

Anthropogenic and natural CO₂ exchange through the Strait of Gibraltar

I. E. Huertas¹, A. F. Ríos², J. García-Lafuente³, A. Makaoui⁴, S. Rodríguez-Gálvez¹, A. Sánchez-Román³, A. Orbi⁴, J. Ruíz¹, and F. F. Pérez²

¹Instituto de Ciencias Marinas de Andalucía, (CSIC), Polígono Río San Pedro, s/n, 11519, Puerto Real, Cádiz, Spain

²Instituto de Investigaciones Marinas, (CSIC), Eduardo Cabello, 6, 36208, Vigo, Spain

³Departamento de Física Aplicada II, Universidad de Málaga, Campus de Teatinos, s/n, Málaga, Spain

⁴Institut National de Recherche Halieutique, (INHR), rue de Tiznit, 2, Casablanca, Morocco

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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 using two methods, the ΔC^* and the TrOCA approach. Applying a two-layer model of water mass exchange through the Strait and using a value of -0.85 Sv for the average 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 25 ± 0.6 Tg C yr⁻¹. A net alkalinity output of 16 ± 0.6 Tg C yr⁻¹ was also observed to occur through the Strait. 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 4.20 ± 0.04 Tg C yr⁻¹ by using the ΔC^* method, which constituted the most adequate approach for this environment. A carbon balance in the Mediterranean was assessed and fluxes through the Strait are discussed in relation to the highly diverse estimates available in the literature for the area and the different approaches considered for C_{ANT} estimation. 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 remain 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 CO₂ (Sabine et al., 2004; Waugh et al., 2006). The ocean absorption of CO₂ contributes to moderate future climate change, but this behavior as a carbon reservoir will however result in deleterious consequences for the marine environment. Quantifying the concentration and distribution of anthropogenic carbon (C_{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 CO₂ world. Accordingly, over the past decade, considerable efforts have been devoted to assess the capacity of the ocean to sequester



Correspondence to: I. E. Huertas
(emma.huertas@icman.csic.es)

CO₂ and the predicted changes brought about by the associated acidification. Nevertheless, the computation of C_{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_{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 CO₂ 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 (³H) and helium (³He). A recent comprehensive analysis based on this method (Δ C* hereafter) has evidenced that the oceanic sink has accounted for ~48% of the overall fossil-fuel and cement-manufacturing emissions and reported a global ocean anthropogenic CO₂ sink of 118±19 PgC (Sabine et al., 2004). This budget was later confirmed by Waugh et al. (2006) using the transit time distribution (TTD) method, a different approach proposed earlier (Thomas et al., 2001; Hall et al., 2002). Even though it appears that comparisons between C_{ANT} estimates obtained with different methods show some substantial differences in both its exact number and spatial distribution (Vázquez-Rodríguez et al., 2009), 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 CO₂ (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; Pérez et al., 2002) or an alternative C_{ANT} assessment model, the TrOCA method, which considers the tracer TrOCA combining oxygen, inorganic carbon and total alkalinity (Touratier and Goyet, 2004b).

On the other hand, within the large-scale scenario of the global ocean as the major reservoir for C_{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 CO₂ has been recognized (IPCC, 2007), not only because of the magnitude of the biogeochemical processes taking place in coastal margins but also because of the considerable human pressure they 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 (Hecht 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 (Ait-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 draw-down of C_{ANT} in the region, assuming a C_{ANT} concentration of 35 μmol kg⁻¹ associated to MOW passing through the Strait of Gibraltar (Álvarez et al., 2005). Applying the TrOCA tracer, Ait-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 CO₂ 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, with carbonate sedimentation appearing to be the major sink for alkalinity. A recent study has 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 Mediterranean 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_{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;

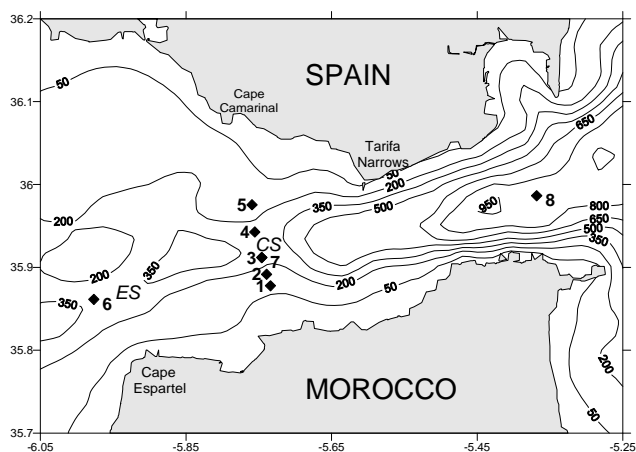


Fig. 1. The Strait of Gibraltar bathymetry and the grid of stations sampled during cruises performed from May 2005 to July 2007. CS and ES indicate the location of the sills of Camarinal and Espartel, respectively.

<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 in the Strait, analyzing the transport of C_{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 km² (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 subjected to the influence of different 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 Water (NASW, salinity of about 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 with mean net transport $Q_0 = Q_A + Q_M \approx 0.05$ Sv (Sverdrups, $1 \text{ Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$), equivalent to a net evaporation of 0.6 m y^{-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

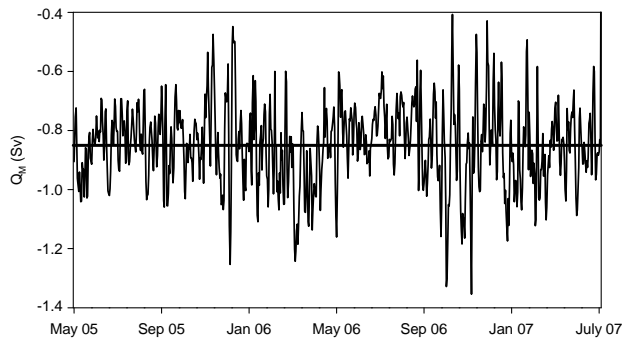


Fig. 2. Time series of the Mediterranean water transport (Q_M) measured in ES section from May 2005 to July 2007. The plotted transport data correspond to daily means during the monitoring period. Solid and horizontal line marks the average value of all data, equivalent to -0.85 Sv.

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 (Ait-Ameur and Goyet, 2006).

2 Material and methods

2.1 Time series of flows

In this study, ES station 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 place located of the Atlantic side of the Strait, tidal currents in the MOW layer are not strong enough to reverse the subinertial flow that is due to tidal effect and consequently the fraction of MOW that returns to the Mediterranean basin can be considered negligible (García-Lafuente et al., 2007). Located at $35^\circ 51.7$ N, $5^\circ 58.6$ 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 above 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 temporary 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 and 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 ± 0.13 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 by considering the net annual evaporation mentioned above, 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 exchange in the area.

3 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 ($5^\circ 44.04$ W, $35^\circ 52.67$ N), ($5^\circ 44.36$ W, $35^\circ 53.50$ N), ($5^\circ 44.75$ W, $35^\circ 54.71$ N), ($5^\circ 45.33$ W, $35^\circ 56.56$ N) and ($5^\circ 45.56$ W, $35^\circ 58.53$ N) and the GIFT section that included the stations 6 ($5^\circ 58.60$ W, $35^\circ 51.68$ N), 7 ($5^\circ 44.75$ W, $35^\circ 54.71$ N) and 8 ($5^\circ 22.10$ W, $35^\circ 59.19$ 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,

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

Campaign ID	Date
CARBOGIB1	2–5 May 2005
CARBOGIB2	7–9 September 2005
CARBOGIB3	12–14 December 2005
CARBOGIB4	20–22 March 2006
CARBOGIB5	21–23 May 2006
GIFT3	23–24 November 2006
CARBOGIB6	13–15 December 2006
CARBOGIB7	7–8 May 2007
CARBOGIB8	4–5 July 2007

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.

3.1 Measurements

3.1.1 Total alkalinity

Total alkalinity (A_T) was determined by titration of seawater using a potentiometric system as described in Mintrop et al. (2002) with a Metrohm 794 Titoprocessor. Water samples were taken from the Niskin bottles in 500 mL borosilicate bottles and poisoned with 100 μ L 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 Prof. Andrew Dickson, Scripps Institution of Oceanography, La Jolla, CA, USA). The accuracy of the A_T measurements on CRMs from 3 batches (batch # 70, 71 and 76) was ± 0.59 , 0.72 and 0.79 $\mu\text{mol kg}^{-1}$, respectively.

3.1.2 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 μ l of the dye was sub-

sequently 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:

$$\text{pH} = pK_{\text{ind}} + \log(R - 0.0069)/(2.222 - 0.133R)$$

where K_{ind} is the dissociation constant for the indicator and R is the ratio of indicator absorbencies at molar absorptivity maxima ($R=A_{578}/A_{434}$) that was corrected for base line absorbance at 730 nm. The method has an accuracy 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).

3.1.3 Dissolved oxygen

Samples for dissolved oxygen (DO) measurements were withdrawn directly from the Niskin 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 $\pm 1 \mu\text{mol kg}^{-1}$.

3.1.4 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, phosphate and silicate were measured in the laboratory using a Skalar San⁺⁺ System autoanalyser following the techniques of Strickland and Parson (1972).

3.2 Calculation of the anthropogenic carbon concentration

In this study, two methods have been used to calculate the concentration of 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) (the ΔC^* method) and the TrOCA approach proposed by Touratier and Goyet (2004a).

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

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

where C_T is the calculated dissolved inorganic carbon concentration in $\mu\text{mol kg}^{-1}$ 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 ($-\Delta\text{O}_2/\Delta\text{C}$)=1.45 and R_N ($-\Delta\text{O}_2/\Delta\text{N}$)=10.6 (Anderson and Sarmiento, 1994) were also used. Additionally, $1/2 (\Delta A_T + AOU/R_N)$ accounts for the C_T change due to CaCO_3 dissolution in deep ocean waters (Broecker and Peng, 1982), where ΔA_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 CO₂ level (Neftel et al., 1994; Sarmiento et al., 1995) using the dissociation constants for carbonic acid of Merzbach et al. (1973) refitted by Dickson and Millero (1987). Finally, ΔC_{DIS} represents the disequilibrium term and stands for the air-sea CO₂ difference expressed in terms of C_T . For the Atlantic water, ΔC_{DIS} on density intervals of 26.8 (NASW) and 27.1 (NACW) calculated by Lee et al. (2003) in $-12 \pm 5 \mu\text{mol kg}^{-1}$ was used. As for the Mediterranean water, ΔC_{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 ΔC_{DIS} in $0 \pm 5 \mu\text{mol kg}^{-1}$. ΔC_{DIS} was obtained for each sample by a mixing analysis using as endmembers the disequilibrium at the salinity maximum of 38.5, corresponding to the MOW, and those of the Atlantic, NASW and NACW. 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 $\pm 6 \mu\text{mol kg}^{-1}$ (Lee et al., 2003).

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

$$C_{ANT(\text{newTrOCA})} = \frac{(\text{TrOCA} - \text{TrOCA}^0)}{a}, \quad (2)$$

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

$$\text{TrOCA} = \text{O}_2 + a \left(C_T - \frac{1}{2} A_T \right),$$

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

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

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

4 Results

4.1 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

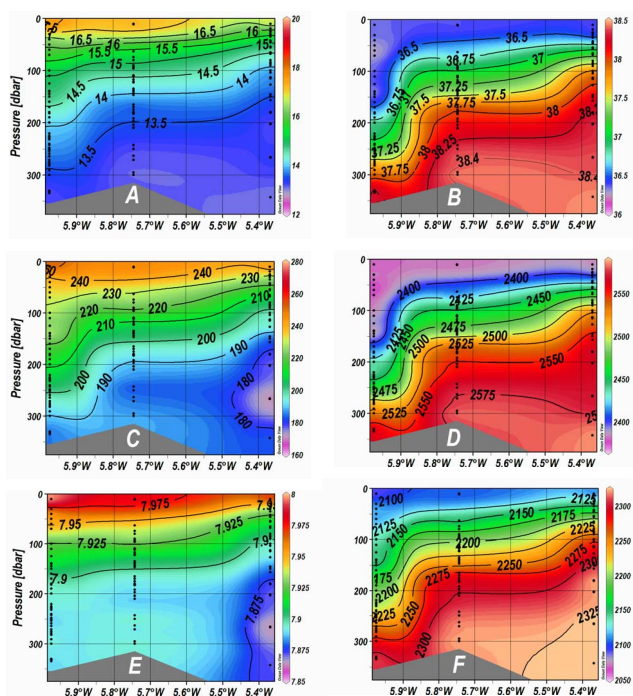


Fig. 3. Distribution of (A) potential temperature (θ , °C), (B) salinity, (C) dissolved oxygen (DO, $\mu\text{mol kg}^{-1}$), (D) alkalinity (A_T , $\mu\text{mol kg}^{-1}$), (E) pH_T and (F) total inorganic carbon (C_T , $\mu\text{mol kg}^{-1}$) along the GIFT leg in the Strait of Gibraltar. Data represent the average values obtained in nine campaigns (more details in the text).

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 $\sim 4^\circ\text{C}$, 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 connect-

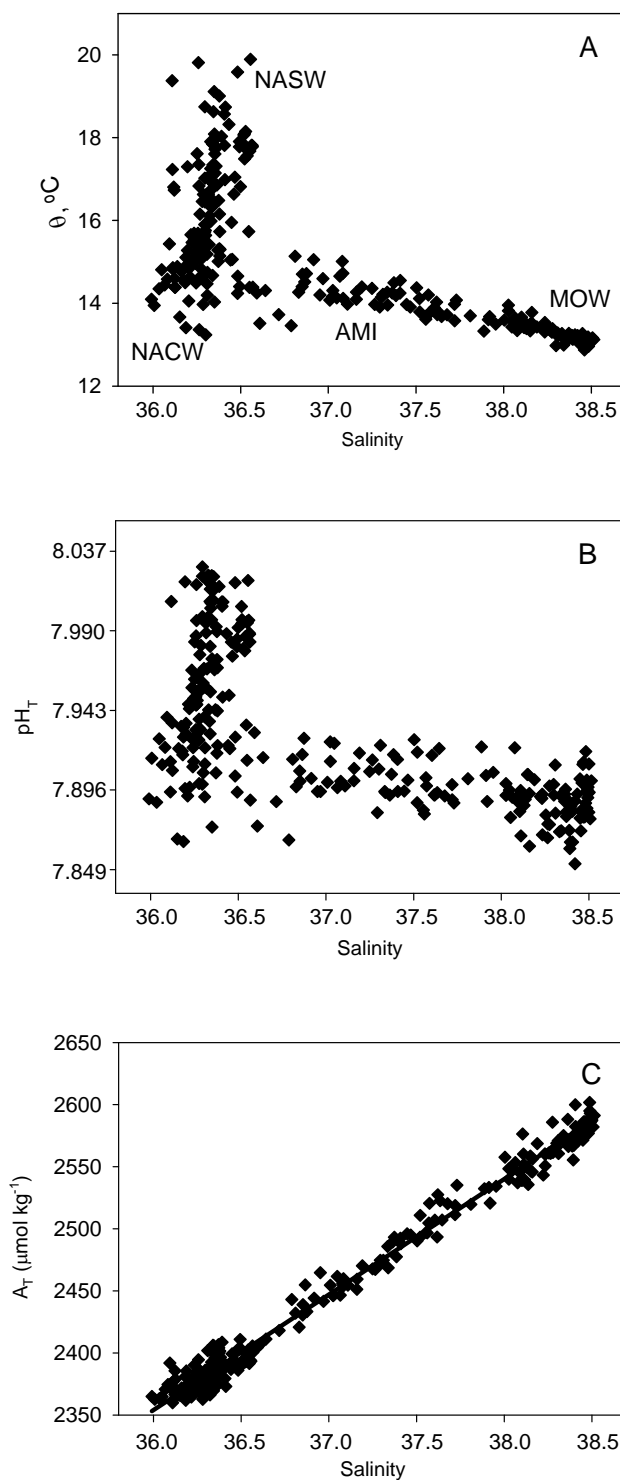


Fig. 4. Potential temperature–salinity plot (A), pH_T at 25°C–salinity diagram (B) and alkalinity (A_T) as a function of salinity (C) in the Strait of Gibraltar. The line with the equation $A_T = 92.95S - 993$ ($n=297$; $r^2=0.989$) results from linear regression in (C).

ing 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, O₂ 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. 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 $2427\pm 9 \mu\text{mol kg}^{-1}$ between surface and 50 m depth whereas C_T varies from 2100 ± 6 to $2176\pm 10 \mu\text{mol kg}^{-1}$ 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; Ait-Ameur and Goyet, 2006). Also, available C_T values for the North East Atlantic Central Water (Ríos 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 $2569\pm 1.5 \mu\text{mol kg}^{-1}$ and C_T levels of $2314\pm 2 \mu\text{mol kg}^{-1}$ 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 (Ait-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).

C_T concentrations reported by Pérez et al. (1986) for the western Mediterranean, Frankignoulle et al. (1990) for the LIW, Copin-Montégut and Begovic (2002) for DYFAMED, all based on indirect computations by using pH and A_T measurements, 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 our study. C_T levels provided here also match other estimates calculated in the MOW passing through the Strait of Gibraltar (Dafner et al., 2001a; Ait-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 O₂ distribution along the Strait of Gibraltar (Fig. 3c), the AI contains O₂ concentrations that ranged from 251 ± 6 to $216\pm 5 \mu\text{mol kg}^{-1}$ (from surface down to 52 m at station 8) whereas the MOW was characterised by lower O₂ levels, with a minimum of $184\pm 2 \mu\text{mol kg}^{-1}$ observed in the bottom layer (328 m) at station 6 (Fig. 3b). Due to mixing, the O₂ concentration progressively diminishes in depth within the AMI throughout the channel (Fig. 3c). These O₂ 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).

4.2 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

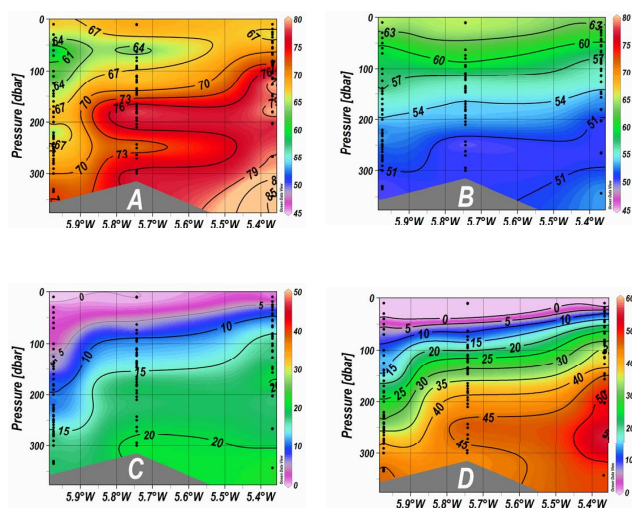


Fig. 5. Distribution of (A) anthropogenic carbon estimated by the TrOCA approach ($C_{ANT(newTrOCA)}$, $\mu\text{mol kg}^{-1}$), (B) anthropogenic carbon calculated by the ΔC^* method ($C_{ANT(C^*)}$, $\mu\text{mol kg}^{-1}$), (C) CaCO_3 dissolution (Ca , $\mu\text{mol kg}^{-1}$) and (D) inorganic carbon resulting from remineralization of organic matter (C_{bio} , $\mu\text{mol kg}^{-1}$) along the GIFT leg in the Strait of Gibraltar. Data represent the average values obtained in nine campaigns (more details in the text).

et al., 2007) and the ΔC^* method (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 $72 \mu\text{mol kg}^{-1}$, 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 $81 \pm 1.6 \mu\text{mol kg}^{-1}$ ($n=9$) are attained in the bottom layer at station 8 (Figs. 5a and 6c). In contrast, the AI presents concentrations close to $65 \mu\text{mol kg}^{-1}$, 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 $71 \pm 7 \mu\text{mol kg}^{-1}$ ($n=9$) at surface to $67 \pm 3 \mu\text{mol kg}^{-1}$ ($n=9$) in the upper limit of the AMI (Fig. 6c), with an average value of $69 \mu\text{mol kg}^{-1}$ within this layer. These differences in the C_{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

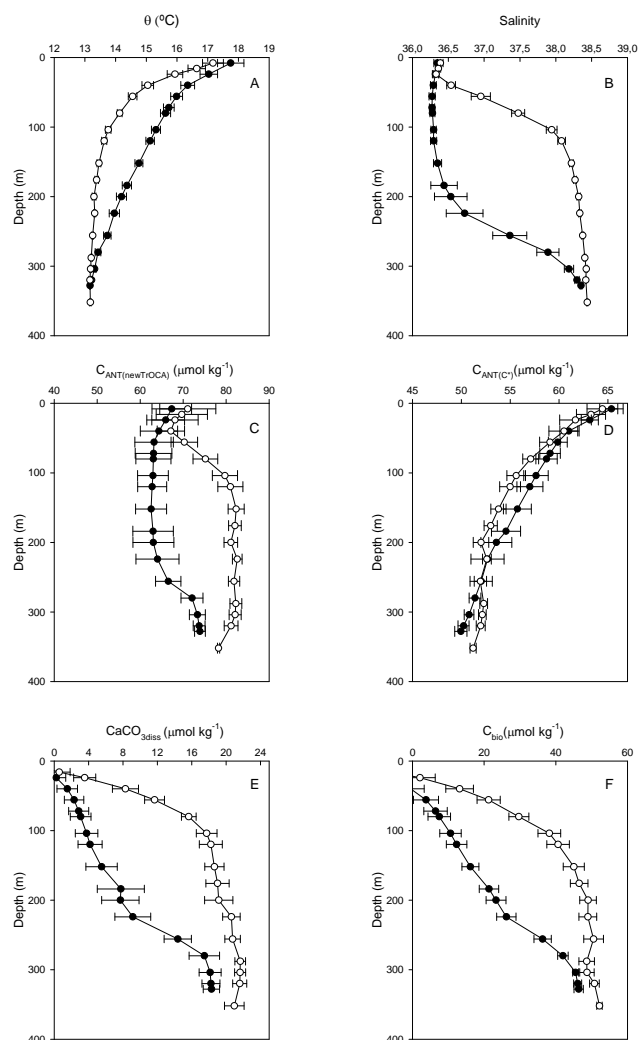


Fig. 6. Vertical profiles of (A) potential temperature (θ , $^{\circ}\text{C}$), (B) salinity, (C) anthropogenic carbon estimated by the TrOCA approach ($C_{ANT(newTrOCA)}$, $\mu\text{mol kg}^{-1}$), (D) anthropogenic carbon calculated by the ΔC^* method ($C_{ANT(C^*)}$, $\mu\text{mol kg}^{-1}$), (E) inorganic carbon resulting from CaCO_3 dissolution (CaCO_{3diss} , $\mu\text{mol kg}^{-1}$) and (F) inorganic carbon resulting from remineralization of organic matter (C_{bio} , $\mu\text{mol kg}^{-1}$) 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).

Strait (Ait-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_{ANT} in the AI entering the Mediterranean Sea with regards to the C_{ANT} concentration in the western entrance (station 6). This explanation, which would also account for the vertical gradient of C_{ANT} through the AMI, has been already proposed by Ait-Ameur and Goyet (2006), who showed an identical distribution pattern, with MOW being also C_{ANT} enriched although in their

study, the calculated values for MOW reached concentrations as high as 111 $\mu\text{mol kg}^{-1}$.

On the contrary, when the ΔC^* method is used, C_{ANT} content in the MOW drops to levels of about 50 $\mu\text{mol kg}^{-1}$ (Fig. 5b), with this concentration being specifically $49 \pm 0.6 \mu\text{mol kg}^{-1}$ ($n=9$) below 300 m depth at station 6 (Fig. 6d). The C_{ANT} concentration in Atlantic waters resembles that computed by the TrOCA approach as values remain close to 65 $\mu\text{mol kg}^{-1}$ within the NASW (Figs. 5b and 6d), which is concordant with the theoretical saturation at the current atmospheric $p\text{CO}_2$ values. Conversely to the previous C_{ANT} estimation, AMI is characterized by a manifest diminution of its C_{ANT} concentration with depth, observation that is noticeable along the entire GIFT leg (Fig. 5b). Also, the C_{ANT} pattern found by using the ΔC^* method 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_{ANT} uptake is calculated by taking into account the inorganic carbon variation due to decomposition of organic matter (C_{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. 5c and d). Consequently, the C_T resulting from CaCO_3 dissolution has been calculated (Figs. 5c and 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 CaCO_3 dissolution and C_{bio} are enhanced processes in the saltier and denser Mediterranean water (Fig. 5c and d). As shown in Fig. 6e, calcium carbonate dissolution in the easternmost part of the Strait ranges from 0 $\mu\text{mol kg}^{-1}$ in near-surface waters corresponding to NASW to a maximum exceeding 20 $\mu\text{mol kg}^{-1}$ 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). The internal hydraulics of the Strait that requires a west-to-east upward slope of the AMI modifies this vertical pattern and thus, lower values can be attained at a same given depth on both sides of the channel (Fig. 6e). As illustrated in Fig. 5c, the spatial distribution of the CaCO_3 dissolution along the GIFT leg reaches a maximum in the bottom layer where the MOW is detected, with NASW containing a much lower CaCO_3 dissolution (Fig. 5c).

Similarly, the inorganic carbon originated from remineralisation of organic matter (C_{bio}) exhibits an analogous pattern on both sides of the Strait than that generated by carbonate dissolution, although concentrations of C_{bio} in the MOW are 2 fold higher than the levels of $\text{CaCO}_3_{\text{diss}}$, with values reaching 40 $\mu\text{mol kg}^{-1}$ in the bottom layer (Fig. 6f). The vertical profile of C_{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).

4.3 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

$$F_N = F_M - F_A = (\rho_M \times Q_M \times C_T^M) - (\rho_A \times Q_A \times C_T^A), \quad (3)$$

where F_M and F_A represent the flux of total inorganic carbon in the Mediterranean and Atlantic layers respectively, with ρ , 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

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.

Station ID	Water Mass Signature	Density ($\text{kg m}^{-3} \times 10^{-3}$)	Q (Sv) ($\mu\text{mol kg}^{-1}$)	A_T ($\mu\text{mol kg}^{-1}$)	C_T ($\mu\text{mol kg}^{-1}$)	$\Delta\text{CaCO}_{3\text{diss}}$ ($\mu\text{mol kg}^{-1}$)	ΔC_{bio} ($\mu\text{mol kg}^{-1}$)	$C_{\text{ANT}(\text{newTrOCA})}$ ($\mu\text{mol kg}^{-1}$)	$C_{\text{ANT}(C^*)}$ ($\mu\text{mol kg}^{-1}$)	DOC ¹
6	NASW	1.027	0.89	2380	2116	2	2	64	60	59
6	MOW	1.030	-0.85	2547	2296	17	42	78	51	45
8	NASW	1.027	0.85	2403	2141	5	8	69	61	59
8	MOW	1.030	-0.81	2578	2331	21	50	81	52	46
		F_N (kmols^{-1})		-44	-67	-13	-35	-8	11	14
		Uncertainty (kmols^{-1})		1.5	1.6	0.3	0.4	1.5	1	1

¹ Data taken from Dafner et al. (2001)

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 (García-Lafuente et al., 2007).

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 $-67 \pm 1.6 \text{ kmol C s}^{-1}$. Therefore, on annual basis, the net export of C_T from the Mediterranean Sea through the Strait accounts for by $2.11 \pm 0.05 \text{ Tmol C yr}^{-1}$ (25 Tg 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 ΔC^* method is considered for C_{ANT} assessment, Atlantic waters constitute a considerable source of anthropogenic carbon to the Mediterranean basin and a net import of $11 \pm 1 \text{ kmol C}_{\text{ANT}} \text{ s}^{-1}$ occurs. This influx corresponds to an annual input of $0.35 \pm 0.03 \text{ Tmol C}_{\text{ANT}}$ ($4.2 \pm 0.04 \text{ Tg C yr}^{-1}$) into the Mediterranean Sea.

In contrast, when the TrOCA approach is applied for C_{ANT} estimation, the flux reverses and Atlantic waters receive a total amount of $0.25 \pm 0.04 \text{ Tmol C}_{\text{ANT}} \text{ yr}^{-1}$ from the Mediterranean (Table 2). This output yields a net export of $3 \pm 0.06 \text{ Tg C yr}^{-1}$ through the Strait.

5 Discussion

According to the analysis performed in our work, 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; Ait-Ameur and Goyet, 2006; de la Paz et al., 2008b). Moreover, the net C_T outflow of $2.11 \text{ Tmol C yr}^{-1}$ 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 – $4.9 \text{ Tmol C yr}^{-1}$ (Dafner et al., 2001a) to 1.64 – 5 Tmol C yr^{-1} (Ait-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 $1.47 \text{ Tmol C yr}^{-1}$. 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 (Ait-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; Ait-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

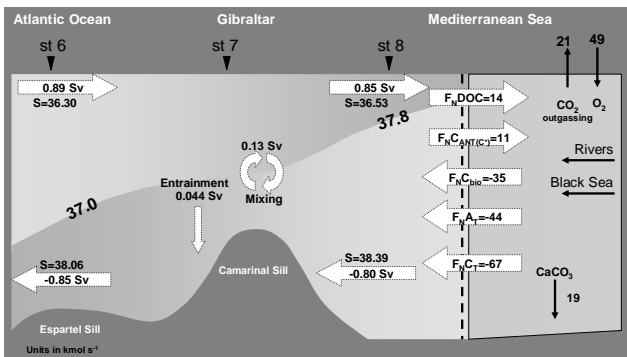


Fig. 7. Diagram of the two-layer model of water mass exchange through the Strait of Gibraltar. Values of the next fluxes of alkalinity (F_{NAT}), inorganic carbon (F_{NCT}), dissolved organic carbon (F_{NDOC}), anthropogenic carbon calculated with the ΔC^* method ($F_{NCANT(C^*)}$) and inorganic carbon resulting from remineralization of organic matter (F_{NCbio}) 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 transferences 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.

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 following the scheme introduced by Dafner et al. (2003) and considering the difference between the outflow and inflow at stations 6 and 8 respectively, 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), $\text{CaCO}_{3\text{diss}}$ (Fig. 5c) and C_{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 Mediterranean basin (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 $-44 \pm 1.5 \text{ kmol s}^{-1}$ ($1.39 \text{ Tmol yr}^{-1}$) occurs through the Strait. This value lies between the one given by Copin-Montégut (1993), who estimated a net alkalinity flux of -77 kmol s^{-1} into the Atlantic, that of -60 kmol s^{-1} provided by Santana-Casiano et al. (2002), and the latest assessment of -25 kmol s^{-1} reported by Schneider et al. (2007). Again, the most plausible explanation for the diversity of estimates available in the literature is due to the values of the water transports considered by the different authors. This cir-

cumstance is evident in the work by Copin-Montégut (1993) that used several water balances whereas Santana-Casiano et al. (2002) applies that given by Tsimplis and Bryden (1999), which is characterized by a high difference between Atlantic inflow and Mediterranean outflow. In contrast, Schneider et al., (2007) employ a Q_M of -0.72 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 Sv observed here, a net alkalinity export of -47 kmol s^{-1} through the Strait is obtained, which strongly matches the alkalinity flux indicated in Table 2. This finding supports that the water transport used for the final computation of fluxes through the Strait is 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 38 kmol s^{-1} and 48 kmol s^{-1} , respectively. Such estimates are in agreement with those mentioned in the prior study by Copin-Montégut (1993) who considered 37 kmol s^{-1} of alkalinity introduced in the basin from the Black Sea and rivers being responsible for an entrance of 53 kmol s^{-1} . 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 86 kmol s^{-1} into the basin from the Black Sea and rivers, and the alkalinity export through the Strait of Gibraltar obtained in our work is taken (-44 kmol s^{-1}), 42 kmol s^{-1} of the alkalinity measured in the Mediterranean do not reach the Atlantic. 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, and the most likely candidate for the loss of the remaining 38 kmol s^{-1} of alkalinity would be CaCO_3 sedimentation. Our results then imply a net carbonate sink of 19 kmol s^{-1} towards the seafloor. However, an export of $-13 \pm 0.3 \text{ kmol s}^{-1}$ of CaCO_3 is observed to occur through Gibraltar (Table 2 and Fig. 7). This output of carbonate can be attributable to the contribution of the biological CaCO_3 pump, which transports downward alkalinity by CaCO_3 particulate from the upper surface layer to deep layer, providing an additional alkalinity gain equivalent to -26 kmol s^{-1} . Although CaCO_3 dissolution is not favoured thermodynamically, the increase of alkalinity can be produced in biological mediated environments (Milliman et al., 1999) or released back from the sediment to the water column (Berelson et al., 2007). The combination of all these processes would result in a gross CaCO_3 formation of 32 kmol s^{-1} . This budget is coherent with the high downward carbonate fluxes measured recently in the NW Mediterranean (Martin et al., 2006), who reported a mean annual flux of sink of $0.40 \text{ mol m}^{-2} \text{ y}^{-1}$ using sediment

traps, which matches strongly our gross estimate. According to Schneider et al. (2007), the alkalinity loss via carbonate sedimentation corresponds to a surface calcification rate of $0.38 \text{ mol m}^{-2} \text{ yr}^{-1}$, which amounts to 32 kmol s^{-1} of a net CaCO₃ precipitation. These authors, however, neglect carbonate dissolution and consider an alkalinity export through the Strait of -25 kmol s^{-1} . In parallel, the gross CaCO₃ formation (32 kmol s^{-1}) in surface waters nearby coastal regions would favour a rise in the oceanic $p\text{CO}_2$. Our estimates point to a CO₂ outgassing of 21 kmol s^{-1} to the atmosphere due to settling of CaCO₃ particles, assuming that $p\text{CO}_2$ is maintained in equilibrium with the atmospheric CO₂ levels (Copin-Montégut, 1993). This latter work also shows an organic matter supply of 4 kmol s^{-1} from the Black Sea to the Mediterranean, which is accompanied by organic carbon inputs of 8 kmol s^{-1} and 5 kmol s^{-1} from the rivers and the atmosphere respectively. According to our calculations, an exportation of $-35 \pm 0.4 \text{ kmol s}^{-1}$ (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 kmol s^{-1} of DOC from the Atlantic (Dafner et al., 2001b; Table 2) and the rest of C_T escaping through the Strait must then come from the Black Sea and rivers, although the contribution of atmospheric deposition cannot be entirely ruled out.

The net exchange of $-67 \pm 2 \text{ kmol s}^{-1}$ of C_T through the Strait is concordant with previous calculations (Aït-Ameur and Goyet, 2006; de la Paz et al., 2008b) and it has been estimated in our 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, 35 kmol s^{-1} of such an export originate 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 CaCO₃ precipitation and the air-sea CO₂ 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 82 kmol s^{-1} (Schneider et al., 2007).

Accordingly, the corresponding C_{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 ($2.5 \times 10^{12} \text{ m}^2$, Menard and Smith, 1966) and the mean penetration depth (MPD, Broecker et al., 1979), which is defined as the quotient between the C_{ANT} water column inventory and the C_{ANT} concentration in the mixed layer (assuming a fully CO₂ equilibrated mixed layer keeping pace with the CO₂ 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 $0.7 \pm 0.1 \mu\text{mol kg}^{-1} \text{ y}^{-1}$. This C_{ANT} storage leads to a rate of $78 \pm 10 \text{ kmol s}^{-1}$, implying an air-sea C_{ANT} uptake of $67 \pm 9 \text{ kmol s}^{-1}$, equivalent to an annual drawdown of $0.8 \pm 0.1 \text{ mol m}^{-2} \text{ y}^{-1}$. Using early data reported in the Alboran Sea by Millero et al. (1979) a concentration of $27 \pm 7 \mu\text{mol kg}^{-1}$ of C_{ANT} in the Mediterranean can be obtained at that time, which represents a 71% of saturation (± 14) with respect to C_{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.

It is worthy to point out that the computed balances are based on C_{ANT} estimations performed by using the ΔC^* method. 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 $-8.0 \pm 1.5 \text{ kmol s}^{-1}$ of C_{ANT} through the Strait is then attained (Table 2), which is equivalent to $3.0 \pm 0.6 \text{ Tg C yr}^{-1}$. This amount is one order of magnitude lower than the previous estimate reported in the area by Aït-Ameur and Goyet (2006).

The discrepancy found between both methods may lay probably on the formulation that each assessment considers for water age calculation. Basically, the TrOCA method applies a global equation that is a function of θ and total alkalinity measured in situ (Eq. 2) whereas the ΔC^* technique includes the computation of the pre-industrial carbon level and the disequilibrium due to the air-sea CO₂ 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 CO₂ 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_{ANT} is already taken into account in the computation (as provided in Eq. 1). In contrast, $C_{\text{ANT}(\text{newTrOCA})}$ profiles augment downward in the water column (Figs. 5a and 6c), resulting in higher concentrations of anthropogenic carbon than

the theoretical C_{ANT} content in saturation with the present atmospheric level. Therefore, the vertical gradient of C_{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, as the tracer was originally defined and evaluated from deep waters in the open ocean and therefore it is not reliable for marginal seas, coastal regions or surface waters.

Until now, the export of inorganic carbon from the Mediterranean Sea through the Strait of Gibraltar was assumed to contribute significantly to C_{ANT} enrichment in the North Atlantic (Álvarez et al., 2005; Ait-Ameur and Goyet, 2006). Our results support those prior observations and explicitly demonstrate that the exchange of both water masses through the Strait alleviates the accumulation of C_{ANT} in the Atlantic basin but this process exacerbates simultaneously C_{ANT} storage into the Mediterranean. Regardless of the approach used for C_{ANT} estimation, the data analysed and provided in our study indicate that the Mediterranean plays a fundamental role in the capture of anthropogenic carbon from the Atlantic, contributing to its storage in a dense layer which in the long term feeds back the deep circulation of the North Atlantic. Hence, the fact that the Mediterranean Sea gains C_{ANT} does not contradict its final function as an additional source of C_{ANT} within deeper Atlantic regions due to the downward entrainment (Ríos et al., 2001; Álvarez et al., 2005).

6 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 (Ait-Ameur and Goyet, 2006; Alvarez et al., 2005). Results presented in our 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 new data gathered in situ 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 on annual basis. According to our estimates, a net export of inorganic carbon equivalent to $25 \pm 0.6 \text{ Tg C yr}^{-1}$ takes place from the Mediterranean Sea to the Atlantic Ocean whereas an annual flux of $4.20 \pm 0.04 \text{ Tg C}_{\text{ANT}}$ towards the Mediterranean basin can be detected. Our study also provides a net alkalinity output of $16 \pm 0.6 \text{ Tg C yr}^{-1}$ through the Strait. This work un-

derlines 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 timeseries GIFT established in the frame of the CAR-BOOCEAN 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.

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