Anthropogenic carbon inventory in the Gulf of Cádiz

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Abstract

The North Atlantic is the most important sink for atmospheric CO₂ although there still remain uncertainties about the total amount stored by this region and the contribution of the anthropogenic CO₂ (CANT) that is exchanged between the Mediterranean Sea and the Atlantic Ocean. During the P₃A₂ cruise performed in October 2008 throughout the oceanic area covered by the Gulf of Cádiz and the Strait of Gibraltar, which channelizes the water exchange between the Atlantic and the Mediterranean, extensive measurements of the carbon system parameters (pH, total alkalinity and total inorganic carbon) and others related (dissolved oxygen and nutrients) were carried out to analyse their distribution in the area. In order to study the CANT spatial variability, three observational methods for CANT concentration assessment (ϕC₀, ΔC* and TrOCA) were applied. The three water masses identified in the area, North Atlantic Central Water (NACW), North Atlantic Deep Water (NADW) and Mediterranean Outflow Water (MOW), were shown to contain different CANT concentration. NADW exhibited the lowest CANT levels whereas NACW was the most CANT enriched. Data also indicate a net import of CANT from the Atlantic towards the Mediterranean through Gibraltar.
Specific $C_{\text{ANT}}$ inventories showed that MOW contributes in 8-12% to the total specific $C_{\text{ANT}}$ inventory of the Gulf of Cádiz.

**Keywords**

Anthropogenic CO$_2$, Carbon storage, Water masses, Gulf of Cádiz, Strait of Gibraltar, Mediterranean Sea.

**1. Introduction**

Since the late 18th Century, carbon dioxide (CO$_2$) concentration in the atmosphere has been rising considerably, which is directly attributable to the fossil fuel burning and changes in land use (deforestation, agriculture, etc.) by human activity (IPCC, 2007). Nevertheless, atmospheric levels are lower than expected if all the CO$_2$ released by anthropogenic sources had remained in the atmosphere. This mismatch is due to the fact that the ocean and land biosphere have taken up a significant amount of CO$_2$, thus acting as sinks for the anthropogenic carbon dioxide ($C_{\text{ANT}}$) (Sarmiento and Gruber, 2002). It is known that the oceans represent the major of these two sinks, storing approximately 48% of the total $C_{\text{ANT}}$ (Sabine et al., 2004). Therefore, quantifying $C_{\text{ANT}}$ distribution and the total amount sequestered by the oceans is crucial to better understand the role of the oceans in the global carbon cycle and how they moderate climate change (IPCC, 2007). This analysis must be, however, conducted through empirical methods based on the use of different tracers since $C_{\text{ANT}}$ can not be directly measured.

Several methods for the indirect estimation of $C_{\text{ANT}}$ have been developed up to date. Those based in the back-calculation technique (Brewer, 1978; Chen and Millero, 1979) are quite extended as they were the first algorithms defined to assess the temporal variation experienced by the measured inorganic carbon since a water mass was originally formed. Such variation is due to the contribution of the organic matter oxidation-reduction processes and the calcium carbonate dissolution-precipitation. Gruber et al. (1996) improved the initial method that was developed for the Atlantic Ocean and defined the quasi-conservative carbon tracer $\Delta C^*$, which reflects the uptake
of \( C_{\text{ANT}} \) and the air-sea disequilibrium present when the water mass loses contact with the atmosphere, assuming that it remains constant over time. A more recent method for \( C_{\text{ANT}} \) computation is the TrOCA approach, which was originally proposed by Touratier and Goyet (2004b) and further improved by Touratier et al. (2007). This technique considers a quasi-conservative tracer TrOCA, which combines Oxygen, inorganic Carbon, and Total Alkalinity and that is based on the conservative NO tracer (Broecker, 1974; Ríos et al., 1989; Touratier and Goyet, 2004a). Both the TrOCA approach and the \( \Delta C^* \) technique assume that below the mixed layer, the decomposition of organic matter follows a constant Redfield stoichiometry and that today’s air-sea \( \text{CO}_2 \) disequilibrium is identical to the one present in pre-industrial times. Current studies have indicated that the TrOCA method considerably overestimates anthropogenic carbon concentrations (Yool et al., 2011). Nevertheless, method has been still applied in our work in order to compare the data obtained with the previous results shown by Aït-Ameur and Goyet (2006) in the Gulf of Cádiz. A new parameterization, has been lately proposed by Vazquez-Rodriguez et al. (2009a), the so-called \( \varphi C_T^o \) method, which represents a revision of \( \Delta C^* \) and it is aimed at improving the assessment of \( C_{\text{ANT}} \) inventory in the Atlantic Ocean. The main contribution of the \( \varphi C_T^o \) method is the use of sub-surface layer data (100-200m) to reconstruct water mass formation conditions, thereby obtaining better estimates of preformed properties instead of using other transient traces, such as CFC, to quantify the effect of the air-sea disequilibrium on the \( C_{\text{ANT}} \) concentration.

However, regardless of the method considered for \( C_{\text{ANT}} \) calculation, several studies have confirmed that the North Atlantic is the most important sink for atmospheric \( \text{CO}_2 \) (Takahashi, 2009; Sabine et al., 2004), although there still remain uncertainties about the total amount stored by this region. In the past, the contribution of areas such as marginal seas, semi-enclosed seas and continental shelves to the global \( C_{\text{ANT}} \) inventories was understudied. Nevertheless, recent studies that evaluate the \( \text{CO}_2 \) sink capacity of these areas have demonstrated that they take up larger amounts of \( C_{\text{ANT}} \) which contribute significantly to the overall global \( C_{\text{ANT}} \) inventories (Tanhua et al., 2009; Schneider et al., 2010; Lee et al., 2011). Therefore, there is a clear research need to accurately quantify the amount of carbon that is captured by the total coastal ocean and subsequently transferred to the open sea. In response to this increasing interest, several studies have been carried out in the coastal area comprised by the Gulf of Cádiz and the
Strait of Gibraltar (Aït-Ameur and Goyet, 2006; Huertas et al., 2006; 2009; de la Paz et al., 2008, 2011; Ribas-Ribas et al., 2011). Data attained by these studies indicate that this region acts as a moderate sink for atmospheric CO$_2$ and that a net export of total inorganic carbon occurs from the Mediterranean to the Atlantic. On the other hand, there have been contradicting results about the concentration of C$_{\text{ANT}}$ that is exchanged between both basins (Aït-Ameur and Goyet, 2006; Huertas et al., 2006; 2009). These discrepancies may be related to the different methods used to obtain C$_{\text{ANT}}$ concentrations, as the TrOCA approach seems to overestimate Mediterranean waters anthropogenic carbon levels. Therefore, the main aim of this work was to examine the spatial variability of the C$_{\text{ANT}}$ in the Gulf of Cádiz considering all the water masses present in the area, in order to gain insights on the role of the Strait of Gibraltar in the fluxes of the anthropogenic carbon. This analysis was performed by applying all the aforementioned C$_{\text{ANT}}$ calculation techniques not only with the aim at comparing the results provided by the different methods currently available and generally applied but also to allow the comparison with data reported in the past in this geographic zone by using the TrOCA approach. Furthermore, a C$_{\text{ANT}}$ inventory for the whole area is provided, with the relative contribution of the outflow of Mediterranean water to the specific inventory being also given.

1.1 Study Area

The oceanic area covered by the Gulf of Cádiz and the Strait of Gibraltar, located southwest of the Iberian Peninsula (Fig. 1), plays a relevant role in the general circulation of the North Atlantic owing to the channelization of the water exchange between the Atlantic and the Mediterranean Sea (Péliz et al., 2009; Criado-Aldeanueva et al., 2009). Thus, the entrainment of North Atlantic Central Water (NACW) by the Mediterranean outflow (MOW) as it descends the northern slope of the Gulf of Cádiz markedly contributes to the generation of the Azores current and also drives upper slope currents in the basin (Péliz et al., 2009).

The Strait of Gibraltar is a narrow and shallow channel with an east-west orientation of a minimum width of 14 km (the Tarifa Narrows, TN in Fig. 1) and an average depth of 600 m, although the main sill of the Strait (Camarinal Sill, CS in Fig. 1) is hardly 300 m depth and imposes a severe constrain for the ventilation of deep Mediterranean waters. On the other hand, the adjacent Gulf of Cádiz is divided into two different portions by
Cape Santa Maria (CSM) (Fig. 1), with each of these halves presenting different
topographic characteristics. West of CSM, the continental shelf is narrow and the sea
bottom is characterized by the presence of submarine canyons. On the contrary, east of
the cape the continental shelf becomes wider and hosts important rivers whose mouths
provide the basin with freshwater and nutrients that control primary production in the
coastal fringe (Prieto et al., 2009). As underlined above, the circulation of water masses
in the Gulf is markedly controlled by the Mediterranean-Atlantic exchange that takes
place in the Strait of Gibraltar. The saltier and denser MOW moves westwards in depth,
being distinguishable through two main cores centred at about 800 and 1200 m depth.
This subdivision is probably due to the bottom topography that channels different
branches along certain isobaths (Ambar and Howe, 1979; Serra and Ambar, 2002). In
addition, a third shallower core can be detected at depths around 500 m in the
continental shelf (Ambar et al., 2002). In contrast, Atlantic waters flow eastward to the
Mediterranean Sea, occupying the upper layer in the Strait of Gibraltar. The confluence
of both water bodies determines the two layer circulation scheme found in the Strait.
The exchange of waters is mainly driven by the water deficit occurring in the
Mediterranean basin, as the excess of evaporation over precipitation and river run off
forces the Atlantic jet to progress towards the Mediterranean Sea to compensate water
losses (Bryden et al., 1994).
The presence of NACW in the area is evident below 100 m depth, as described in
previous studies (Navarro et al., 2006). This water mass has been categorized in two
varieties, such as the warmer Eastern North Atlantic Central Water of subtropical origin
(ENACₜ) and the colder subpolar Eastern North Atlantic Central Water (ENACₛ) (Ríos
et al., 1992; Pollard et al., 1996; Pérez et al., 2001; Alvarez et al., 2005). At shallower
depths, NACW is modified by the atmospheric interaction and it has been defined as
North Atlantic Surface Water (Gascard and Richez, 1985). Furthermore, the North
Atlantic Deep Water (NADW) can be found at depths greater than 1500 m (Emery and
Meincke, 1986; Alvarez et al., 2005) associated with a depth-decreasing thermohaline
properties (Ambar et al., 2002).

2. Material and Methods

2.1. Sampling
The P₃A₂ oceanographic cruise was conducted on board the R.V. Hespérides from the 16th to the 22nd of October 2008. A macroscale study was completed in a sampling grid composed by 45 stations distributed from CSM to the Strait of Gibraltar (Fig. 1). At each station CTD profiles were obtained with a SeaBird SBE 911, followed by collection of water samples with rosette at different depths (from 5 m up to ~2000 m or bottom depth) in order to determine the spatial distribution of several biogeochemical variables, such as total alkalinity, pH, dissolved oxygen and inorganic nutrients (nitrite, nitrate, phosphate and silicate).

2.2. Measurements

2.2.1. Total Alkalinity

Total alkalinity (Aₜ) was measured with a Metrohm 794 Titroprocessor following the method described by Mintrop et al. (2000). Water samples were taken from the Niskin bottles and preserved in 500 mL borosilicate bottles poisoned with 100 µL of HgCl₂ saturated aqueous solution and kept until subsequent onboard and onshore analysis. Accuracy of Aₜ determination was calculated from regular measurements of 2 batches (batch # 85 and 89) of Certified Reference Material (CRM supplied by Prof. Andrew Dickson, Scripps Institution of Oceanography, La Jolla, CA, USA), resulting in ±2 µmol kg⁻¹.

2.2.2 pH

pH was measured following the spectrophotometric method of Clayton and Byrne (1993) using m-cresol purple as the indicator, and consequently, the scale used was the total scale. Samples were collected directly from the rosette in 10 cm path-length optical glass cells and measurements were carried out onboard with a Shimadzu UV-2401PC spectrophotometer containing a 25°C-thermostated cells holder. This method has been proved to have an accuracy of ±0.003 pH units (Clayton and Byrne, 1993). Accuracy of our pH determinations was calculated from regular measurements of 2 CRMs batches (# 85 and # 89). From both pH and Aₜ values, the concentration of inorganic carbon (Cₜ) was calculated using the dissociation constants from Mehrbach et al. (1973) refitted by Dickson and Millero (1987).
2.2.3 Dissolved Oxygen

Dissolved oxygen was determined following the Winkler method (Winkler, 1888). Seawater was taken in sealed flasks directly from the Niskin bottles and stored in darkness for at least 24 h. Analysis was performed by potentiometric determination using a Metrohm 794 Titroprocessor, with an estimated error of ±1 µmol kg\(^{-1}\).

2.2.4 Nutrients

Two 5 mL replicates of filtered seawater (GF/F Whatman filters) were taken and stored at -20°C until onshore laboratory analysis. Concentration of NO\(_2\), NO\(_3\), PO\(_4\) and Si\((OH)_4\) were obtained following the techniques described by Grasshoff et al. (1983) with a Skalar San++System autoanalyser.

2.3. Calculation of C\(_{\text{ANT}}\) concentration

As already indicated, several methods were applied to calculate C\(_{\text{ANT}}\) in the study region: the TrOCA approach with the set of parameters proposed by Touratier and Goyet (2004b) and with the latter improvements of Touratier et al. (2007), designated here as TrOCA\(_{2004}\) and TrOCA\(_{2007}\) respectively; the back-calculation technique (\(\Delta C^*\)) and the \(\phi C_T\) method. The original TrOCA\(_{2004}\) parameterization (Touratier and Goyet 2004b) was exclusively used to compare the results attained in this study with previous estimations reported in the area based on such method (Aït-Ameur and Goyet, 2006). Regardless of the calculation technique applied, the first 100 m of the water column were excluded for C\(_{\text{ANT}}\) assessments and hence only data obtained in stations with waters deeper than 100 m were considered.

C\(_{\text{ANT}}\) (TrOCA) has been computed using the following relationship

\[
C_{\text{ant}}(\text{TrOCA}_{2004,2007}) = \frac{\text{TrOCA} - \text{TrOCA}^0}{a}, \quad (2)
\]

where TrOCA represents a semi-conservative tracer based on the Redfield oxidation-reduction ratios of organic matter, calculated as follows:

\[
\text{TrOCA}_{2004} = O_2 + aC_T - 0.6A_T, \quad \text{TrOCA}_{2007} = O_2 + a(C_T - 1/2A_T), \quad (3, 4)
\]

and TrOCA\(^0\) is defined as the pre-industrial TrOCA:
\[
\text{TrOCA}^\circ_{2004} = 1505.04e^{-0.904}, \quad \text{TrOCA}^\circ_{2007} = e^{(7.511 + (1.087 \times 10^{-3} \theta - (7.81 \times 10^{-7} / A^\circ_T))},
\]

where the constant \(a\) is equal to 1.2 and 1.279 for the TrOCA\(_{2004}\) and the TrOCA\(_{2007}\) parameterizations respectively.

For the back-calculation technique, the following equation was used:

\[
C_{\text{ANT}}(\Delta C^\circ) = C_T - \text{AOU}/R_C - 1/2(\Delta A_T + \text{AOU}/R_N) - C^\circ_{T278} - \Delta C_{\text{dis}},
\]

where \(C_T\) is the dissolved inorganic carbon concentration of the sample expressed in \(\mu\text{mol kg}^{-1}\) and AOU stands for Apparent Oxygen Utilization, which was calculated using the oxygen saturation equation of Benson and Krause (1984). The stoichiometric coefficients \(R_C\) \((-\Delta O_2/\Delta C) = 1.45\) and \(R_N\) \((-\Delta O_2/\Delta N) = 10.6\) of Anderson and Sarmiento (1994) were taken. \(\text{AOU}/R_C\) corresponds to the \(C_T\) increase due to organic matter oxidation and \(\frac{1}{2}(\Delta A_T + \text{AOU}/R_N)\) accounts for the \(C_T\) change due to CaCO\(_3\) dissolution-precipitation, where \(\Delta A_T = A_T^\circ - A_T\) is the total alkalinity variation since the water mass was formed. Preformed alkalinity \((A_T^\circ)\) and the disequilibrium term that stands for the air-sea \(\text{CO}_2\) difference expressed in terms of \(C_T(\Delta C_{\text{dis}})\), were obtained for each water sample from the mixing proportion of the different water masses. This was carried out by an extended optimum multiparameter analysis (eOMP) (Poole and Tomczak, 1999). The \(A_T^\circ\) type values for the Atlantic Waters were calculated using the approach proposed by Perez et al. (2002) while those by Rhein and Hinrichsen (1993) and Santana-Casiano et al. (2002) were used for the MOW. \(C^\circ_{T278}\) represents the \(C_T\) in equilibrium with the preindustrial atmospheric \(\text{CO}_2\) molar fraction of 278 ppm and was calculated using the dissociation constants of Merbach et al. (1973) refitted by Dickson and Millero (1987). \(\Delta C_{\text{dis}}\) for both NACW and NADW was considered to be \(-12\pm5\) \(\mu\text{mol kg}^{-1}\) and \(-10\pm8\) \(\mu\text{mol kg}^{-1}\), respectively (Lee et al. 2003) whereas for the MOW \(\Delta C_{\text{dis}}\) was obtained from Huertas et al. (2009), which sets \(\Delta C_{\text{dis}}\) in \(0\pm5\) \(\mu\text{mol kg}^{-1}\) using the CFC data given by Rhein and Hinrichsen (1993). As for the \(\varphi C_T^\circ\) method (Vazquez-Rodriguez et al. 2009a), new \(A_T^\circ\) and \(\Delta C_{\text{dis}}\) parameterizations were included in the equation based on a 100-200 m depth surface layer that is taken as a reference for reconstructing water mass formation conditions. Accordingly, the NO and PO conservative tracers defined by Broecker (1974) and the preformed silicate (\(S_i^\circ\)) provided by Perez et al. (2002) were used. For the term \(\Delta C_{\text{dis}}\), a distinction depending on different potential temperature (\(\theta\)) intervals was made in the case of Atlantic waters.
whereas for the MOW (S>36.5), $A_T^*$ and $\Delta C_{\text{dis}}$ were obtained by eOMP analysis. The different water masses found in the area were defined in the eOMP analysis by several water types (WT): WT1 and WT2 correspond to the two different varieties of NACW (ENACWt and ENACWs, respectively), WT3 designs NADW and WT4 marks MOW, as summarized in Table 1.

Therefore, the $C_{\text{ANT}}^*$ calculation equation can be summarized as follows

$$C_{\text{ANT}}(\varphi C_T^0) = \frac{\Delta C^* - \Delta C_{\text{dis}}^0}{1 + \varphi |\Delta C_{\text{dis}}^*| C_{\text{sat}}^{\text{ant}}}, \quad (8)$$

with $\Delta C^* = C_T - \text{AOU/R}_C - \Delta C_a - C_{T278}^*$ where $\Delta C_a$ is the term related to the CaCO$_3$ dissolution, since $\Delta C_a = 0.5(\text{PA}_T, \text{observed} - \text{PA}_T^*)$ with $\text{PA}_T = A_T + \text{NO}_3 + \text{PO}_4$ and $\text{PA}_T^* = A_T^* + \text{NO}_3^* + \text{PO}_4^*$, being $\text{NO}_3^* = \text{NO}_3 - \text{AOU/9}$ and $\text{PO}_4^* = \text{PO}_4 - \text{AOU/135}$. The O$_2$-N=9 and O$_2$-P=135 Redfield ratios proposed by Broecker (1974) were taken.

Furthermore, in the $C_{\text{ANT}}(\varphi C_T^0)$ equation, the constant term $\varphi$ is a proportionality factor and equals the ratio between the temporal variability of the air-sea disequilibrium of CO$_2$ from the time of pre-industrial water mass formation to the time “t” ($\Delta \Delta C_{\text{dis}}$), with the disequilibrium at the time “t” being $\Delta C_{\text{dis}}^t$. Finally, $C_{\text{sat}}^{\text{ant}}$ represents the anthropogenic carbon saturation referred to a $x$CO$_2$ air of 384 ppm, which is taken from measurements performed at the meteorological station of the Lampedusa (Italy, Cooperative Air Sampling Network of the NOAA/ESRL Global Monitoring Division) and it is included to account for the effects of temperature and salinity on the solubility of $C_{\text{ANT}}$ in the different water masses.

In order to estimate the uncertainty associated to the $C_{\text{ANT}}$ calculation techniques an error propagation analysis was conducted for each method. The error for $C_{\text{ANT}}$ assessments using the TrOCA$_{2004}$ and the TrOCA$_{2007}$ parameterizations were $\pm 5.3$ $\mu$mol kg$^{-1}$ and $\pm 5.5$ $\mu$mol kg$^{-1}$, respectively; $\pm 6.1$ $\mu$mol kg$^{-1}$ when the $\Delta C^*$ technique was applied and $\pm 5.6$ $\mu$mol kg$^{-1}$ in the case of the $\varphi C_T^0$ method. In previous works, the overall estimated $C_{\text{ANT}}$ uncertainties ranged from $\pm 3$ to $5.9$ $\mu$mol kg$^{-1}$ for the TrOCA$_{2004}$ approach (Touratier et al. 2004b), $\pm 6.2$ for the TrOCA$_{2007}$ parameterization (Touratier et al. 2007), $\pm 9$ for the $\Delta C^*$ technique (Gruber et al. 1996) and $\pm 5.2$ for the $\varphi C_T^0$ method (Vazquez-Rodriguez et al. 2009a).
3. Results and Discussion

3.1. Water masses and carbon system parameters in the study area.

Three water masses were clearly identified in the Gulf of Cádiz according to their different thermohaline properties (Fig. 2a): NACW, NADW and MOW. NACW, located above 500 m depth, was well defined with a temperature range from 11 to 18 °C and salinity values around 35.5-36.3. This water mass showed a linear behaviour for the isopycnals interval of 26.6 kg m\(^{-3}\) ≤ \(\sigma_0\) ≤ 27.3 kg m\(^{-3}\), as described in Criado-Aldeanueva et al. (2006). The MOW signal could be detected throughout the entire study area and up to 1500 m depth (Figs. 5f, 6f). In particular, MOW in the Strait of Gibraltar is defined by a salinity of 38.5 and a temperature value of 13°C (Figs. 4b-c) (Gascard and Richez 1985; Garcia-Lafuente et al. (2007) whereas in the Gulf of Cadiz was clearly evident at a pressure of around 1000 dbar because of a salinity and potential temperature increase (Fig. 3b-c). This signal corresponds to the lower core of the MOW (Fig. 5f) (Ambar and Howe, 1979; Serra and Ambar, 2002). In contrast, NADW was found in a reduced number of deep stations (depth>1500 m) located in the southwestern part of the surveyed region (Fig. 5e, 6e). This water mass was previously described in the Iberian Basin by Alvarez et al. (2005) with salinity and temperature values around 34.9 and 2.4 °C, respectively. In our study, NADW was slightly modified as it showed salinity and temperature values around 35°C and 5°C respectively (Figs. 3b-c, 4b-c).

All the water masses identified were also characterized by specific carbonate properties, as the variability of \(A_T\), AOU and \(C_T\) (Figs. 2b-d) was well correlated with the distribution of the different water masses. Due to the shallower location of the NACW (Figs. 5d, 6d), its thermohaline properties suffer modifications caused by the air-sea interactions and river discharges (Criado-Aldeanueva et al., 2009), which resulted in the highest variability found for these parameters within the same water mass (Figs. 2b-d).

Moreover, the pattern of AOU allowed to distinguish the presence of the two varieties of the NACW described in the area: the ENAC\(_s\), which is oxygen saturated, was thereby characterized by the lowest AOU levels at about 6 µmol kg\(^{-1}\) (Fig. 2c), coinciding with previous reports (Aït-Ameur and Goyet, 2006) and the ENAC\(_t\), which is located below the former, and exhibited an increase in the AOU levels (Fig. 2c). Perez et al. (2001)
attributed this deeper AOU maximum to the remineralization of organic matter in the African coast linked to the northwest African upwelling system. Within the NACW layer, $A_T$ and $C_T$ showed intermediate levels in relation to the total measurements, with average values around $2360\pm2$ and $2130\pm2 \mu \text{mol kg}^{-1}$, respectively (Figs. 2b,d, 3d-e, 4d-e). As expected, the highest $A_T$ ($2576\pm6 \mu \text{mol kg}^{-1}$) and $C_T$ contents ($2317 \pm 5 \mu \text{mol kg}^{-1}$) were found in the MOW located in the western side of the Strait (Figs. 2b-d). In the vertical sections of the N-S and W-E transects, the biogeochemical properties of the MOW were also evident in the lower core (Figs. 3d-f, 5f) and in the western part of the Strait (Figs. 4d-f, 6f), with values that coincide with those reported by Aït-Ameur and Goyet (2006) and Huertas et al. (2009) in the area. The elevated AOU levels of about $80 \mu \text{mol kg}^{-1}$ within this layer indicated the lower oxygen concentrations present in the MOW due to the active remineralisation of organic matter occurring in the Mediterranean basin (Huertas et al., 2009).

On the other hand, the $A_T$ and $C_T$ signatures inside the NADW showed lower values equivalent to $2329\pm7 \mu \text{mol kg}^{-1}$ and $2167\pm2 \mu \text{mol kg}^{-1}$, respectively (Fig. 2b, d). In fact, data plotted in the vertical sections of the transects revealed a decrease of these properties with depth (Figs. 3d-e, 4d-e) due to the presence of this water mass (Figs. 5e, 6e). It is also worth mentioning that the high AOU values (~$80 \mu \text{mol kg}^{-1}$) detected in this water mass (Fig. 2c) can be related to the ageing of water masses that results in a simultaneous increase in AOU, nitrate and phosphate owing to the mineralization of organic matter (van Aken, 2000).

The linear relationship between salinity and $A_T$ obtained for the whole region was calculated at a salinity reference of 35 in order to remove spatio-temporal changes. The equation obtained ($A_T= [(84.3\pm1.6)*(S-35)-(2277\pm2)$, $r^2=0.95$, $n=156$] indicated that mixing is the main controlling factor for the $A_T$ distribution, in a similar way as in Santana-Casiano et al., (2002) and Huertas et al., (2009). These authors reported linear relationships of $A_T=2353(\pm0.4) +92.28(\pm0.31)$ (S-36.0) ($r^2=0.998$) and $A_T =92.98\times S-993$ ($r^2=0.989$) for the Gulf and the Strait, respectively. The new relationship attained here was based on data collected in a wider area, which is influenced by the presence of water masses with lower salinity, such as the NADW, which is absent in the Strait. This circumstance may explain the reduction in the slope and the slight diminution in the correlation coefficient compared to the ones reported by previous works.
3.2. $C_{ANT}$ distribution

The vertical distribution of $C_{ANT}$ calculated using the TrOCA$_{2007}$, the $\Delta C^*$ and the $\phi C_t^o$ methods is plotted in Fig. 5 for a N-S section and in Fig. 6 for an E-W section. The red transects indicated in Figs. 3a and 4a were chosen as representatives of all the legs sampled.

In the N-S section, the spatial pattern of $C_{ANT}$ was similar regardless of the method used for computation, as all of them resulted in a vertical decreasing gradient (Figs. 5a-c). The maximum concentrations of $C_{ANT}$ were consistently located in 100 m depth waters (50-60 $\mu$mol kg$^{-1}$), where the highest proportion of NACW was present (Fig. 5d). In contrast, the lowest $C_{ANT}$ values were found at depths below 1500 dbar (Figs. 5a-c) due to the slight $C_{ANT}$ penetration into the domain of the NADW (Fig. 5e), as described by Ríos et al., 2001). Within this layer, $C_{ANT}$ concentrations showed concordant values between 9 and 12 $\mu$mol kg$^{-1}$ for all the methods applied (Figs. 5a-c). The higher salinity zone found at about 1000-1200 dbar in the continental slope (Fig. 3b) and corresponding to the lower MOW core (Fig. 5f), was characterized by an increase in $C_{ANT}$ concentration, especially when the TrOCA$_{2007}$ parameterization was used (Fig. 5c), resulting in concentrations of 50 $\mu$mol kg$^{-1}$ approximately.

In the E-W section, the distribution of $C_{ANT}$ (Figs. 6a-c) revealed a similar trend for the three parameterizations used except for that obtained in the Strait of Gibraltar with the TrOCA$_{2007}$ approach. According to this method, the MOW located in the Strait was characterised by the highest $C_{ANT}$ content (Fig.6c), particularly waters with salinities >37.5 (Fig.4b). $C_{ANT}$ TrOCA$_{2007}$ concentration in the easternmost part displayed values around 63±1 $\mu$mol kg$^{-1}$ (Fig.6c), which declined westwards and upwards in the water column. Moreover, when the original TrOCA$_{2004}$ parameterization was applied in order to compare with previous estimates (not shown), MOW exhibited average $C_{ANT}$ levels of 92±1 $\mu$mol kg$^{-1}$, whereas NADW and NACW showed 24 ±4 $\mu$mol kg$^{-1}$ and 55 ±1 $\mu$mol kg$^{-1}$ in good agreement with the values reported by Aït-Ameur et al. (2006). Therefore, comparing both TrOCA parameterizations, the initial TrOCA$_{2004}$ method yielded values around 40% higher than those attained by the technique subsequently refined (Fig. 6c).

On the contrary, when both the $\phi C_t^o$ and $\Delta C^*$ methods were applied in the Strait, higher $C_{ANT}$ concentrations were detected within the NACW located in the upper layer of the
water column, with a decreasing vertical pattern being also evidenced (Figs. 6a, c). This discrepancy can be explained by the nature of the equations, as the general TrOCA approach applies a global formula that is a function exclusively of $\theta$, $O_2$ and $A_T$ measured in situ (Eqs. 3, 4) whereas the back-calculation techniques include the computation of the pre-industrial carbon level and the disequilibrium due to the air-sea CO$_2$ difference (Eqs. 5, 6), which are adapted regionally considering the formation of each particular water mass. This feature was already highlighted in the early analysis performed in the Strait by Huertas et al., (2009). In the rest of the surveyed region, the ranges of $C_{ANT}$ concentration within the NACW and NADW coincide with those observed in the N-S transect independent of the approach applied.

### 3.3. $C_{ANT}$ inventory

The specific inventory of $C_{ANT}$ for the entire area was determined by integrating the average vertical $C_{ANT}$ profiles attained at each station from surface down to the bottom depth. Because $C_{ANT}$ concentrations were calculated from 100 dbar to the sea bottom, the surface layer above this depth was assumed to contain a constant $C_{ANT}$ level equal to that present at this upper limit, which also marks the winter mixing layer for Atlantic subtropical waters (Vázquez-Rodríguez et al., 2009a). This artefact for inventory computations allows to avoid the influence of the seasonal biogeochemical variability on surface $C_{ANT}$ estimates (Lo Monaco et al., 2005; Vázquez-Rodríguez et al., 2009a). Specific inventories calculated in the region by the different techniques showed small differences (Table 2). Nevertheless, should be taken into account in the inventory results obtained that they represent average values for the totality of the waters masses present in the area (not shown). As is shown in the Table 2, the initial TrOCA$_{2004}$ method yielded the highest specific inventory with 38.0±3.1 mol C m$^{-2}$, whereas the rest of calculation techniques resulted in similar values, with the minimum provided by the $\phi C_T^o$ method equivalent to 33.5±3.2 mol C m$^{-2}$. Estimates were statistically analyzed by a student’s t test and averaged results obtained showed no statistical differences between the different methods applied.

These values are comparable to the specific inventory presented by Lee at al. (2011) for the East/Japan Sea and equal to 34±5.1 mol C m$^{-2}$. The specific inventory for the entire Eastern North Atlantic comprised in the 30ºN-40ºN latitude band, where our study area
is contained, has been estimated in 66.2 mol C m$^{-2}$, using the $\Delta C^*$ (Lee et al., 2003) and in 75 mol C m$^{-2}$ with the $\varphi C_T^0$ method (Vázquez-Rodríguez et al., 2009b). The differences between such estimates and those obtained here are due to the lower volume of water contained in the surveyed region in relation to that of the Eastern North Atlantic, as the vertical interpolation markedly depends on the water column volume.

Since the main differences in the $C_{\text{ANT}}$ contents observed in our study were related to the presence of the Mediterranean waters (Figs. 6a-c), the contribution of the MOW to the specific $C_{\text{ANT}}$ inventory was also calculated with each technique. Results summarized in Table 2 indicate that the Mediterranean supplies 8% of the total $C_{\text{ANT}}$ specific inventory when the $\varphi C_T^0$ and $\Delta C^*$ methods were used. A small increase in this contribution (11-12%) was attained with the two TrOCA approaches, as a result of the higher concentration of $C_{\text{ANT}}$ assigned to the MOW by both parameterizations (Fig. 6c).

4. Conclusions

The analysis of the spatial distribution of the carbon system parameters in the area covered by the Gulf of Cádiz and the Strait of Gibraltar reflected the presence of different water masses that were characterized by distinct biogeochemical properties. The concentration of $C_{\text{ANT}}$ calculated for each water mass according to three estimation methods resulted in small variations. The main discrepancies between the results obtained by all the methods were found in the MOW, as both TrOCA approaches seem to overestimate $C_{\text{ANT}}$ concentration within this water mass. Accordingly, slight differences were found in the specific inventories with the exception of the value provided by the TrOCA$_{2004}$ approach. Furthermore, the quantification of the additive effect of the $C_{\text{ANT}}$ contained in the MOW on that measured in Atlantic waters at intermediate depths has been evidenced in this study. This work also presents new data on the $C_{\text{ANT}}$ levels present in a coastal ocean region, whose role in the capture and storage of CO$_2$ had been underestimated in the past. These results also represent a contribution to the North Atlantic specific carbon inventories.

5. Acknowledgments

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Fig. 1 Map of the location of the Gulf of Cadiz and the Strait of Gibraltar and sampling grid during the P3A2 cruise.

Fig. 2 θ/S diagram of the study area from 100 dbar depth to the bottom: a) CTD data. Red stars represent the water types (WT) for the different water bodies (NACW, NADW and MOW) used for the eOMP analysis; b) $A_T$ ($\mu$mol kg$^{-1}$); c) AOU ($\mu$mol kg$^{-1}$); d) $C_T$ ($\mu$mol kg$^{-1}$). Contour lines represent density anomaly expressed in kg m$^{-3}$.

Fig. 3 Vertical distributions of a N-S transect from 100 dbar to the bottom: a) Map of the selected stations; b) Salinity; c) Potential temperature (°C), d) Total Alkalinity ($A_T$) in $\mu$mol kg$^{-1}$, e) Total Inorganic Carbon ($C_T$) in $\mu$mol kg$^{-1}$ and e) Apparent Oxygen Utilization (AOU) in $\mu$mol kg$^{-1}$.

Fig. 4 Vertical distributions of an E-W transect from 100 dbar to the bottom: a) Map of the selected stations; b) Salinity; c) Potential temperature (°C), d) Total Alkalinity ($A_T$) in $\mu$mol kg$^{-1}$, e) Total Inorganic Carbon ($C_T$) in $\mu$mol kg$^{-1}$ and e) Apparent Oxygen Utilization (AOU) in $\mu$mol kg$^{-1}$.

Fig. 5 Vertical distributions of a N-S transect from 100 dbar to the bottom: a-c) Estimates of $C_{ANT}$ ($\mu$mol kg$^{-1}$) from the $\varphi C_T^o$, $\Delta C^*$ and TrOCA2007 methods respectively; d-f) percentage of NACW, NADW and MOW obtained by the eOMP analysis.

Fig. 6 Vertical distributions of an E-W transect from 100 dbar to the bottom: a-c) Estimates of $C_{ANT}$ ($\mu$mol kg$^{-1}$) from the $\varphi C_T^o$, $\Delta C^*$ and TrOCA2007 methods respectively; d-f) percentage of NACW, NADW and MOW obtained by the eOMP analysis.
Table 1. Biogeochemical characteristics of the water types selected as end-members in the eOMP analysis.

<table>
<thead>
<tr>
<th></th>
<th>NACW</th>
<th>NADW</th>
<th>MOW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WT1</td>
<td>WT2</td>
<td>WT3</td>
</tr>
<tr>
<td>Θ (°C)</td>
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<td>11.3</td>
<td>2.4</td>
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<td>S</td>
<td>36.50</td>
<td>35.55</td>
<td>34.93</td>
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<tr>
<td>O₂ (µmol kg⁻¹)</td>
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<td>PO₄ (µmol kg⁻¹)</td>
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<tr>
<td>Α₁° (µmol kg⁻¹)</td>
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<td>2327</td>
<td>2300</td>
</tr>
<tr>
<td>ΔC₅ₐ₅ (µmol kg⁻¹)</td>
<td>-17</td>
<td>-6</td>
<td>-8</td>
</tr>
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</table>
Table 2. Specific C\textsubscript{ANT} inventories in the area and the specific Mediterranean contribution (number of stations used=31, surface area=14,082 Km\textsuperscript{2}).

<table>
<thead>
<tr>
<th>Method</th>
<th>Specific Inventory (mol C m\textsuperscript{2})</th>
<th>Contribution of MOW to the specific inventory (%)</th>
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<tbody>
<tr>
<td>(\varphi C_T) &lt;sup&gt;t&lt;/sup&gt;</td>
<td>33.5±3.2</td>
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</tr>
<tr>
<td>(\Delta C^*)</td>
<td>34.2±3.2</td>
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</tr>
<tr>
<td>TrOCA\textsubscript{2007}</td>
<td>33.7±3.0</td>
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</tr>
<tr>
<td>TrOCA\textsubscript{2004}</td>
<td>38±3.1</td>
<td>12</td>
</tr>
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</table>
Figure 4

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