Anthropogenic and natural CO₂ exchange through the Strait of Gibraltar

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Abstract

The exchange of both anthropogenic and natural inorganic carbon between the Atlantic Ocean and the Mediterranean Sea through Strait of Gibraltar was studied for a period of two years under the frame of the CARBOOCEAN project. A comprehensive sampling program was conducted, which was design to collect samples at eight fixed stations located in the Strait in successive cruises periodically distributed through the year in order to ensure a good spatial and temporal coverage. As a result of this monitoring, a time series namely GIFT (GIbraltar Fixed Time series) has been established, allowing the generation of an extensive data set of the carbon system parameters in the area. Data acquired during the development of nine campaigns were analyzed in this work. Total inorganic carbon concentration (\( C_T \)) was calculated from alkalinity-pH \( T \) pairs and appropriate thermodynamic relationships, with the concentration of anthropogenic carbon (\( C_{ANT} \)) being also computed. Applying a two-layer model of water mass exchange through the Strait and using the transport of the outflowing Mediterranean water recorded in situ during the considered period, a net export of inorganic carbon from the Mediterranean Sea to the Atlantic was obtained, which amounted to 0.025 Pg C yr\(^{-1}\). In contrast, the Atlantic water was found to contain a higher concentration of anthropogenic carbon than the Mediterranean water, resulting in a net flux of \( C_{ANT} \) towards the Mediterranean basin of 4.2 Tg C yr\(^{-1}\). A carbon balance through the Strait was assessed and fluxes are discussed in relation to the highly diverse estimates available in the literature for the area. This work unequivocally confirms the relevant role of the Strait of Gibraltar as a controlling point for the biogeochemical exchanges occurring between the Mediterranean Sea and the Atlantic Ocean and emphasizes the influence of the Mediterranean basin in the carbon inventories of the North Atlantic.
1 Introduction

1.1 The oceanographic setting

Although there still remains large uncertainties in relation to the final fate of the carbon dioxide that is released to the atmosphere as a result of human activities, solid evidence has arisen indicating that the oceans represent the major sink for anthropogenic CO$_2$ (Sabine et al., 2004; Waugh et al., 2006). The ocean absorption of CO$_2$ contributes to moderate future climate change, but this behavior as a carbon reservoir will however result in deleterious consequences for the marine environment. Seawater acidification and its subsequent impact on both marine biota and biogeochemical cycles are expected to be the most immediate and severe effects derived from the oceanic CO$_2$ uptake (Caldeira and Wickett, 2005; Orr et al., 2005; Iglesias-Rodriguez et al., 2008; Fabry et al., 2008). Quantifying the concentration and distribution of anthropogenic carbon ($C_{\text{ANT}}$) in the oceans has become thereby a crucial issue in the understanding of the global carbon cycle and its future evolution in a high CO$_2$ world. Accordingly, over the past decade, considerable efforts have been devoted to assess the capacity of the ocean to sequester CO$_2$ and the predicted changes brought about by the associated acidification. Nevertheless, the computation of $C_{\text{ANT}}$ that is taken up by the oceans faces a considerable constrain, which is the impossibility to be measured directly in situ, as it can not be chemically discriminated from the bulk of natural carbon present in seawater. In order to overcome this limitation, several models for the indirect estimation of $C_{\text{ANT}}$ based on different tracers have been developed (Touratier et al., 2007 and references therein).

Among these models, those denominated back-calculation techniques were the first to estimate anthropogenic CO$_2$ from discrete inorganic carbon measurements, considering their variability due to remineralization of organic matter and carbonate dissolution (Brewer, 1978; Chen and Millero, 1979). Gruber et al. (1996) improved later this method by adding the quasi-conservative tracer $C$, derived from the estimate of the water mass age from tracers such as CFC-11, CFC-12, tritium ($^3$H) and helium ($^3$He).
Several studies based on the back-calculation technique indicated that the ocean had absorbed between 30–40% of the total $C_{\text{ANT}}$ released into the atmosphere from the beginning of the industrial period (Siegenthaler and Sarmiento, 1993; Feely et al., 2001; Sarmiento and Gruber, 2002; Takahashi et al., 2002) whereas a more recent comprehensive analysis applying this approach has evidenced that the oceanic sink has accounted for $\sim$48% of the overall fossil-fuel and cement-manufacturing emissions (Sabine et al., 2004). These differences in $C_{\text{ANT}}$ estimation seem to be due to the various improvements introduced in the method over the last years. The work by Sabine et al. (2004) reported a global ocean anthropogenic CO$_2$ sink of 118±19 Pg C. This budget was later confirmed by Waugh et al. (2006) using the transit time distribution (TTD) method, a different approach proposed by Hall et al. (2002). Even though it appears that comparisons between $C_{\text{ANT}}$ estimates obtained with different methods show some substantial differences in both its exact number and spatial distribution (Vazquez-Rodriguez et al., 2008), the majority of the analysis performed up to date have agreed to conclude that the North Atlantic represents the oceanic region containing the highest vertically integrated concentrations of anthropogenic CO$_2$ (Lee et al., 2003; Key et al., 2004; Sabine et al., 2004; Waugh et al., 2006). This finding has been also confirmed by regional studies using either the back-calculation technique (Ríos et al., 2001; Perez et al., 2002) or an alternative $C_{\text{ANT}}$ assessment model, the TrOCA method, which considers the tracer TrOCA combining oxygen, inorganic carbon and total alkalinity (Touratier and Goyet, 2004a, b).

On the other hand, within the large-scale scenario of the global ocean as the major reservoir for $C_{\text{ANT}}$ storage, there have been certain areas traditionally excluded from carbon budget inventories. This has been the case of marginal seas, semi-enclosed seas and continental shelves, which were ignored due to the reduced number of accurate data available for these regions and the fact that their specific surface was considered insignificant in relation to the open ocean domain (Borges et al., 2006). Recently, the need to include the role of such areas in the capture of anthropogenic CO$_2$ has been recognized (IPCC, 2007), not only because of the magnitude of the biogeochem-
ical processes taking place in coastal margins but also because of the considerable human pressure that suffer. These two circumstances make these areas especially vulnerable to global change, and particularly those located in middle latitudes where seasonal temperature fluctuations markedly regulate the temporal dynamics of the carbon system.

Among these regions, it is a generally accepted opinion that the Mediterranean Sea plays a relevant role in the global circulation of the Atlantic Ocean (Hetch et al., 1997; Serra and Ambar, 2002; Carton et al., 2002), contributing significantly to the biogeochemical inventory of the North Atlantic (Dafner et al., 2001a; Dafner et al., 2003) and being recognized as a source of inorganic carbon for the Atlantic open ocean (Aît-Ameur and Goyet, 2006; de la Paz et al., 2008a). In fact, Ríos et al. (2001) showed that the $C_{ANT}$ advected by Mediterranean Water (MW) was the most important contributor to the total $C_{ANT}$ advected into the Eastern North Atlantic, representing 59%. Furthermore, a later study demonstrated that the transport of Mediterranean outflowing water (MOW) across the Gulf of Cádiz drove a considerable drawdown of $C_{ANT}$ in the region, assuming a $C_{ANT}$ concentration of 35 $\mu$mol kg$^{-1}$ associated to MOW passing through the Strait of Gibraltar (Álvarez et al., 2005). Applying the TrOCA tracer, Aît-Ameur and Goyet (2006) calculated the net export of $C_{ANT}$ from the Mediterranean Sea to the Atlantic Ocean through the Strait of Gibraltar, obtaining that the former constituted a significant source of anthropogenic CO$_2$ for the latter, because of the elevated $C_{ANT}$ concentration contained in the MOW. In addition, it is well established that the Mediterranean Sea is characterized by a high alkalinity (Santana-Casiano et al., 2002; Schneider et al., 2007; de la Paz et al., 2008a), being also supersaturated with respect to calcite and aragonite (Schneider et al., 2007). Moreover, results presented by Schneider et al. (2007) show that main alkalinity inputs come into the basin from the Black Sea along with river discharge whereas the Strait of Gibraltar behaves as a net sink for alkalinity mainly due to carbonate sedimentation. A recent study have pointed that the higher inorganic carbon concentration present in the MOW in relation to the Atlantic inflow (AI) as a result of the intense remineralization occurring in the Mediter-
ranean basin (Dafner et al., 2001b; Béthoux et al., 2005), is responsible for a net carbon transport to the North Atlantic, with the exchange being markedly sensitive to the interface definition between both water bodies (de la Paz et al., 2008a). Therefore, evidence from a variety of sources seems to indicate that the Mediterranean participates significantly in the export of carbon to the Atlantic, which would exacerbate the accumulation of $C_{\text{ANT}}$ into this carbon enriched region. Consequently, in the present context of global change, assessing carbon transport through the Strait of Gibraltar has become a relevant issue both for the Mediterranean environment and for ocean circulation and climate variability.

With the aim to quantify carbon exchange between the Atlantic and the Mediterranean and evaluate concomitantly the response of the Mediterranean basin to global change, a joint Spanish-Moroccan monitoring time series namely GIFT (Gibraltar Fixed Timeseries) has been implemented in the Strait of Gibraltar (CARBOOCEAN project; http://www.carboocean.org). Here, data obtained during more than two years of measurements (from May 2005 to July 2007) performed in the area are presented. This work then focuses on the dynamics of the inorganic carbon system in the Strait, analyzing the transport of $C_{\text{ANT}}$ that occurred between the Atlantic and the Mediterranean through different approaches and considering the mechanisms governing the carbon balance in this key oceanic node.

1.2 The study area

The Strait of Gibraltar is the only dynamically relevant connection of the Mediterranean Sea with the World’s Ocean. It is a narrow and shallow channel with an east–west orientation that possesses a minimum width of 14 km on the Tarifa Narrows (Fig. 1) and an average depth of about 600 m. Thirteen kilometers westward of the Tarifa Narrows lies the main bathymetric sill of the Strait, the Camarinal sill (CS, Fig. 1), with a maximum depth of about 285 m and a cross-area of about 7.86 km$^2$ (Guimerans et al., 1988). A second sill, the Espartel sill (ES, Fig. 1) is situated 21 km west of the former and has a maximum depth of 358 m (La Violette and Lacombe, 1988). The
circulation in the Strait has been classically described as a two-layer system: a surface eastward Atlantic water inflow (AI) and a deep westward outflow of saltier (and denser) Mediterranean water (MOW). In the long term, the former is slightly greater than the latter in order to balance the freshwater deficit of the Mediterranean basin.

Water exchange through the Strait is strongly influenced by a wide variety of mechanisms that present diverse frequency of variability, from daily to seasonal or interannual scale, such as tidal currents, winds or atmospheric pressure variations (García-Lafuente et al., 2002; Vargas et al., 2006). The AI is formed by the mixing of the North Atlantic Surface Waters (NASW, salinity about of 36.46), North Atlantic Central Water (NACW, salinity less than 36.06) and Spanish Coastal Water (with salinity <36.10), which is basically NASW residing in the continental shelf of the Gulf of Cadiz that has been modified by coastal processes (Criado-Aldeanueva et al., 2006). Similarly, the MOW is a mixture of intermediate and deep waters residing in the Mediterranean Sea, basically Levantine Intermediate Water (LIW) formed in the eastern Mediterranean basin, which flows across the Strait of Sicily into the western basin, and the Western Mediterranean Deep Water (WMDW) formed in the Gulf of Lions that occupies the bottom layer. Due to the complexity of the hydrodynamic processes within the Strait, water masses contributing to the AI or to the MOW appear either intermittently, as it is the case of the less abundant NACW in the AI (Gascard and Richez, 1985; Macías et al., 2006, 2008), or mixed in changing proportions throughout the year, as is the case of WMDW in the MOW (García-Lafuente et al., 2007), creating considerable spatial and temporal variations in the position and intensity of the water bodies. In addition, mixing and water entrainment between AI and MOW in the Strait originate an interfacial layer where oceanographic properties change gradually. This interfacial layer, often called Atlantic-Mediterranean interface (AMI), has a significant thickness and contributes appreciably to the exchanged flows (Bray et al., 1995). The AMI is characterized by a well-developed halocline through which salinity changes by about 2 units (Candela et al., 1989). However, the inverse-estuarine exchange can still be approximated as a two-layer system of reduced gravity $g \sim 0.02 \text{ m s}^{-2}$ and mean
net transport \( Q_0 = Q_A + Q_M \approx 0.05 \text{ Sv} \) (Sverdrups, 1 Sv=\(10^6 \text{ m}^3 \text{ s}^{-1}\)), equivalent to a net evaporation of 0.6 m yr\(^{-1}\) in the Mediterranean and where \( Q_A \) is positive and represents the AI transport and \( Q_M \) negative and equivalent to the MOW transport. In this work, this two-layer system scheme will be used for computation of carbon fluxes through the Strait and sub indices A and M will then designate the upper Atlantic layer and the lower Mediterranean layer, respectively.

It is worthy to point out that the complexity of the water circulation in the Strait of Gibraltar, particularly the strong tidal variability, complicates the assessment of the water fluxes through the channel (and the concomitant computation of exchange of substances) and debate has arisen traditionally about which site is the most adequate for monitoring the transport in the area. In fact, the high uncertainty associated to the estimation of the exchange of biogeochemical properties through the Strait has been attributed to the value of the water flux or transport that is used for computation (Gomez, 2003). For instance, values of water transport may vary significantly in the literature from 0.69/−0.65 Sv to 1.77/−1.73 Sv, with a broad range of values in between (Bryden et al., 1994; García-Lafuente et al., 2007). Many are the reasons behind these discrepant values, such as seasonal or inter-annual variations, an insufficient spatial or temporal coverage of the measurements, the omission of the interface movement, or inaccurate estimations of the balance between precipitation and evaporation in the Mediterranean Sea based on budget models. The value of water transport also depends on the section where the measurements are taken along with the salinity criteria chosen to determine the interfacial layer that limits both layers. Therefore, depending upon the magnitude of this key parameter, the exchange of any substance through the Strait of Gibraltar can exhibit variations of even 5-fold for an identical concentration of a given substance (Aït-Ameur and Goyet, 2006).
2 Material and methods

2.1 Time series of flows

In this study, ES section has been considered the reference spot for monitoring carbon exchange through the Strait. The selection criterion lies on the hydrodynamics of the area since at this particular section located on the Atlantic side of the Strait, tidal currents in the MOW layer are not strong enough to reverse the subinertial flow and consequently the fraction of MOW that returns to the Mediterranean basin can be considered negligible (García-Lafuente et al., 2007). Located at 35°51.7 N, 5°58.6 W (station 6 in Fig. 1), the permanent presence of a monitoring station allowed the acquisition of the complete bulk of data needed to assess \( Q_M \) during the monitoring period. The mooring, equipped with an uplooking Acoustic Doppler Current Profiler (ADCP), a point-wise currentmeter and an autonomous Conductivity-Temperature-Depth (CTD) probe located at 20 m, 15 m and 10 m above seafloor, respectively, was installed in September 2004 and it still records data continuously. More details of the instrumentation and mooring line are available in García-Lafuente et al. (2007). The transport of MOW (\( Q_M \)) through the Strait of Gibraltar after removing tidal contribution (the so-called subinertial flow) estimated at ES during the period of study, from May 2005 to July 2007, is plotted in Fig. 2. From this data series, it is evident that \( Q_M \) varies temporarily quite markedly, which may be attributed to the influence of processes with different timescales, from the meteorological and tidal-fortnightly time scale to the seasonal variability (García-Lafuente et al., 2007). These rapid and sudden fluctuations observed in the magnitude of the Mediterranean outflow might result in unrealistic values of the carbon fluxes through the Strait if instantaneous values of \( Q_M \) are used for computations, as both variables (water transport and inorganic carbon concentration) have been sampled at very different rates, which prevents the computation of realistic time series of carbon fluxes. Therefore, in order to minimize the considerable aliasing that would be introduced when calculating carbon exchange through the Strait an avoid misinterpretations, a mean value of \( Q_M \) has been used in this study, which was attained averaging...
the daily mean of the transport obtained from the complete bulk of data shown in Fig. 2 \((n=780)\). This yields an outflow of \(-0.85\pm0.13\) Sv, which is in good agreement with that previously reported in the area for another two years period, from October 2004 to October 2006 (García-Lafuente et al., 2007). From \(Q_M\) and taking into account the fresh water balance in the Mediterranean basin, the inflow of Atlantic water \(Q_A\) was also estimated. Calculations of the water transport were performed on both sides of the Strait (represented by stations 6 and 8, Fig. 1) with the aim of establishing a carbon balance in the area.

2.2 Sampling

In order to evaluate the exchange of carbon between the Mediterranean basin and the North Atlantic through the Strait of Gibraltar as one of the objectives of the CARBOOCEAN project, 8 stations (Fig. 1) were sampled periodically between May 2005 and July 2007 during nine campaigns conducted on board either the RV Al Amir Moulay Abdellah (8) or the BO García del Cid (1). The exact dates of the cruises and their identifying acronyms are indicated in Table 1. The 8 stations that constituted the fixed sampling grid were distributed in two perpendicular sections (Fig. 1): one that was formed by stations 1 to 5 \((5°44.04\text{ W}, 35°52.67\text{ N}), (5°44.36\text{ W}, 35°53.50\text{ N}), (5°44.75\text{ W}, 35°54.71\text{ N}), (5°45.33\text{ W}, 35°56.56\text{ N})\) and \((5°45.56\text{ W}, 35°58.53\text{ N})\) and the GIFT section that included the stations 6 \((5°58.60\text{ W}, 35°51.68\text{ N})\), 7 \((5°44.75\text{ W}, 35°54.71\text{ N})\) and 8 \((5°22.10\text{ W}, 35°59.19\text{ N})\). As indicated above, the GIFT leg has been established in the framework of the CARBOOCEAN Project as a timeseries where to assess the temporal variability of the carbon fluxes through the Strait of Gibraltar. Therefore, sampling and on going monitoring are still maintained. At each station, a temperature and salinity profile was obtained with a Seabird 911Plus CTD probe, followed by water sampling using oceanographic Niskin bottles within a rosette. Seawater samples were taken subsequently at five variable depths, which were selected on board according to the information provided by the CTD cast on the instant position of the AMI. This strategy was aimed at collecting samples within the different water bodies present in the Strait,
which permitted to acquire a proper vertical profile of the variables studied through the water column. Total alkalinity ($A_T$), pH, dissolved oxygen (DO) and inorganic nutrients were measured in the samples as explained below.

2.3 Measurements

2.3.1 Total alkalinity

Total alkalinity ($A_T$) was determined by titration of seawater using a potentiometric system as described in Pérez et al. (2000) with a Metrohm 794 Titoprocessor. Water samples were taken from the Niskin bottles in 500 mL borosilicate bottles and poisoned with 100 µL of a saturated aqueous solution of mercuric chloride for later shore-based analysis. The accuracy of the $A_T$ determination was assessed by regular measurements of Certified Reference Material (CRM, supplied by Andrew Dickson, Scripps Institution of Oceanography, La Jolla, CA, USA). The precision of the $A_T$ measurements on CRMs from 3 batches (batch # 70, 71 and 76) was ±0.59, 0.72 and 0.79 µmol kg$^{-1}$, respectively.

2.3.2 pH

The pH was measured by two different techniques. For campaigns CARBOGIB 1, 4, 5, 6, 7, 8 and GIFT3, pH was obtained following the spectrophotometric method of Clayton and Byrne (1993) using m-cresol purple as indicator, and consequently, the scale used was total. Samples were collected directly from the rosette in 10 cm path-length optical glass cells and measurements were carried out on board with a Shimadzu UV-2401PC spectrophotometer containing a 25°C-thermostated cells holder. Seawater, also previously thermostated to 25°C, was analyzed for a blank determination at 730, 578 and 434 nm and 50 µl of the dye was subsequently injected and the measurements repeated. Three photometric replicates were carried out for each injection in order to
remove any dye effect. The pH values were then calculated according to:

\[
pH = pK + \log\left(\frac{R - 0.0069}{2.222 - 0.133R}\right)
\]

where \(K_{\text{ind}}\) is the dissociation constant for the indicator and \(R\) is the ratio of indicator absorbencies at molar absorptivity maxima \(R=A578/A434\) that was corrected for base line absorbance at 730 nm. The method has a precision of ±0.003 pH units and measurements were shown to be internally consistent with other carbon dioxide measurements by using the above mentioned certified reference materials.

On the other hand, for campaigns CARBOGIB 2 and 3, pH was measured using a Metrohm 780 pH meter equipped with a combined glass electrode (Metrohm Model 6.0258.010) that included a temperature sensor, which was calibrated following the protocol described by Del Valls and Dickson (1998) with an accuracy of 0.004 pH units. The pH values were then obtained in SWS scale but they were subsequently transformed to total scale for consistency. Thus, all pH data shown in this work are then expressed in total scale at a temperature reference of 25°C. From such data and \(A_T\) values, the concentration of inorganic carbon \((C_T)\) was calculated afterward using the dissociation constants from Mehrbach et al. (1973) refitted by Dickson and Millero (1987).

2.3.3 Dissolved oxygen

Samples for dissolved oxygen (DO) measurements were withdrawn directly from the Nisking bottles in sealed flasks and stored in darkness for at least 24 h, as described by the Winkler method. Analysis was performed by potentiometric titration using a Metrohm 794 Titoprocessor, with an estimated error of ±1 µmol kg\(^{-1}\).

2.3.4 Nutrients

Three replicates of filtered seawater (12 mL, Whatman GF/F filters) were taken at each sampling station and stored at –20°C for inorganic nutrient concentration determination, which is required for the \(C_T\) calculation. Concentrations of nitrate, nitrite, phos-
phosphate and silicate were measured in the laboratory using a Skalar San++ System autoanalyser following the techniques of Strickland and Parson (1972).

2.4 Calculation of the anthropogenic carbon concentration

In this study, two methods have been used to calculate the concentration of anthropogenic carbon ($C_{ANT}$) in the water column along the Strait of Gibraltar: the back-calculation technique initially developed by Brewer (1978) and Chen and Millero (1979) and later improved by Gruber et al. (1996) and the TrOCA approach proposed by Touratier and Goyet (2004a, b).

According to the first method, $C_{ANT}$ has been estimated here as

$$C_{ANT} = C_T - AOU/R_C - 1/2 \left( A_T - A_T^0 + AOU/R_N \right) - C_{T278}^0 - \Delta C_{DIS},$$

where $C_T$ is the calculated dissolved inorganic carbon concentration in µmol kg$^{-1}$ and $AOU/R_C$ corresponds to the $C_T$ increase due to organic matter oxidation. Apparent Oxygen Utilization (AOU) was calculated with the oxygen saturation equation of Benson and Krause (UNESCO, 1986) and the stoichiometric coefficients $R_C$ ($-\Delta O_2/\Delta C$)=1.45 and $R_N$ ($-\Delta O_2/\Delta N$)=10.6 (Anderson and Sarmiento, 1994) were also used. Additionally, $1/2(A_T + AOU/R_N)$ accounts for the $C_T$ change due to CaCO$_3$ dissolution in deep ocean waters (Broecker and Peng, 1982), where $\Delta A_T$ is the total alkalinity variation from the initial value during water mass formation ($A_T^0$). $A_T^0$ stands then for preformed alkalinity and was calculated using the approach proposed by Pérez et al. (2002) for the Atlantic inflow and by Schneider et al. (2007) for the Mediterranean water. $C_{T278}^0$ corresponds to the initial $C_T$ of any water mass in the pre-industrial era, which is calculated from time-independent $A_T^0$ and the atmospheric CO$_2$ level (Neftel et al., 1994; Sarmiento et al., 1995) using the dissociation constants for carbonic acid of Merhbach et al. (1973) refitted by Dickson and Millero (1987). Finally, $\Delta C_{DIS}$ represents the disequilibrium term and stands for the air-sea CO$_2$ difference expressed in terms of $C_T$. For the Atlantic water, $\Delta C_{DIS}$ on density intervals of 26.8 and 27.1 calculated 1033
by Lee et al. (2003) in $-12 \pm 5 \mu$mol kg$^{-1}$ was used. As for the Mediterranean water, $\Delta C_{DIS}$ was obtained using the CFC data given by Rhein and Hinrichsen (1993). From CFC data, the age of the Mediterranean outflow was stabilized in 20 years, which sets $\Delta C_{DIS}$ in $0 \pm 5 \mu$mol kg$^{-1}$. $\Delta C_{DIS}$ was obtained for each sample by a mixing analysis.

This method for $C_{ANT}$ estimation is submitted to a number of uncertainties. Using an error propagation analysis as in Gruber et al. (1996) and Sabine et al. (1999), the maximum error associated with the $C_{ANT}$ calculation was $\pm 6 \mu$mol kg$^{-1}$ (Lee et al., 2003).

The second assessment applied to estimate $C_{ANT}$ in this study, the TrOCA approach (Touratier and Goyet, 2004a, b), was used in order to compare the results obtained with a previous estimation reported in the area based on such method (Aït-Ameur and Goyet, 2006). In particular, the latest version of the method as in Touratier et al. (2007) was considered. Thus, $C_{ANT(new\text{TrOCA})}$ has been computed using the following relationship

$$C_{ANT(new\text{TrOCA})} = \frac{(\text{TrOCA} - \text{TrOCA}^0)}{a},$$

(2)

where TrOCA represents a semi-conservative tracer calculated using DO, $A_T$, and $C_T$ as follows

$$\text{TROCA} = O_2 + a \left( C_T - \frac{1}{2} A_T \right),$$

and $\text{TrOCA}^0$ is similar to TrOCA without any anthropogenic contribution, i.e. the $\text{TrOCA}^0$ is defined as the pre-industrial TrOCA:

$$\text{TrOCA}^0 = e^{\left( b + c\theta + \frac{d}{A_T} \right)},$$

where $a$, $b$, $c$ and $d$ are the set of parameters established in Touratier et al. (2007).
3 Results

3.1 The carbon system parameters in the Strait of Gibraltar

The spatial distribution of the variables measured along the GIFT leg during the monitoring period is shown in Fig. 3, where values have been interpolated through the entire water column from the average of all data obtained at the five sampling depths in each station during the nine cruises conducted in the area (Table 1). In the westernmost part of the E–W section, corresponding to ES (station 6, Fig. 1), the MOW can be detected between 300 and 358 m depth, being characterized by temperatures close to 13°C (Fig. 3a) and maxima in salinity (>38 in Fig. 3b). These distinctive thermohaline properties have been earlier reported and define the outflowing of the Mediterranean water in the Strait (Santana-Casiano et al., 2002; García-Lafuente et al., 2007). The upper layer at ES, located between surface and about 200 m, is occupied by the NASW, which possesses 36.46 salinity (Fig. 3b) and high average temperatures between 18°C and 16°C (Fig. 3a). The interfacial layer between both water masses where binary mix occur, the AMI, is evidenced by the presence of a striking halocline, distinguishable throughout the whole channel of the strait (Fig. 3b). Also worth mentioning is the remarkable horizontal gradient of all properties between Camarinal and Espartel sills, which is the result of the enhanced mixing and turbulence related to the internal hydraulic jump formed during most tidal cycles downstream of Camarinal between both sills (Armi and Farmer, 1989; Weson and Gregg, 1994; Bruno et al., 2002). Actually, this energetic hydrodynamic feature induces sharper horizontal gradients than those showed in Fig. 3, which must be understood as a smoothed, time-averaged version of the actual pattern that, otherwise, is highly time dependent.

Considering this, it can be observed that the depth and thickness of the interface layer along the E-W section moves upwards toward the easternmost part of the Strait, shifting from 200 m at station 6 to around 75 m at station 8 (Fig. 3b), as the Atlantic water accelerates in the Camarinal Sill area and entrains the Mediterranean water. Due to mixing between Atlantic and Mediterranean waters, average temperature in the AMI
exhibits a range of variation of 2°C approximately, fluctuating from 15°C to 13°C and being also influenced by surface processes as it ascends, effect particularly noticeable at station 8 (Fig. 3a). Accordingly, MOW occupies a larger volume in the water column on the eastern side of the GIFT section and its presence is marked again by salinities higher than 38 and temperatures of 13°C, which occur at about 175 m in station 8 (Fig. 3a and b). Similarly, the occurrence of the diverse types of waters interacting in the Strait of Gibraltar can be derived from the analysis of the typical potential temperature-salinity (θ-S) plot shown in Fig. 4a. In this case, the complete bulk of data acquired in CTD casts performed at the 8 stations sampled during the 9 campaigns analysed in this work has been plotted. NASW is easily detected on the upper left side of the plot, with salinity nearly constant (~36.4) and temperature fluctuations of ~4°C, as a result of seasonal fluctuations due to heat fluxes through the sea surface. The salinity minimum in the lower left part (~36.0) is the footprint of the NACW. It is a recurrent signal in the westernmost station 6 that progressively fades out toward the east due to mixing and entrainment. MOW can be located in the lower right corner, with the AMI connecting both water bodies, as indicated by a change in salinity of about 2 units (Fig. 4a).

The water masses present in the area also show distinctive features in their carbonate properties (Fig. 3d–f). Along the Strait, DO, $A_T$, $pH_T$ and $C_T$ display a patent vertical gradient. As expected and regardless of the station considered, $O_2$ decreases with depth (Fig. 3c) whereas both $A_T$ and $C_T$ rise downward in the water column (Fig. 3d and f, respectively). In addition, $pH_T$ follows a pattern of diminution with depth, exhibiting a range of variation comprised between 8.037 in surface waters and 7.875 above the seafloor throughout the whole longitudinal section (Fig. 3e). A more comprehensive analysis of the pH variability in relation to salinity using data collected in the 8 stations during the whole monitoring period ($n=298$) provides a distribution (Fig. 4b) that mimics the shape of the θ-S plot (Fig. 4a), similarity that allows to assign a certain pH range to each water mass. As illustrated in Fig. 4b, NASW appearing at salinities of around 36.4 and shallower in the water column (Fig. 3b), is characterized by higher and greatly variable $pH_T$ values (ranging from 7.895 to 8.037), circumstance possibly
related to the biological processes taking place into the photic zone (as described in Macías et al., 2008) and to seasonal atmospheric variations that affect both mixing and evaporation. Furthermore, the exchanges of CO$_2$ with the atmosphere involve a modification of pH and although this effect is weak, the seasonal variability of the CO$_2$ fugacity described recently in the Strait (de la Paz et al., 2008b) may contribute slightly to the variation registered in the surface layer. A pH$_T$ minimum (7.849) is observed at the high saline deep waters ($S$>38) (Fig. 3e), reflecting the active remineralization of organic matter that takes place in the Mediterranean Sea (Copin-Montégut, 1993; Dafner et al., 2001b; Béthoux et al., 2005). The mixing in the interfacial layer and the influence of tidal processes on its position in the water column may be claimed as the responsible factors for the apparent scattering in the pH$_T$ values observed inside the AMI (Fig. 4b) due to the influence of the biological processes when the AMI reaches the photic zone. Nevertheless, the pH within this layer is still comprised in a narrow interval of variation, between 7.848 and 7.94 approximately.

Likewise, the distribution of both $A_T$ and $C_T$ presents a noticeable variability in the water column along the Strait. Thus, NASW contains the lowest $A_T$ and $C_T$ contents. In the easternmost part of the E–W section where the AI penetrates into the Mediterranean basin, $A_T$ fluctuates from 2381±5 to 2427±9 µmol kg$^{-1}$ between surface and 50 m depth whereas $C_T$ varies from 2100±6 to 2176±10 µmol kg$^{-1}$ inside the same layer (Fig. 3d and f, respectively). The $A_T$ concentrations measured and associated to the occurrence of NASW have been observed previously in the Strait of Gibraltar as well as in the nearby Gulf of Cadiz (Santana-Casiano et al., 2002; Aït-Amour and Goyet, 2006). Also, available $C_T$ values for the North East Atlantic Central Water (Rios et al., 1995, González-Dávila et al., 2003) are consistent with those reported here in the inflow of the Atlantic water passing through the Strait.

By contrast, the MOW is characterized by the highest $A_T$ and $C_T$ concentrations, as illustrated in Fig. 3d and f, respectively. In particular, the MOW recorded at station 6 yields a $A_T$ content of 2569±1.5 µmol kg$^{-1}$ and $C_T$ levels of 2314±2 µmol kg$^{-1}$ above the seafloor. The $A_T$ values found in this study reflect quite closely those measured
earlier in the outflowing of the Mediterranean water in the Strait (Aît-Ameur and Goyet, 2006) and in the Western Mediterranean (Schneider et al., 2007). Regarding $C_T$, it is worthy to mention that the consumption of inorganic carbon by photosynthesis within the photic layer also would contribute to the drop in $C_T$ detected in NASW as compared to the carbon-enriched MOW. In fact, Macías et al. (2008) recently described the presence of deep chlorophyll maxima in the Strait associated to the water interfaces, finding likely due to a reduction in their settling velocity caused by either the density gradient created by the strong halocline or modifications in turbulence levels (Ruiz et al., 2004).

Experimental data fully describing the carbonate system in the Mediterranean are available only at the DYFAMED station, situated in the northwest side of the basin and under a considerable influence of coastal processes. Moreover, no direct measurements of $C_T$ have been conducted in the Mediterranean and all the available data are based on indirect computations by using pH and $A_T$ measurements. Even so, and assuming these limitations in the assessment of inorganic carbon, $C_T$ concentrations reported by Pérez et al. (1986) for the western Mediterranean, Frankignoulle et al. (1990) for the LIW, Copin-Montégut and Begovit (2002) for DYFAMED and the satellite-based computations summarized in D’Ortenzio et al. (2008) for the whole Mediterranean are in good agreement to the values obtained in this study. $C_T$ levels provided here also match other estimates calculated in the MOW passing through the Strait of Gibraltar (Dafner et al., 2001a; Aît-Ameur and Goyet, 2006; de la Paz et al., 2008a). As already pointed out, because of the confluence of the two water bodies and the resulting mixing, all carbonate properties display a gradient within the AMI. This gradual change can be directly derived when a relationship between the alkalinity and salinity is established (Fig. 4c). In fact, a robust correlation between salinity and $A_T$ ($r^2=0.989$, $n=298$) is obtained, confirming that mixing is the main controlling factor for the variability of $A_T$ in the area. The linear relationship resulting from data acquired in the 8 stations sampled during the nine campaigns analysed in this work was found to be $A_T=92.98 \times S–993$, which is similar to other relationships found earlier in the Strait (Santana-Casiano et
al., 2002).

Concerning O$_2$ distribution along the Strait of Gibraltar (Fig. 3c), the AI contains O$_2$ concentrations that ranged from 251±6 to 216±5 µmol kg$^{-1}$ (from surface down to 52 m at station 8) whereas the MOW was characterised by lower O$_2$ levels, with a minimum of 184±2 µmol kg$^{-1}$ observed in the bottom layer (328 m) at station 6 (Fig. 3b). Due to mixing, the O$_2$ concentration progressively diminishes in depth within the AMI throughout the channel (Fig. 3c). These O$_2$ levels are again an indication of the active remineralization of organic matter occurring in the Mediterranean basin (Copin-Montégut, 1993; Dafner et al., 2001b; Béthoux et al., 2005).

3.2 Anthropogenic carbon in the Strait of Gibraltar

The anthropogenic carbon concentration in the Strait of Gibraltar has been calculated here using two different methods: the latest version of the TrOCA approach (Touratier et al., 2007) and the back-calculation technique (Gruber et al., 1996). Hence, the C$_{ANT}$ distribution along the GIFT leg obtained by both methods is illustrated in Fig. 5. Any of the method considered for C$_{ANT}$ computation provides a vertical dependence (Fig. 5a and b) that is more apparent when interpolated values obtained at both entrances of the Strait (stations 6 and 8) are plotted (Fig. 6c and d). However, results attained by both approaches reveal a complete opposite trend. According to the TrOCA method, the MOW is characterized by the highest C$_{ANT}$ concentrations (Fig. 5a), as observed at station 6 below 300 m depth (Fig. 6c). In particular, in waters of salinities >38 located at Espartell Sill, C$_{ANT}$ levels reach values higher than 72 µmol kg$^{-1}$, which gradually decline upwards in the water column (Fig. 5a). In the easternmost part of the Strait, C$_{ANT}$ concentration in MOW even increases (Fig. 5a) and values as high as 81±1.6 µmol kg$^{-1}$ ($n$=9) are attained in the bottom layer at station 8 (Figs. 5a and 6c). In contrast, the AI presents concentrations close to 65 µmol kg$^{-1}$, as observed in surface waters along the E–W section (Fig. 5a). Specifically, the AI that penetrates into the Mediterranean basin at station 8 contains C$_{ANT}$ values ranging from 71±7 µmol kg$^{-1}$
(n=9) at surface to 67±3 µmol kg⁻¹ (n=9) in the upper limit of the AMI (Fig. 6c), with an average value of 69 µmol kg⁻¹ within this layer. These differences in the $C_{\text{ANT}}$ content of Atlantic waters between the eastern and western sides obtained by the TrOCA approach have been attributed in the past to the influence of Mediterranean waters on the anthropogenic CO₂ content of the Atlantic Ocean as the former crosses the Strait (Aït-Ameur and Goyet, 2006). The entrainment that the fast AI exerts on the MOW in the eastern part (station 8) would increase the concentration of $C_{\text{ANT}}$ in the AI entering the Mediterranean Sea with regards to the $C_{\text{ANT}}$ concentration in the western entrance (station 6). This explanation, which would also account for the vertical gradient of $C_{\text{ANT}}$ through the AMI, has been already proposed by Aït-Ameur and Goyet (2006), who showed an identical distribution pattern, with MOW being also $C_{\text{ANT}}$ enriched although in their study, the calculated values for MOW reached concentrations as high as 111 µmol kg⁻¹.

On the contrary, when the back-calculation technique is used, $C_{\text{ANT}}$ content in the MOW drops to levels of about 50 µmol kg⁻¹ (Fig. 5b), with this concentration being specifically 49±0.6 µmol kg⁻¹ (n=9) below 300 m depth at station 6 (Fig. 6d). The $C_{\text{ANT}}$ concentration in Atlantic waters resembles that computed by the TrOCA approach as values remain close to 65 µmol kg⁻¹ within the NASW (Figs. 5b and 6d), but and conversely to the previous $C_{\text{ANT}}$ estimation, AMI is characterized by a manifest diminution of its $C_{\text{ANT}}$ concentration with depth, observation that is noticeable along the entire GIFT leg (Fig. 5b). Also, the $C_{\text{ANT}}$ pattern found by using the back-calculation technique is similar on both entrances of the Strait (Fig. 6d), with the vertical profile exhibiting a more homogeneous behaviour throughout the channel than that resulting from the TrOCA approach (Fig. 6c).

As the oceanic $C_{\text{ANT}}$ uptake is calculated by taking into account the inorganic carbon variation due to decomposition of organic matter ($C_{\text{bio}}$) and dissolution of particulate carbonates in the water column ($\text{CaCO}_3\text{diss}$), the contribution of these processes to the carbon balance in the Strait of Gibraltar has been also analysed (Fig. 5). Consequently, the $C_T$ resulting from $\text{CaCO}_3$ dissolution has been calculated (Fig. 6e) along with that
produced by the remineralisation of organic matter (Figs. 5d and 6f). Calculations were again made for the whole area, being also plotted on both sides of the Strait, represented by stations 6 and 8. Nevertheless, regardless of the station, it appears clear that CaCO₃ dissolution and \( C_{\text{bio}} \) are enhanced processes in the saltier and denser Mediterranean water (Fig. 5a and c). As shown in Fig. 6e, the input of carbon originated from carbonate dissolution in the easternmost part of the Strait ranges from 0 µmol kg\(^{-1}\) in near-surface waters corresponding to NASW to a maximum exceeding 20 µmol kg\(^{-1}\) in the MOW, being affected by the mixing with Atlantic waters inside the AMI upwards in the water column (around 75 m depth, Fig. 6b). This vertical pattern is also evident in the western entrance, although the internal hydraulics of the Strait that requires a west-to-east upward slope of the AMI (Fig. 3b) is responsible for the lower values attained at a same given depth (Fig. 6e). Another piece of evidence that confirms the occurrence of a small dissolution of hard material in the Mediterranean basin comes from the concentration of calcium ions that can be found throughout the Strait (Schneider et al., 2007). As illustrated in Fig. 5c, the spatial distribution of calcium along the GIFT leg reaches a maximum in the bottom layer where the MOW is detected, with NASW containing a much lower calcium concentration (Fig. 5c).

Similarly, the inorganic carbon originated from remineralisation of organic matter (\( C_{\text{bio}} \)) exhibits an analogous pattern on both sides of the Strait than that generated by carbonate dissolution, although concentrations of \( C_{\text{bio}} \) in the MOW are 2 fold higher than the levels of CaCO₃\(_{\text{diss}}\), with values reaching 40 µmol kg\(^{-1}\) in the bottom layer (Fig. 6f). The vertical profile of \( C_{\text{bio}} \) reflects the different oxidation state of the Atlantic waters in relation to the deeper Mediterranean waters (Figs. 5d and 6f) that experience a longer time in the basin unexposed to exchange with the atmosphere, which favours the deep degradation of organic matter. The O₂ concentration measured along the GIFT leg corroborates this feature (Fig. 3c).
3.3 Exchange of natural and anthropogenic carbon through the Strait of Gibraltar

In order to estimate the net transport of carbon through the Strait of Gibraltar, identification of the upper Atlantic layer and the lower Mediterranean layer is required. In addition, the interaction between inflow and outflow results in strong shear that induces vertical exchange between layers (Bray et al., 1995). Therefore, an interface definition is necessary to carry out a two-layer decomposition. However, as seen in Figs. 3b and 6b, the depth of the AMI varies significantly along the channel of the Strait and its position in the water column is under the influence of a wide variety of processes at a different time scale (García-Lafuente et al., 2002; Vargas et al., 2006). Taking into account previous works (García-Lafuente et al., 2002 and references therein) the interface is identified here by using fixed values of salinity as references. In particular, the limit between the two layers at the western entrance of the Strait (equivalent to station 6) was marked by a value of 37.0 whereas a salinity of 37.8 was adopted at the eastern entrance (equivalent to station 8) to discriminate between both layers. Water with salinity lower than the selected values was incorporated to the inflowing Atlantic layer and the respective portions of the water column with a higher salinity were included into the Mediterranean outflow. The net exchange or flux of $C_T$ ($F_N$) through the Strait of Gibraltar has been computed using the equation

$$F_N = F_M - F_A = (\rho_M \times Q_M \times C_T^M) - (\rho_A \times Q_A \times C_T^A),$$

where $F_M$ and $F_A$ represent the flux of total inorganic carbon in the Mediterranean and Atlantic layers, respectively, with $\rho$, $Q$ and $C_T$ standing for water density, volume transport and the $C_T$ concentration calculated in the two layers. Average concentrations of $C_T$ were used for both water masses (Table 2), taking into account the definition of the AMI established at stations 6 and 8 and the $C_T$ distribution obtained (Fig. 3f). Likewise, average densities of 1029 and 1027 kg m$^{-3}$ were taken for the MOW and for the AI, respectively (Table 2). The mean value of $Q_M$ of $-0.85$ Sv (Fig. 2) measured at Espartel sill during the monitoring period was used. There appears to be several different water transport estimates in the literature for this area since the water exchange through the
Strait of Gibraltar is affected by an ample variety of processes. Nonetheless, the value considered in this study is the most recent and appropriate since it has been computed from two years of observations that span the period of sampling. In addition, the $Q_M$ reported here coincides quite closely with that earlier provided by García-Lafuente et al. (2007) based on a prior data set. It must be mentioned however that north of the main ES channel there is a shallower, secondary channel through which a small fraction of the MOW could be flowing out. Recent numerical model of the Strait indicates that this fraction would be around 10% of the main bulk of MOW flowing out by the main channel where the monitoring station is located.

Using the above referred value of $Q_M$, the defined values of salinity that mark the separation between the two water layers and applying the mass conservation equation at both entrances of the Strait, the transport of the Atlantic water ($Q_A$) has been estimated (Table 2). Substituting in Eq. (3), the exchange of inorganic carbon through the Strait of Gibraltar is obtained. According to these calculations, a net transport of $C_T$ from the Mediterranean basin to the North Atlantic takes place (Table 2), with this output corresponding to $-67$ kmol C s$^{-1}$. Therefore, on annual basis, the net export of $C_T$ from the Mediterranean Sea through the Strait accounts for by $2.11$ Tmol C yr$^{-1}$ ($0.025$ Pg C yr$^{-1}$). All these estimates could be increased by 10% in order to account for the minor fluxes taking place through the northern channel of Espartel section.

An identical procedure has been applied to assess the exchange of $C_{ANT}$ through the Strait of Gibraltar, although in this case the average values of $C_{ANT}$ taken from the vertical profiles calculated by the two approaches used in this study (Fig. 6c and d) were introduced in Eq. (3). Results summarized in Table 2 indicate that when the backcalculation technique is considered for $C_{ANT}$ assessment, Atlantic waters constitute a considerable source of anthropogenic carbon to the Mediterranean basin and a net import of $11$ kmol $C_{ANT}$ s$^{-1}$ occurs, with an uncertainty of $1$ kmol s$^{-1}$ associated to the calculation. This influx corresponds to an annual input of $0.35$ Tmol $C_{ANT}$ ($4.2$ Tg C yr$^{-1}$) into the Mediterranean Sea.
In contrast, when the TrOCA approach is applied for $C_{\text{ANT}}$ estimation, the flux reverses and Atlantic waters receive a total amount of 0.25 Tmol $C_{\text{ANT}}$ yr$^{-1}$ from the Mediterranean (Table 2), with an uncertainty of 1.5 kmol s$^{-1}$. This output yields a net export of 3 Tg C yr$^{-1}$ through the Strait.

4 Discussion

Results presented in this study highlight the relevant role of the Strait of Gibraltar as a controlling point for the biogeochemical exchanges occurring between the Mediterranean Sea and the Atlantic Ocean and emphasize the influence of the Mediterranean basin in the carbon inventories of the North Atlantic. Data shown here arise from an extensive set of measurements collected during nine campaigns conducted in the area over a monitoring period of two years (Table 1). Therefore, our estimates are based on a comprehensive analysis of a broad time series that includes both physical and biogeochemical variables gathered in successive sampling cruises evenly distributed to cover a thorough temporal coverage.

According to the analysis performed, the most evident pattern of the carbon exchange through the Strait of Gibraltar is the export of $C_T$ from the Mediterranean Sea (Table 2). This behaviour of the Mediterranean as a source of $C_T$ for the Atlantic has been previously described in a number of papers (Dafner et al., 2001a; Aït-Ameur and Goyet, 2006; de la Paz et al., 2008b). Moreover, the net $C_T$ outflow of 2.11 Tmol C yr$^{-1}$ obtained here (Table 2) falls within the range of those reported in the aforementioned studies (even if increased by 10%), although substantial differences in the gross estimates are observed. In particular, assessments of $C_T$ exchange through the Strait vary from 3.8–4.9 Tmol C yr$^{-1}$ (Dafner et al., 2001a) to 1.64–5 Tmol C yr$^{-1}$ (Aït-Ameur and Goyet, 2006), with the most recent estimation proposed by de la Paz et al. (2008b) yielding a $C_T$ export to the Atlantic of 1.47 Tmol C yr$^{-1}$. Since $C_T$ concentrations reported formerly in the Strait (Dafner et al., 2001a; Santana-Casiano et al., 2002; de la Paz et al., 2008b) or in the MOW at the western entrance of the channel (Aït-Ameur...
and Goyet, 2006) are quite similar to those observed here (Fig. 3f, Table 2), the discrepancies existing between the carbon exchanges in the literature can be attributable to the values of the water transport associated to each water layer. High values of carbon exchange result when water transports given by Béthoux (1979) are used for fluxes computation, as already underlined by other authors (Gómez, 2003; Aït-Ameur and Goyet, 2006). This circumstance may be due to the fact that the early work by Béthoux (1979) did not consider properly the interface definition for calculations. Conversely, more similar values for the carbon exchange through the Strait are achieved when fluxes are estimated using either the transports provided by Baschek et al. (2001) or in situ measurements, such as those depicted in Fig. 2.

Figure 7 shows the diagram of the two-layers model of water mass exchange through the Strait of Gibraltar that has been used in this work to compute the carbon fluxes. Salinity values taken to define the interfacial layer on both sides of the Strait along with those derived from mixing analysis calculated along the GIFT leg are also illustrated. These values mark the balance of salinity in the Strait and considering the difference between the outflow and inflow in surface waters at stations 6 and 8, a water entrainment equivalent to 0.044 Sv is attained. Similarly, a vertical mixing of 0.13 Sv between the upper Atlantic layer and the lower Mediterranean layer can be derived from this balance, a value that is coherent with preceding calculations in the channel (Dafner et al., 2003). From this scheme and introducing in Eq. (3) the average of data resulting from the vertical profiles of alkalinity (Fig. 3d), CaCO$_3$$_{\text{diss}}$ (Fig. 5c) and $C_{\text{bio}}$ (Fig. 5d), the corresponding exchange of these variables through the Strait can be calculated (Table 2). This assessment allows establishing a carbon balance in the area (Fig. 7), which has been completed by adding the levels of dissolved organic carbon (DOC) provided by Dafner et al. (2001b).

As summarized in Table 2, a net alkalinity output of $-44$ kmol s$^{-1}$ (1.39 Tmol yr$^{-1}$) occurs through the Strait. This value is comprised between that given by Copin-Montégut (1993), who estimated a net alkalinity flux of $-77$ kmol s$^{-1}$ into the Atlantic, and the latest assessment of $-25$ kmol s$^{-1}$ reported by Schneider et al. (2007). Furthermore,
the alkalinity export presented here is much lower as compared to that of \(-60 \text{ kmol s}^{-1}\) provided by Santana-Casiano et al. (2002). Again, the most plausible explanation for the diversity of estimates available in the literature lies on the values of the water transports considered by the different authors. Thus, Copin-Montégut (1993) used the water balance described by Béthoux (1979) whereas Santana-Casiano et al. (2002) applies that given by Tsimpilis and Bryden (1999), both characterized by a high difference between Atlantic inflow and Mediterranean outflow. In contrast, Schneider et al. (2007) employ a \(Q_M\) of \(-0.72\text{ Sv}\) that is considerably much lower than that recorded in ES (Fig. 2), the most adequate spot for monitoring Mediterranean water transport (García-Lafuente et al., 2007). In fact, recalculating fluxes using the \(A_T\) concentrations measured by Schneider et al. (2007) and the \(Q_M\) of \(-0.85\text{ Sv}\) observed here, a net alkalinity export of \(-47 \text{ kmol s}^{-1}\) through the Strait is obtained, which strongly matches the alkalinity flux indicated in Table 2. This finding supports that is the water transport used for the final computation of fluxes through the Strait the main responsible factor for the discrepancies found between assessments.

The work by Schneider et al. (2007) also underlines that main alkalinity inputs come into the Mediterranean from the Black Sea and river discharge, which supply \(39 \text{ kmol s}^{-1}\) and \(41 \text{ kmol s}^{-1}\), respectively. Such estimates are in agreement with those mentioned in the prior study by Copin-Montégut (1993) who considered \(37 \text{ kmol s}^{-1}\) of alkalinity introduced in the basin from the Black Sea, with rivers being responsible for an entrance of \(53 \text{ kmol s}^{-1}\). This latter work also shows an organic matter supply of \(4 \text{ kmol s}^{-1}\) from the Black Sea to the Mediterranean, which is accompanied by organic carbon inputs of \(8 \text{ kmol s}^{-1}\) and \(5 \text{ kmol s}^{-1}\) from the rivers and the atmosphere. According to our calculations, an exportation of \(-35 \text{ kmol s}^{-1}\) (1.1 Tmol yr\(^{-1}\)) of inorganic carbon, originated from remineralization of organic matter within the Mediterranean basin, takes place through the Strait (Table 2). However, approximately 40% of this output is compensated by the entrance of \(14 \text{ kmol s}^{-1}\) of DOC from the Atlantic (Dafner et al., 2001b; Table 2). The rest of \(C_T\), originated by oxidation of organic matter, escaping through the Strait must then come from the Black Sea and rivers, although the con-
tribution of atmospheric deposition cannot be entirely ruled out. Using the net export of nitrate through the Strait given by Dafner et al. (2003), a consumption of 4 kmol s\(^{-1}\) of alkalinity is expected to be associated to the remineralization of the organic matter present in the Mediterranean Sea. In addition, the dissolution of calcium carbonate in the water column (−13 kmol s\(^{-1}\), Table 2 and Fig. 7) provides an alkalinity input equivalent to −26 kmol s\(^{-1}\) in the Mediterranean. Therefore, if the alkalinity budget for the Mediterranean Sea described in Schneider et al. (2007) is taken into account, which considers a joint alkalinity entrance of 80 kmol s\(^{-1}\) into the basin from the Black Sea and rivers, and the change in alkalinity due to both the consumption of organic matter and carbonate dissolution obtained here is accounted, −58 kmol s\(^{-1}\) of the alkalinity measured in the Mediterranean do not reach the Atlantic. The most likely candidate for this loss of alkalinity is CaCO\(_3\) sedimentation, which would consequently account for by 29 kmol s\(^{-1}\) inside the water column. According to Schneider et al. (2007), the alkalinity loss via carbonate sedimentation corresponds to a surface calcification rate of 0.38 mol m\(^{-2}\) yr\(^{-1}\), which amounts to 16 kmol s\(^{-1}\) of CaCO\(_3\) that precipitate. Therefore, the remaining 13 kmol s\(^{-1}\) of CaCO\(_3\) would dissolve in the water column before the MOW crosses the Strait, resulting in the alkalinity input of 26 kmol s\(^{-1}\) recorded here due to such process (Table 2) and where 4 kmol s\(^{-1}\) were consumed for organic matter remineralization as explained above. This inventory implies that approximately 22 kmol s\(^{-1}\) out of the net alkalinity flux of −44 kmol s\(^{-1}\) recorded through the Strait must have a riverine origin. This budget is coherent with the very high downward carbonate fluxes measured recently in the NW Mediterranean close to the coast (Martin et al., 2006). In parallel, the CaCO\(_3\) formation in surface waters nearby coastal regions would favour a rise in the oceanic \(pCO_2\). Our estimates points to a CO\(_2\) outgassing of 19 kmol s\(^{-1}\) to the atmosphere due to settling of CaCO\(_3\) particles, assuming that \(pCO_2\) is maintained in equilibrium with the atmospheric CO\(_2\) levels (Copin-Montégut, 1993).

The net exchange of −67 kmol s\(^{-1}\) of \(C_T\) through the Strait concordant with previous calculations (Aït-Ameur and Goyet, 2006; de la Paz et al., 2008b) is estimated in this study including the input of anthropogenic carbon. If the import of Atlantic \(C_{ANT}\) towards
the Mediterranean equivalent to 11 kmol s\(^{-1}\) (Table 2, Fig. 7) is considered, a natural export of 78 kmol s\(^{-1}\) of \(C_T\) would be then obtained. Nevertheless, 45% of such an export originates from the remineralization of organic matter within the Mediterranean, which corresponds to an oxygen consumption of 49 kmol s\(^{-1}\) (Fig. 7). Consequently, the resulting budget once the continental supply of inorganic carbon, the \(\text{CaCO}_3\) precipitation and the air-sea \(\text{CO}_2\) exchange are combined, accounts for the rest of the carbon balance. The first process integrates the \(C_T\) that is introduced into the Mediterranean by both the Black Sea and the rivers, which amounts to 77 kmol s\(^{-1}\) (Schneider et al., 2007).

Accordingly, the corresponding \(C_{\text{ANT}}\) storage in the Mediterranean Sea can be calculated by using the rates of increase of the anthropogenic carbon in equilibrium with the atmosphere, the average area of the Mediterranean Sea (2.5\(\times\)10\(^{12}\) m\(^2\), Menard and Smith, 1966) and the mean penetration depth (MPD, Broecker et al., 1979), which is defined as the quotient between the \(C_{\text{ANT}}\) water column inventory and the \(C_{\text{ANT}}\) concentration in the mixed layer (assuming a fully \(\text{CO}_2\) equilibrated mixed layer keeping pace with the \(\text{CO}_2\) atmospheric increase). Given that the mean depth of the Mediterranean corresponds to 1370 m and the fact that the basin constitutes a region for deep water mass formation, it can be assumed that the majority of the water volume experiences an increase in anthropogenic carbon of 0.7±0.1 \(\mu\text{mol kg}^{-1}\) yr\(^{-1}\). This \(C_{\text{ANT}}\) storage leads to a rate of 78±10 kmol s\(^{-1}\), implying an air-sea \(C_{\text{ANT}}\) uptake of 67±9, equivalent to an annual drawdown of 0.8±0.1 mol m\(^{-2}\) yr\(^{-1}\).

It is worthy to point out that the computed balances are based on \(C_{\text{ANT}}\) estimations performed by using the back-calculation technique. When the TrOCA approach is applied the exchange tendency reverses and the Mediterranean behaves as a net source of anthropogenic carbon to the Atlantic. A net export of \(-8\) kmol s\(^{-1}\) of \(C_{\text{ANT}}\) through the Strait is then attained (Table 2), which is equivalent to 0.003 Pg C yr\(^{-1}\). This amount is one order of magnitude lower than the previous estimate reported in the area by Aït-Ameur and Goyet (2006) using the same approach for \(C_{\text{ANT}}\) computation.

The discrepancy found between both methods may lay probably on the formula-
tion that each assessment considers for water age calculation. Basically, the TrOCA method applies a global equation that is a function of $\theta$ and total alkalinity measured in situ (Eq. 2) whereas the back-calculation technique includes the computation of the pre-industrial carbon level and the disequilibrium due to the air-sea CO$_2$ difference (Eq. 1), which are adapted regionally considering the formation of each particular water mass. Thus, according to Rhein and Hinrichsen (1993), the age of the MOW that crosses the Strait coming from the Alboran Sea is estimated in 14–20 years, being characterised by low concentrations of CFC and oxygen levels below saturation. The $C_{\text{ANT}}(C')$ profiles obtained in this work (Figs. 5b and 6d) decrease with depth as does oxygen concentration (Fig. 3c), in agreement with the CFCs vertical distribution provided by Rhein and Hinrichsen (1993) in the Mediterranean. This semi-enclosed sea is characterized by an inverse circulation where surface waters nearly saturated of gases sink, circulate around the basin to finally return to the North Atlantic after crossing the Strait. Therefore, the outflowing water that has experienced a long residence time in the Mediterranean basin prevented from any contact with the atmosphere is expected to contain lower levels of CFC and CO$_2$ than those present in the current surface water, as the former was exposed to a less anthropogenic carbon enriched atmosphere. The change in oxygen concentration with time in the water column is caused by remineralisation process although its impact on $C_{\text{ANT}}$ is already taken into account in the computation (as provided in Eq. 1). In contrast, $C_{\text{ANT(newTrOCA)}}$ profiles augment downward in the water column (Figs. 5a and 6c), resulting in higher concentrations of anthropogenic carbon than the theoretical $C_{\text{ANT}}$ content in saturation with the present atmospheric level. Therefore, the vertical gradient of $C_{\text{ANT}}$ should not be expected to rise with depth, as that would turn in reaching a superior concentration than that contained in water recently equilibrated with the atmosphere. An adaptation of the TrOCA approach to the Mediterranean water residence time would possibly fade the discrepancy detected.

Until now, the export of inorganic carbon from the Mediterranean Sea through the Strait of Gibraltar was assumed to contribute significantly to $C_{\text{ANT}}$ enrichment in the
North Atlantic (Álvarez et al., 2005; Aït-Ameur and Goyet, 2006). Results presented here support those prior observations and explicitly demonstrate that the exchange of both water masses through the Strait alleviates the accumulation of $C_{\text{ANT}}$ in the Atlantic basin but this process exacerbates simultaneously $C_{\text{ANT}}$ storage into the Mediterranean. Regardless of the approach used for $C_{\text{ANT}}$ estimation, the data analysed in this study indicate that the Mediterranean plays a fundamental role in the capture of anthropogenic carbon, contributing to its storage in a dense layer which in the long term feeds the deep circulation of the North Atlantic. Hence, the fact that the Mediterranean Sea gains $C_{\text{ANT}}$ does not contradict its final function as a pump that injects $C_{\text{ANT}}$ within deeper Atlantic regions. The approach applied results in different net values but this only affects the magnitude of the drawdown but not its ultimate fate. According to the back calculation technique, the sequestered $C_{\text{ANT}}$ would be equivalent to 80% of the saturation level whereas the $C_{\text{ANT}}$ obtained by the TrOCA tracer would support an export of $C_{\text{ANT}}$ in excess with the saturation value. Using early data reported in the Alboran Sea by Millero et al. (1979) a concentration of $27\pm7$ kmol s$^{-1}$ of $C_{\text{ANT}}$ in the Mediterranean can be obtained at that time, which represents a 71% of saturation ($\pm14$) with respect to $C_{\text{ANT}}$ in equilibrium with the atmosphere twenty years ago, in good agreement with our estimates at present and seems to confirm the computed vertical decreasing gradient.

5 Conclusions

The Strait of Gibraltar constitutes the only connection of the Mediterranean Sea with the Atlantic Ocean. Previous works have indicated the relevant role played by the Mediterranean in the global circulation of the Atlantic (Hetch et al., 1997; Serra and Ambar, 2002; Carton et al., 2002), in its biogeochemical inventory (Dafner et al., 2001a; Dafner et al., 2003) and in its carbon content (Aït-Ameur and Goyet, 2006; Alvarez et al., 2005). Results presented in this work highlight the significance of the Strait as a key area for evaluating the interactions between both oceanic regions, and particularly in
the current context of global change. The extensive analysis performed using data gathered during the development of nine cruises evenly distributed over a two years period in conjunction with continuous measurements of the transport of the outflow of Mediterranean water through the Strait of Gibraltar provides a comprehensive view of the carbon exchange occurring in this area. According to our estimates, a net export of inorganic carbon equivalent to 0.025 Pg C yr$^{-1}$ takes place from the Mediterranean Sea to the Atlantic Ocean whereas an annual flux of 4.2 Tg $C_{\text{ANT}}$ towards the Mediterranean basin can be detected. This study also underlines the necessity to maintain measurements of both water transport and carbon system parameters in the area with the aim to compute possible variations in the carbon inventories of the Atlantic and the Mediterranean. In this sense, the GIFT timeseries established in the frame of the CARBOOCEAN project constitutes a powerful tool for monitoring future changes expected to proceed in the biogeochemical cycles of both ocean regions in response to the anthropogenic pressure.

Acknowledgements. The excellent co-operation of the captains and the crews of R/V Al Amir Moullay Abdellah and BO Garcia del Cid are gratefully acknowledged. We also thank M. Ferrer-Marco, A. Agouzouk, M. Castaño and M. Arjonilla for collection and measurement of the samples and G. Navarro for helpful discussions. Mrs. S. Zizah kindly assisted in project management. Funding for this work was provided by the CARBOOCEAN IP of the European Commission (511176GOCE) and by the Spanish Ministry of Education and Sciences (CTM2006-26206-E/MAR and CTM2006-27116-E). Authors JGL and ASR acknowledge the financial support of the Spanish Ministry of Education and Science through projects REN2003-01618/MAR and CTM2006-02326/MAR in whose frame the ES monitoring station is presently collecting data.

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Table 1. Acronyms and sampling dates of the campaigns conducted in the Strait of Gibraltar under the umbrella of the CARBOOCEAN Project.

<table>
<thead>
<tr>
<th>Campaign ID</th>
<th>Date</th>
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<tbody>
<tr>
<td>CARBOGIB1</td>
<td>02–05 May 2005</td>
</tr>
<tr>
<td>CARBOGIB2</td>
<td>07–09 September 2005</td>
</tr>
<tr>
<td>CARBOGIB3</td>
<td>12–14 December 2005</td>
</tr>
<tr>
<td>CARBOGIB4</td>
<td>20–22 March 2006</td>
</tr>
<tr>
<td>CARBOGIB5</td>
<td>21–23 May 2006</td>
</tr>
<tr>
<td>GIFT3</td>
<td>23–24 November 2006</td>
</tr>
<tr>
<td>CARBOGIB6</td>
<td>13–15 December 2006</td>
</tr>
<tr>
<td>CARBOGIB7</td>
<td>07–08 May 2007</td>
</tr>
<tr>
<td>CARBOGIB8</td>
<td>04–05 July 2007</td>
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Table 2. Concentration of the carbon system parameters on both sides of the Strait of Gibraltar, represented by stations 6 and 8 for the western and the eastern entrance, respectively. The net flux of each parameter through the Strait is also indicated. The mean Mediterranean water transport ($Q_M$) measured at Espartell sill during the monitoring period (from May 2005 to July 2007) has been used for computation of fluxes (more details are given in the text). Uncertainty associated to the calculations is shown.

<table>
<thead>
<tr>
<th>Station ID</th>
<th>Water Mass Signature</th>
<th>Density ($kg m^{-3} 10^{-3}$)</th>
<th>$Q$ (Sv)</th>
<th>$A_T$ (µmol kg$^{-1}$)</th>
<th>$C_T$ (µmol kg$^{-1}$)</th>
<th>$\Delta C_{CaCO_3}^{diss}$ (µmol kg$^{-1}$)</th>
<th>$\Delta C_{bio}$ (µmol kg$^{-1}$)</th>
<th>$C_{ANT(new+POCA)}$ (µmol kg$^{-1}$)</th>
<th>$C_{ANT(C^-)}$ (µmol kg$^{-1}$)</th>
<th>DOC$^a$ (µmol kg$^{-1}$)</th>
<th>Uncertainty (kmols$^{-1}$)</th>
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</thead>
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<tr>
<td>6 NASW</td>
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<td>0.89</td>
<td>2380</td>
<td>2116</td>
<td>2</td>
<td>2</td>
<td>64</td>
<td>60</td>
<td>59</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
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<td>−0.85</td>
<td>2547</td>
<td>2296</td>
<td>17</td>
<td>42</td>
<td>78</td>
<td>51</td>
<td>45</td>
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<td>0.3</td>
</tr>
<tr>
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<td>0.85</td>
<td>2403</td>
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<td>5</td>
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<td>2331</td>
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<td>Uncertainty (kmols$^{-1}$)</td>
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</tbody>
</table>

$^a$ Data taken from Dafner et al. (2001).
Fig. 1. The Strait of Gibraltar bathymetry and the grid of stations sampled during cruises performed from May 2005 to July 2007. CS and ES indicate the location of the sills of Camarinal and Espartel, respectively.
Fig. 2. Time series of the Mediterranean water transport ($Q_M$) measured in ES section from May 2005 to July 2007. Solid line marks the average value of all data included in the plot, equivalent to $-0.85$ Sv.
Fig. 3. Distribution of (A) potential temperature ($\theta$, °C), (B) salinity, (C) dissolved oxygen (DO, $\mu$mol kg$^{-1}$), (D) alkalinity ($A_T$, $\mu$mol kg$^{-1}$), (E) pH$_T$ and (F) total inorganic carbon ($C_T$, $\mu$mol kg$^{-1}$) along the GIFT leg in the Strait of Gibraltar. Data represent the average values obtained in nine campaigns (more details in the text).
Fig. 4. Potential temperature-salinity plot (A), pH$_T$ at 25°C-salinity diagram (B) and alkalinity ($A_T$) as a function of salinity (C) in the Strait of Gibraltar. The line with the equation $A_T = 92.95S - 993$ ($n=297$; $r^2=0.989$) results from linear regression in (C).
Fig. 5. Distribution of (A) anthropogenic carbon estimated by the TrOCA approach ($C_{\text{ANT(newTrOCA)}}$, $\mu$mol kg$^{-1}$), (B) anthropogenic carbon calculated the back-calculation technique ($C_{\text{ANT(C)}}$, $\mu$mol kg$^{-1}$), (C) CaCO$_3$ dissolution (Ca, $\mu$mol kg$^{-1}$) and (D) inorganic carbon resulting from remineralization of organic matter ($C_{\text{bio}}$, $\mu$mol kg$^{-1}$) along the GIFT leg in the Strait of Gibraltar. Data represent the average values obtained in nine campaigns (more details in the text).
Fig. 6. Vertical profiles of (A) potential temperature ($\theta$, °C), (B) salinity, (C) anthropogenic carbon estimated by the TrOCA approach ($C_{\text{ANT(newTrOCA)}}$, $\mu$ mol $\text{kg}^{-1}$), (D) anthropogenic carbon calculated the back-calculation technique ($C_{\text{ANT(C*)}}$, $\mu$mol $\text{kg}^{-1}$), (E) inorganic carbon resulting from CaCO$_3$ dissolution (CaCO$_3$$_{\text{diss}}$, $\mu$mol $\text{kg}^{-1}$) and (F) inorganic carbon resulting from remineralization of organic matter ($C_{\text{bio}}$, $\mu$mol $\text{kg}^{-1}$) at stations 6 (black symbols) and 8 (open symbols) of the GIFT leg in the Strait of Gibraltar. Data represent the average values obtained in nine campaigns and have been interpolated through the water column (more details in the text).
Fig. 7. Diagram of the two-layer model of water mass exchange through the Strait of Gibraltar. Values of the next fluxes of alkalinity ($F_{N_A}$), inorganic carbon ($F_{N_C}$), dissolved organic carbon ($F_{N_{DOC}}$), anthropogenic carbon calculated with the back-calculation technique ($F_{N_{C_{ANT(C)}}}$) and inorganic carbon resulting from remineralization of organic matter ($F_{N_{C_{bio}}}$) that take place between the Atlantic Ocean and the Mediterranean Sea are indicated on the dash line. Precipitation rate of CaCO$_3$ in the Mediterranean basin is also shown, along with air-sea transfers of O$_2$ and CO$_2$ according to the carbon budget considered (more details in the text). Water transports, entrainment and mixing between the Atlantic and Mediterranean waters are given as well as salinity values on both sides of the Strait and those used to establish the limit between the two layers at stations 6 and 8.