No $C_{\text{ANT}}$ annual rate was found in the deep layer (2000 db-bottom). In this layer the average $C_{\text{ANT}}$ concentration for the whole the period and cruises was $1.9 \pm 2.0$ $\mu$mol kg$^{-1}$. This value is within the range of uncertainty of the method for estimating anthropogenic carbon.

The annual rate of $C_{\text{ANT}}$-uptake in the upper layer seems to keep pace with the atmospheric $p$CO$_2$ increase. However, if we integrate the $C_{\text{ANT}}$ concentrations down to 2000 m, we obtain the same inventory (0.95 mol m$^{-2}$ yr$^{-1}$) as if considering an atmospheric-equilibrated upper mixed layer 1000 m deep. However, according to Paillet and Arhan (1996) and Pollard et al. (1996), the upper mixed layer or “annually ventilated” layer in this area comprises about the upper 500 m, being deeper (~ 700 m) north of 42°N and shallower (~ 200 m) south of 41°N. Consequently, the total uptake rates of $C_{\text{ANT}}$ have a portion of $C_{\text{ANT}}$ accumulated by advection through thermohaline circulation.

Combining data from different cruises for a temporal-series analysis references a good quality control check in order to avoid systematic offsets in the several databases. We have addressed this point in the Database and Method sections. However, we would like to emphasise the consistency of our analysis and results; both the obtained rate of $C_{\text{ANT}}$-uptake in the upper mixed layer and the mean values of $C_{\text{ANT}}$ below 2000 db lead us to consider our data set as suitable and consistent for estimating the $C_{\text{ANT}}$ inventory in the eastern North Atlantic Ocean. Another source of error could be the spatial normalisation, we have estimated it to be lower than 0.5 as explained in Appendix A. The highest errors in this study come from the estimation of the advection rates, and are mainly ascribed to the 30% error in the volume fluxes. A propagation error analysis for the advected $C_{\text{ANT}}$ rates was also carried out (Table 2).

The examination of the $C_{\text{ANT}}$ rates (Table 2) within depth intervals showed for the upper layer (0–700 db) a $C_{\text{ANT}}$ advection rate of 0.12 mol m$^{-2}$ yr$^{-1}$, and therefore, an atmospheric $C_{\text{ANT}}$-uptake rate of 0.47 mol m$^{-2}$ yr$^{-1}$. This rate is exactly the same if considering an average upper mixed layer of 500 m (Pollard et al., 1996; Paillet and Arhan, 1996) keeping pace with the $p$CO$_2$ increase in the atmosphere. Besides, this net $C_{\text{ANT}}$-uptake rate is similar to the net CO$_2$ flux across the air–sea interface of 0.44 mol m$^{-2}$ yr$^{-1}$ on the North Atlantic for the 0–40°N latitude interval given by Roos and Gravenhorst (1984). Takahashi et al. (1999) gave combined flux of natural and anthropogenic CO$_2$ of 2 mol m$^{-2}$ yr$^{-1}$ for the area 38–46°N by 10–20°W.

The results given in Table 2 show that half of the entry of $C_{\text{ANT}}$ in the study area corresponds to a direct uptake of atmospheric CO$_2$ (0.48 mol m$^{-2}$ yr$^{-1}$). The other half enters the box by advection. Contrary to expectations, the $C_{\text{ANT}}$ advected by MW is the most important input of advected $C_{\text{ANT}}$ in the area, contributing 59% (0.27 mol m$^{-2}$ yr$^{-1}$) of the total advected $C_{\text{ANT}}$, while the LSW contributes only 15% (0.07 mol m$^{-2}$ yr$^{-1}$). According to Cunningham and Haine (1995), the LSW core in our study area estimated by CFC data is about 15 years old. MW is an older water mass, with a residence time in the Mediterranean Sea of about 70 years (Pickard and Emery, 1990); presumably, LSW should be loaded with a higher $C_{\text{ANT}}$ content, which it is advected into our area.

The formation mechanism of MW explains its high content of advected $C_{\text{ANT}}$. Mediterranean overflow water (MOW) with 38.4 salinity enters the North Atlantic, dragging down Central Waters
salinities to around 35.7, sinking until reaching the appropriate density level, forming MW with 36.2 final salinity. According to Bryden et al. (1994), 0.78 Sv of Central Water flow into the Mediterranean Sea through the Strait of Gibraltar, and 0.67 Sv are exported out as MOW. Slater and Bryden (2000), in a 3-sided box around the Gulf of Cadiz, found a net outflow from the box in the MW depth range of about 4.4 Sv. We calculate the amount of entrained Central Water as 3.73 Sv. This value is within the range estimated by Mazé et al. (1997), 3–4 Sv, and by Rhein and Hinrichsen (1993), 3.6 Sv using CFC and nutrient data. Therefore, MW is composed of 85% Central Water and 15% MOW. A small portion of Central Water also penetrates through the Strait of Gibraltar at the Mediterranean Sea where deep water is formed in the Levantine zone and Lion Gulf.

The downward entrainment of upper water in the Gulf of Cadiz is a particular mechanism contributing to the eastern boundary ventilation (Pedlosky, 1983; Arhan et al., 1994). According to this mechanism and considering a current C\textsubscript{ANT} concentration of about 50\mu mol kg\(^{-1}\), we obtain that 0.07 Gt C yr\(^{-1}\) of Central Waters are drawn down to form MW. Although this rate seems to be small, it represents 26% of the rate of the C\textsubscript{ANT} transported by the thermohaline circulation in the North Atlantic, considering a transport of 14 Sv (Schmitz, 1996) in the North Atlantic. In summary, our results demonstrate that the C\textsubscript{ANT} sequestered by MW through the downward entrainment of Central Water is sufficiently important to be considered in the global carbon budgets and in models of oceanic circulation.

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**Appendix A. Spatially normalisation of the C\textsubscript{ANT} average profiles**

In order to normalise the C\textsubscript{ANT} average profiles spatially for each cruise to the same central position (42°N, 15°W), we first “moved” each profile to the central position using the latitude and longitude differences between each profile (i) and the reference point (r). Then, the corresponding C\textsubscript{ANT} anomaly (ΔC\textsubscript{ANT}) was calculated from salinity differences (ΔS) between the profile and the central point in the North–South and West–East directions. In order to do this a ΔC\textsubscript{ANT}/ΔS regression line was calculated by depth intervals and N–S, W–E directions (Table 3):

\[
\Delta C_{\text{ANT}} = \left[ (\Delta C_{\text{ANT(LONG)}} \cdot \Delta \text{Long}(i-r)) + (\Delta C_{\text{ANT(LAT)}} \cdot \Delta \text{Lat}(i-r)) \right]/(\Delta \text{Long}(i-r) + \Delta \text{Lat}(i-r)),
\]

where \(\Delta C_{\text{ANT(LONG)}} = (S_i - S_r)[\Delta C_{\text{ANT(W-E)}}/\Delta S_{(W-E)}]\)

and \(\Delta C_{\text{ANT(LAT)}} = (S_i - S_r)[\Delta C_{\text{ANT(N-S)}}/\Delta S_{(N-S)}]\).
Table 3
Slopes and determination coefficients between $\Delta C_{\text{ANT}}$ and $\Delta S$ for the West–East and North–South variation obtained from data showed in Fig. 3

<table>
<thead>
<tr>
<th>Level (db)</th>
<th>$\frac{\Delta C_{\text{ANT(W-E)}}}{\Delta S_{(W-E)}}$</th>
<th>$R^2$ (W–E)</th>
<th>Error of the $\frac{\Delta C_{\text{ANT(LONG)}}}{\Delta S_{(N-S)}}$ estimate ($\mu$mol kg$^{-1}$)</th>
<th>$\frac{\Delta C_{\text{ANT(N-S)}}}{\Delta S_{(N-S)}}$</th>
<th>$r^2$ (N–S)</th>
<th>Error of the $\frac{\Delta C_{\text{ANT(LAT)}}}{\Delta S_{(N-S)}}$ estimate ($\mu$mol kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–700</td>
<td>$-66 \pm 34$</td>
<td>0.49</td>
<td>$\pm 1.9$</td>
<td>$-11.4 \pm 0.3$</td>
<td>0.97</td>
<td>$\pm 0.05$</td>
</tr>
<tr>
<td>700–1400</td>
<td>$9.6 \pm 1.4$</td>
<td>0.85</td>
<td>$\pm 0.49$</td>
<td>$15.3 \pm 2.0$</td>
<td>0.87</td>
<td>$\pm 0.8$</td>
</tr>
<tr>
<td>1400–2000</td>
<td>$22.4 \pm 5.8$</td>
<td>0.74</td>
<td>$\pm 0.26$</td>
<td>$5.8 \pm 0.01$</td>
<td>0.998</td>
<td>$\pm 0.003$</td>
</tr>
</tbody>
</table>

The error on $C_{\text{ANT}}$ generated by this normalisation is given by the sum of the relative errors of salinity and the slopes. The salinity analytical error is $\pm 0.005$, with a relative error of about 0.014%. The maximum north–south and west–east gradients of salinity were 0.38 and 0.35, respectively, which represent errors of $5.3 \times 10^{-5}$ and $5 \times 10^{-5}$ psu. Therefore, these errors can be considered as negligible with regard to the error of the slopes. The error of the $\Delta C_{\text{ANT(LONG)}}$ and $\Delta C_{\text{ANT(LAT)}}$ estimates were calculated from the relative error of the slope and the north–south and west–east gradients. These errors are given in Table 3.

References


