Anthropogenic carbon dioxide in the South Atlantic western basin

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Abstract

The meridional WOCE line A17 was conducted during the austral summer of 1994 parallel to the eastern South American coast, from 55°S to 10°S, where one of the main limbs of the North Atlantic Deep Water (NADW), i.e., the southward-flowing Deep Western Boundary Current (DWBC) is found. Full–depth profiles of pH, total alkalinity and total inorganic carbon were measured and checked with analytical CO₂ certified reference materials (CRMs), providing a high-quality dataset with good internal consistency for the CO₂ system parameters that is well suited for anthropogenic CO₂ (CANT) estimation. For the first time in the western Atlantic basin the CANT has been calculated using four independent approaches and results are compared. The methods considered are the CFC-based TTD method and the ϕCT⁰, TrOCA and ∆C* carbon-system-based back-calculation methods. All four methods have produced CANT distribution patterns that are in general good agreement: maximum concentrations of CANT (50-60 µmol kg⁻¹) are predicted for the upper warm South Atlantic central waters from the tropical gyres, while the minima (~5 µmol kg⁻¹) are located in the old northward-flowing branch of Circumpolar Deep Water. There are, however, some discrepancies detected. The TrOCA method yields the highest overall [CANT] values, even over the theoretical limit of CANT saturation for 1994 in the upper layers. The ∆C* approach consistently yielded negative estimates of CANT below 2800 dbar, even after correcting a reported -8 µmol kg⁻¹ bias in the alkalinity measurements of the WOCE A17 line. The main overall difference between the four methods corresponds to the relative CANT maximum associated with the lower limb of NADW: this structure is well identified in the ϕCT⁰ and TTD methods but seems to disappear in the case of TrOCA and ∆C*. In agreement with other intercomparison studies of CANT, the specific inventories are significantly higher (~45%) than those reported in the GLODAP database obtained from the ∆C* method. This suggests that the South Atlantic stores more CANT than initially expected, particularly towards the southernmost tip of the WOCE A17 line, close to the Southern Ocean. The ϕCT⁰, TrOCA and TTD methods confirm an increasing tendency of CANT specific inventories south from the Equator, while the ∆C* method shows a decreasing trend south from 35°S.
1. Introduction

The ocean plays a major role in the global carbon cycle by sequestering annually 2.2 ±0.4 Pg C out of the total 8.0 ±0.5 Pg yr\(^{-1}\) of anthropogenic CO\(_2\) (C\(_{\text{ANT}}\)) emitted to the atmosphere as a result of activities such as fossil fuel burning, land use changes, deforestation and cement production (Canadell et al., 2007). The Atlantic Ocean alone contributes with a share of 38% to the anthropogenic oceanic carbon storage, even though it only represents 29% of the global ocean surface area (Sabine et al., 2004). The formation of deep waters in the North Atlantic (NADW) and Southern Ocean (Antarctic Bottom Water; AABW) enhances significantly the Atlantic storage of C\(_{\text{ANT}}\) (Lo Monaco et al., 2005). An important branch of the NADW, the Deep Western Boundary Current (DWBC), flows southwards from the Irminger and Labrador Seas and communicates with the South Atlantic basin through the Equatorial channel (Steinfeldt et al. 2007). The DWBC splits into eddies at 8°S such that, southwards from this latitude, the NADW is carried into the South Atlantic Ocean by migrating eddies, rather than by a continuous flow (Dengler et al., 2004). The eastward deflection of the southward-flowing DWBC has also been observed in the NADW domain (Weiss et al., 1985; Richardson and Schmitz, 1994; Rhein et al., 1995; Andrié, 1996; Mercier and Arhan, 1997; Arhan et al., 1998) along and just south of the Equator. On the other hand, model-based studies have suggested that a weakening in the thermohaline circulation and increases of sea surface temperature can potentially reduce ocean carbon uptake by up to 50% and that such reductions are only partly counterbalanced by changes in the marine biological cycle (Sarmiento and Le Quéré, 1996; Sarmiento et al., 1998).

The Atlantic sector of the Southern Ocean withholds moderate concentrations of C\(_{\text{ANT}}\) yet its massive volume turns it into one of the largest carbon reservoirs of this basin (Vázquez-Rodríguez et al., 2009b). Manabe and Stouffer (1993) spotted from model results a potential modification of the ocean carbon sink in a vast region of the Southern Ocean, where increased rainfall would lead to surface freshening and increased stratification. The increased stratification
reduces the downward flux of carbon and hinders the air-sea heat exchanges causing an overall
decrease of the oceanic $C_{\text{ANT}}$ uptake in the Southern Ocean (Sarmiento et al. 1998). Recent
estimates of CO$_2$ sink in the Southern Ocean showed a weakening between 1981 and 2004
which was attributed to the observed increase in Southern Ocean winds resulting from human
activities (Le Quére et al., 2007). The response of the carbon sink in the Southern Ocean to the
changes in the wind stress is currently under debate (Böning et al., 2008). Most of the above-
mentioned results were obtained from model-based studies and, given the importance of the
Southern Ocean in the context of global ocean carbon sink, the acquisition and analysis of high-
quality field data remain essential tasks to obtain the best possible $C_{\text{ANT}}$ estimates.

Over the years, a series of methods have been developed to retrieve the relatively small
(3%) $C_{\text{ANT}}$ signal from the large total inorganic carbon (CT) pool in the oceans. One of the issues
concerning $C_{\text{ANT}}$ is that it cannot be measured directly. Consequently, the so-called back-
calculation techniques were developed to estimate $C_{\text{ANT}}$ indirectly from direct observation of
other tracers. This technique was first applied in the pioneering works of Brewer (1978) and
Chen and Millero (1979). The methodology basis consists in separating from the measured CT
the individual contributions or background signals from Organic Matter Remineralization
(OMR) and dissolution of calcium carbonate species that had occurred since the water mass
formed (it was last in contact with the atmosphere). Following the earlier concept of preformed
nutrient defined by Redfield et al. (1963), the preformed total inorganic carbon ($C_T^p$) was
analogously defined ($C_T$ of the water mass right after formation). This term and the air-sea CO$_2$
disequilibrium ($\Delta C_{\text{dis}}$) are also subtracted from the measured $C_T$. The $C_T^p$ term has not remained
constant after the pre-industrial era. The water masses have gradually formed in contact with a
continuously altered atmosphere by human activity. Therefore, the $C_T^p$ term tracks the imprint
of $C_{\text{ANT}}$, which can be retrieved by subtracting a “zero-$C_{\text{ANT}}$” reference from this preformed
property.
Lo Monaco et al. (2005) reevaluated the specific inventories of C\textsubscript{ANT} for the Southern Ocean using an observational carbon-dependent back-calculation technique based on the one from Körtzinger et al. (1998) that had been applied in the North Atlantic. They found higher values (52-70 mol C m\textsuperscript{-2}) than those computed from the $\Delta$C* method (Gruber et al., 1996) (29-46 mol/m\textsuperscript{2}) at latitudes between 30-47ºS in the Atlantic. Recently, a series of different C\textsubscript{ANT} methods like the TTD, TrOCA and $\varphi$C\textsubscript{T}° approaches (Waugh et al., 2006; Touratier et al., 2007; Vázquez-Rodríguez et al., 2009a) have confirmed Lo Monaco et al.'s (2005) findings and corroborate that C\textsubscript{ANT} inventories in the Southern Ocean could be, in fact, much larger than previously estimated (Vázquez-Rodríguez et al., 2009b).

The present work uses data from the WOCE A17 cruise, which runs parallel to the eastern South American coast, to obtain the C\textsubscript{ANT} distribution and inventories by applying a recent observational carbon-based approach, the $\varphi$C\textsubscript{T}° method (Vázquez-Rodríguez et al., 2009a) and the TrOCA method (Touratier et al., 2007). The obtained results are then compared with C\textsubscript{ANT} estimates from other back-calculation techniques, namely: the $\Delta$C* (Gruber et al., 1996) and the CFC–based TTD approach (Waugh et al., 2006). This practice was never performed before in the western Atlantic basin.

2. Dataset and methodology

The measurements used in this work were performed onboard the R/V Maurice Ewing from January 4th until March 21st 1994 during the CITHER-2 / WOCE A17 cruise, framed within the WOCE/French Project CITHER (Circulation THERmohaline). This quasi-meridional section was complemented by three short transverse lines to the continental slope at nominal latitudes 35ºS, 13ºS, and 10ºN (Fig. 1a). These transversal legs are not considered for the estimation of C\textsubscript{ANT} in the present study. The water samples were collected at 32 depth levels, from the surface down to 15 m above the bottom. The average horizontal spatial resolution of 30 nautical miles between stations was increased near the Equator and prior to stations that
displayed steep bathymetric profiles. A general presentation of the cruise, and a thorough
description of the data used in this paper is provided in Groupe CITHER-2 (1995, 1996). Also,
the quality-controlled database is publicly available (http://cdiac.ornl.gov/oceans/woce_a17c.html) as well as the PI recommend corrections (section 3.7 at http://cdiac.ornl.gov/oceans/ndp_084/ndp084.html).

The pH measurements were originally reported in the NBS scale, as described in Pérez
and Fraga (1987a). Total alkalinity (A_T) measurements were performed every three stations
using a single end point titration technique (Pérez and Fraga, 1987b; Mintrop et al., 2002). Total
inorganic carbon (C_T) was directly measured onboard with a coulometric method using a
“Single Operator Multi–Parameter Metabolic Analyzer (SOMMA)” (Johnson et al., 1993).
Where not measured, C_T was calculated additionally from A_T and pH_{NBS} measurements using
the thermodynamic equations of the carbon system and the CO_2 dissociation constants from
Dickson and Millero (1987; refit from Mehrbach et al. 1973). The measured and calculated C_T
values agreed within ±1.6 µmol kg^{-1} (Ríos et al., 2005). Additional physical-chemical properties
used in the present work such as salinity, temperature, dissolved oxygen, nutrients and CFC-11
were measured using standard methodologies, which are detailed in the cited data reports. The
accuracy of the measured CO_2 parameters was evaluated using “Certified Reference Materials”
(CRMs) supplied by Dr. A.G. Dickson (Univ. of California). The CRM samples were analyzed
routinely for a total of 163 C_T measurements during the cruise, with an average difference from
the certified C_T value (2115.15 µmol kg^{-1}) of ±1.6 µmol kg^{-1}. The average of 146 CRM
analyses for A_T was also in good agreement with the certified value to ±1.7 µmol kg^{-1} (Ríos et
al., 2005). An offset in the A_T data of -8 µmol kg^{-1} (i.e., -0.32%) was later detected for the
WOCE A17 line and reported by Ríos et al. (2005). The nutrients were determined by
segmented flow analysis with a Technicon II Autoanalyzer (Mouriño and Fraga,1985; Alvarez-
Salgado et al.,1992). The accuracy of nitrate and phosphate was ±0.1 and ±0.01 µmol kg^{-1},
respectively.
Regarding $C_{\text{ANT}}$ estimation, four methods have been considered in this study: the TTD (Waugh et al., 2006), $\Delta C^*$ (Gruber et al., 1996), TrOCA (Touratier et al., 2007) and $\varphi_{C_T^o}$ (Vázquez-Rodríguez et al., 2009a,b). The $\Delta C^*$ method was previously applied to the GLODAP dataset and results were accessed from the GLODAP website (http://cdiac.ornl.gov/oceans/glodap/Glodap_home.htm), as well as the CFC12-age data. The results of the $C_{\text{ANT}}$ estimates from the TTD method were downloaded from the following website: https://jshare.johnshopkins.edu/dwaugh1/public_html/Cant/. On the basis of the variables needed to compute $C_{\text{ANT}}$, the methods here mentioned can be classified into two groups: a) the carbon-based methods ($\Delta C^*$, TrOCA and $\varphi_{C_T^o}$), which typically require measurements of $C_T$, $A_T$, oxygen, temperature, salinity and eventually some nutrient analysis. The reported $A_T$ offset of -8 µmol kg$^{-1}$ has been considered when calculating $C_{\text{ANT}}$ from back-calculation methodologies. In the case of the GLODAP-$\Delta C^*$ results, the -8 µmol kg$^{-1}$ $A_T$ offset translates directly into a 4 µmol kg$^{-1}$ $C_{\text{ANT}}$ offset (according to the formulation in Gruber et al., 1996), which has been added to the original GLODAP estimates of $C_{\text{ANT}}$; b) the Transient-Tracer-based methods (TTD) that commonly use CFC-11 or CFC-12 concentration measurements as proxies of the anthropogenic CO$_2$ signal. The uncertainties in $C_{\text{ANT}}$ estimates for the $\Delta C^*$, TrOCA, $\varphi_{C_T^o}$, and TTD methods are ±7.9, ±6.2, ±5.2, and ±5.0, µmol kg$^{-1}$, respectively. A summary of the $C_{\text{ANT}}$ methods used in this work can be found in Vázquez-Rodríguez et al. (2009b).

The amount of dissolved CaCO$_3$ ($\Delta C$) in the water column is one of the fundamental terms in $C_{\text{ANT}}$ back-calculation methodologies. The $\Delta C$ is defined as $\Delta C = \frac{1}{2} (P_{A_T} - P_{A_T^o})$ in terms of the measured $A_T$ and preformed $A_T$ ($A_T^o$), i.e., the alkalinity of the considered water mass at the moment of formation, when it was last in contact with the atmosphere. The potential alkalinity term ($P_{A_T}$) is defined as $P_{A_T} = A_T + NO_3 + PO_4$ (Robertson et al., 1994). The OMR does not affect the $P_{A_T}$ in the water column but carbonate shifts caused by CaCO$_3$ dissolution still increase $P_{A_T}$ by a factor of two. (Vázquez-Rodríguez et al., 2009a). A plot showing the
vertical distribution of $\Delta Ca$ along the WOCE A17 line is shown in Fig. 2. The corresponding $PA_T^*$ term in the $\Delta Ca$ expression was calculated as in Vázquez-Rodríguez et al. (2009a).

3. Results

The main water masses found on the WOCE A17 section are clearly identified from the temperature, salinity and silicate distributions (Figure 2). The warm and saline South Atlantic Central Water (SACW) is predominantly present above 1000 dbar along the whole section. There exist several varieties of this water mass that are well described in Mémery et al. (2000) (hereinafter M’00). The Antarctic Intermediate Water (AAIW) is characterised by its salinity minimum (34.1-34.5) that extends from the Subantarctic Front (46ºS) northwards, between 800 and 1000 dbar. Under the AAIW at ~1000 dbar and south from 20ºS there is a relative maximum of temperature (3.2 ºC) and silicate (45 µmol kg$^{-1}$) corresponding to the upper Circumpolar Deep Water ($u$CDW). The North Atlantic Deep Water (NADW) extends southwards along the section, characterised by an ample salinity maximum (>34.9) located between 1000 and 3500 dbar. Several varieties of NADW have also been thoroughly described in M’00, most importantly its upper and lower limbs ($u$NADW and $l$NADW, respectively) that are identified in Fig. 2. In the Equatorial region at about 1800 dbar there is a relative salinity maximum (~34.95) associated to a minimum silicate signal (~20 µmol kg$^{-1}$) that identifies the $u$NADW branch. The $l$NADW limb is located immediately below (~3500 dbar), with slightly lower salinity and higher silicate values (~34.90 and 35 µmol kg$^{-1}$, respectively) than the upper branch. The maximum silicate values recorded are located at the southern end of the section. They are associated to the lower limb of the CDW ($l$CDW; [SiO$_2$]≥120 µmol kg$^{-1}$) and to the Antarctic Bottom Water (AABW) ([SiO$_2$] >125 µmol kg$^{-1}$ and $\theta$ <0 ºC) (M’00).

The biological component ($AOU/R_C$) in the general back-calculation equation represents a measure of the OMR contribution to the measured $C_T$ signal. This term reaches values of up to
85 μmol kg⁻¹ in the case of AABW and has two relative minima (∼49 μmol kg⁻¹, when using the
$R_c=1.45$ proposed by Anderson and Sarmiento, 1994) associated to the upper and lower NADW
limbs that evolve into a single relative AOU minima south from 20°S (Fig. 2; M’00). The
absolute AOU maximum is located at the core of the SACW, between 500 and 700 dbar north
from 15°S. This layer of the ocean accumulates high loads of organic matter from the Equatorial
upwelling regions, and the AOU/$R_c$ term can amount up to 120 μmol kg⁻¹ of $C_T$. The lowest
AOU values in the section correspond to young recently ventilated surface waters (lowest
observed CFC12 age) around 40°S (M’00). Similarly, both limbs of NADW are characterised
by their relative CFC12 age minima of ∼40 yr. However, it must be noted that using CFC12
concentrations to infer water mass ages tends to underestimate ages in waters older than 25
years (Matear et al., 2003). In spite of the methodological biases, the waters found in the band
between 40°S and the Equator and below 2000 db are indeed very old water masses.

As introduced earlier, the dissolution of CaCO₃ ($\Delta$Ca) also affects the $C_T$ content of a
water parcel. The $\Delta$Ca is largest in the AABW and bottom waters in general throughout the
section, where the oldest water masses are found (Chung et al., 2003). Although there is a
general trend of $\Delta$Ca to increase with depth, an evident relative minimum of $\Delta$Ca (12 μmol kg⁻¹)
is observed associated to the moderately young $\nu$NADW. These values are in contrast with the
relative $\Delta$Ca maximum from the little-ventilated SACW/AAIW between 600 and 800 dbar,
placed immediately above the $\nu$NADW. Alternatively, the fairly good correlation between the
observed $\Delta$Ca and silicate fields indicates that most dissolved CaCO₃ is advected from Antarctic
waters (namely, AABW and CDW). This relationship is well documented in the literature
(Broecker and Peng, 1982; Ríos et al., 1995; Pérez et al., 2002) and draws a clear line of
demarcation between waters with strong Antarctic influence and the rest. The high correlation
stems from the relationship between the dissolution of opal and calcium carbonate.
Independently of the $C_{\text{ANT}}$ reconstruction method used, the maximum values of $C_{\text{ANT}}$ (50-60 $\mu$mol kg$^{-1}$, i.e., around the corresponding $C_{\text{ANT}}^{\text{sat}}$ for 1994) are always found in the warm upper waters from the subtropical gyres (Fig. 3). In the $C_{\text{ANT}}$ distribution obtained with the $\varphi C_{T}^{o}$ method the minimum values ($\sim$5 $\mu$mol kg$^{-1}$) are located at the oldest water masses (CFC12 age $\sim$50 yr) near the 3500 dbar level between the $u$NADW and $l$NADW, where the influence of $l$CDW is slightly more noticeable (M’00). Asides from this, there exists a relative minimum of $C_{\text{ANT}}$ at 1000 dbar north of 15ºS. It coincides with the penetration northwards of $u$CDW (M’00), which erodes the relative maxima of the slightly more ventilated, younger, southward-flowing $u$NADW and $l$NADW. South from 30ºS, the high burdens of $C_{\text{ANT}}$ in subsurface waters reach down to 1200 dbar, while bottom waters show $C_{\text{ANT}}$ concentrations of approximately 10 $\mu$mol kg$^{-1}$. In the deepest end of the section, south of 40ºS, there is a slight increase of $C_{\text{ANT}}$ with respect to the surrounding waters that is likely caused by the penetration northwards of the AABW.

The $C_{\text{ANT}}$ estimates from the TTD approach do not depend on the measurements of carbon system parameters yet its results are in remarkable resemblance with the ones from the $\varphi C_{T}^{o}$, most notably: the $C_{\text{ANT}}$ distributions at the subsurface, at the $u$NADW and $l$NADW associated maxima north of 15ºS, and the relative minima from the spreading of $u$CDW, $l$CDW and the deep AABW. There are, however, discrepancies between the TTD and $\varphi C_{T}^{o}$ results. Amongst the most relevant discrepancies there is the larger penetration of the high-$C_{\text{ANT}}$ from the uppermost layers waters down to $\sim$1200 dbar uppermost layers south from 30ºS predicted by the TTD, compared with the $\varphi C_{T}^{o}$ method. On the contrary, under 2000 dbar the $\varphi C_{T}^{o}$ estimates are higher on average ($3\pm2$ $\mu$mol kg$^{-1}$) than the TTD ones, except in the case of the $l$NADW where the TTD approach has produced the highest $C_{\text{ANT}}$ estimates.
The $C_{\text{ANT}}$ fields produced by the $\Delta C^*$ method included in the GLODAP database (Key et al., 2004) were corrected by the $A_T$ offset (Ríos et al., 2005). Although this correction removes 23% of the negative values of $C_{\text{ANT}}$, the $\Delta C^*$ method keeps showing negative $C_{\text{ANT}}$ concentrations below the 2800 dbar level in the WOCE A17 section (Fig. 3). These negative $C_{\text{ANT}}$ estimates were not considered for inventory calculations. Above this depth level the estimates are relatively similar to those from the $\varphi C_T^o$ method, reproducing the relative maximum associated to the $\nu$NADW north of 15°S and the relative minimum of the $\nu$CDW. However, south from 30°S the layers with the largest concentrations of $C_{\text{ANT}}$ are thicker (by ~250 meters, likely due to the AAIW influence) than those predicted by the $\varphi C_T^o$ method (Fig. 3).

The TrOCA approach has the convenience of being a very straightforward $C_{\text{ANT}}$ method to apply, since it is based on one simple equation that can be applied to the global ocean. The obtained $C_{\text{ANT}}$ fields through this method follow the same general trends described above for the rest of methods. It reproduces well the $\nu$CDW relative minimum north of 15°S and the moderate $C_{\text{ANT}}$ values from the AABW. The thickness of the high-$C_{\text{ANT}}$ upper layers is similar to that from the TTD and reaches deeper than in the case of the $\varphi C_T^o$ and $\Delta C^*$ methods. Nonetheless, the TrOCA method has generally yielded the highest $C_{\text{ANT}}$ estimates. The absolute maximum $C_{\text{ANT}}$ values in the upper SACW are the highest of all four methods, reaching even over the theoretical upper-limit of $C_{\text{ANT}}^{\text{sat}}$ for 1994 ($C_{\text{ANT}}^{\text{sat}}$ is the theoretical saturation concentration of $C_{\text{ANT}}$ for surface waters in equilibrium with the atmospheric CO$_2$ levels when the cruise was conducted). The main differences with the other methodologies are found in the slightly higher values associated to the relative minimum of the $\nu$CDW and in the lower values (~5 μmol kg$^{-1}$) spreading between 3000 and 4000 dbar all along the section, especially with respect to the $\varphi C_T^o$ and TTD methods. In addition, the relative maximum of the $\nu$NADW predicted by the latter two methods disappears in the case of TrOCA, while the $C_{\text{ANT}}$ estimates for the AABW fall halfway...
in the range between the \( \varphi C_T^o \) and TTD results. Finally, the relative maximum in the \( uNADW \) is also the highest of all four methods.

4. Discussion

One of the main goals in \( \text{C}_{\text{ANT}} \) estimation is to be able to come up with an educated guess of how much of it is stored in the ocean. Since \( \text{C}_{\text{ANT}} \) cannot be measured directly and there is no absolute reference against which results can be checked unequivocally, a comparison of the latitudinal variability (according to different estimation methodologies) of the specific \( \text{C}_{\text{ANT}} \) inventories is well justified (Fig. 4).

The vertically integrated \( \text{C}_{\text{ANT}} \) fields from the \( \varphi C_T^o \) and TrOCA methods are found to be in outstanding agreement, always within the uncertainties of either method. It is remarkable to see such a concurrence given the different \( \text{C}_{\text{ANT}} \) vertical gradients described by the two methods (Fig. 3). The observed differences stem mainly from the particular zero-\( \text{C}_{\text{ANT}} \) references in each approach. The similarities between the \( \varphi C_T^o \) and TrOCA specific inventories of \( \text{C}_{\text{ANT}} \) likely comes from a compensation of \( \text{C}_{\text{ANT}} \) between the uppermost and deeper layers: while the \( \varphi C_T^o \) method predicts lower \( \text{C}_{\text{ANT}} \) concentrations in the upper layers than TrOCA, the opposite occurs in deeper layers. When vertically integrated in the water column, the concentration values get, therefore, compensated. The lower surface concentrations in the \( \varphi C_T^o \) approach derive from considering the temporal variability of the air-sea CO\(_2\) disequilibrium (\( \Delta \Delta C_{\text{air}} \)), compared to the TrOCA approach. On the other hand, the slightly higher bottom estimates of the \( \varphi C_T^o \) method are the outcome of the \( A_T^o \) parameterization that was obtained taking subsurface layer observations as a reference of water mass formation conditions.
The C\textsubscript{ANT} intercomparison work from Vázquez-Rodríguez et al. (2009b) included an analogous comparison for the $\varphi$C\textsubscript{T$^o$} and TrOCA methods (amongst others) in the WOCE A14, which runs parallel to the west African coast along 10$^\circ$W covering a similar latitudinal range to the WOCE A17. In that work, the specific inventories of C\textsubscript{ANT} calculated from the $\varphi$C\textsubscript{T$^o$} are higher than the ones from the TrOCA method south from 20$^\circ$S, unlike in the WOCE A17, where results are more alike. This discrepancy likely stems from the fact that, unlike in the present study, the TrOCA method showed large volumes of C\textsubscript{ANT}-depleted waters in the deep South Atlantic region (south from 20$^\circ$S) of the WOCE A14 section. A recent publication (Yool et al., 2010) based on a comparison of C\textsubscript{ANT} estimates from the TrOCA method with model outputs questions the theoretical foundations of the TrOCA approach and reveals very large biases (up to 50%) at regional level, suggesting that a satisfactory universal TrOCA parameterisation is not achievable.

The $\varphi$C\textsubscript{T$^o$} and TrOCA methods give specific inventories of C\textsubscript{ANT} over the TTD ones, most notoriously in the latitudinal band between the Equator and 25$^\circ$S. This seems to be the direct result of the lower C\textsubscript{ANT} values predicted in this region by the TTD between 1000 and 2000 dbar (Fig. 3), compared with the TrOCA and $\varphi$C\textsubscript{T$^o$} methods. Contrastingly, the opposite occurs with the high TTD values for the lNADW. In spite of these discrepancies, the results obtained for the WOCE A14 in Vázquez-Rodríguez et al. (2009b) for the eastern Atlantic basin showed very similar specific inventories of C\textsubscript{ANT} for the TTD and $\varphi$C\textsubscript{T$^o$} methods. This is likely due to the fact that the deep waters in the eastern basin are older than those in the western one, and have therefore smaller amounts of C\textsubscript{ANT} and CFCs (Vázquez-Rodriguez et al., 2009b) that would yield lower methodological discrepancies. Regarding the difference of results here obtained for the WOCE A17 line, they are likely caused by the fact that the TTD approach assumes a globally constant mixing ($\Delta$) to advection ($\Gamma$) ratio $\Delta/\Gamma=1$ that might not be particularly representative of the ocean dynamics in the North Atlantic given the strong influence of the Meridional Overturning Circulation. Actually, it is most probable that the two NADW branches
would not share the same \( \Delta / \Gamma \) ratio since advection is likely to gain relevance over mixing in the upper NADW (\( u \text{NADW} \)) compared to the lower NADW (\( l \text{NADW} \)) (Steinfeldt et al., 2009).

With respect to the inventory estimates from GLODAP-\( \Delta C^* \) the results are similar to the TTD ones north of 30ºS, mind the large amount of negative \( C_{\text{ANT}} \) estimates in the \( \Delta C^* \) approach caused by the high zero-\( C_{\text{ANT}} \) reference considered (Gruber et al., 1996; Matsumoto and Gruber, 2005). South of 30ºS the \( \Delta C^* \) method also shows low specific inventories of \( C_{\text{ANT}} \) (Fig. 4). Regarding these results, Lo Monaco et al. (2005) had already pointed out that the \( \Delta C^* \) yielded close to zero or even negative \( C_{\text{ANT}} \) values in AABW, while the rest of methods predicted concentrations \( \sim 10 \mu \text{mol kg}^{-1} \). Compared with the specific inventories of \( C_{\text{ANT}} \) in the WOCE A14 (Vázquez-Rodríguez et al., 2009b), the results here obtained are very alike: in the equatorial and subtropical regions of the western Atlantic basin the \( \Delta C^* \) and TTD methods predict very similar inventory values and trends, but this similarity ceases south from 40ºS, where the influence of Antarctic origin waters starts to be sizeable. The here-accounted alkalinity offset and the corresponding increase in \( C_{\text{ANT}} \) specific inventory (\( \sim 12 \text{ mol} \ C \text{ m}^{-2} \)) brings closer together the \( \Delta C^* \) inventory and all others (differences reduce by 35%, especially south of 40ºS) in Fig. 4. However, there are non-negligible remnant discrepancies, especially south of 35ºS, with the inventories from TTD, \( \varphi C_{\Gamma^o} \) and TrOCA.

Lee et al. (2003) provided \( C_{\text{ANT}} \) inventories applying a slightly modified version of the \( \Delta C^* \) method and computed \( C_{\text{ANT}} \) specific inventories by latitude bands separately for the eastern and western Atlantic basins. The western Atlantic \( C_{\text{ANT}} \) inventories from Lee et al. (2003) (included in Fig. 4) are based on several cruises, including the WOCE A17. The basin wide inventories there described follow the same latitudinal trends as the WOCE A17 ones, except for the lower values south of 30ºS when compared to the \( \varphi C_{\Gamma^o} \), TTD and TrOCA estimates. Part of these lower values south of 30ºS (where only the section A17 was used to calculate inventories in
Lee’s work) can also be justified from the unaccounted -8 µmol kg\(^{-1}\) offset in \(A_T\) data previously mentioned. On this regard, Ríos et al. (2003) had also described for the eastern Atlantic basin an increasing trend of \(C_{\text{ANT}}\) inventories southwards from the Equator up to the Southern Ocean. They used a carbon-based back-calculation method for their \(C_{\text{ANT}}\) estimates that yielded results in agreement with model outputs (Sarmiento et al., 1995). In addition to this reference, a set of different Ocean Global Circulation Models (Princeton/GFDL, MPI and Hadley OGCMs) have reproduced \(C_{\text{ANT}}\) specific inventories showing similar trends of southward increment, i.e., an increase of 20-25 mol C m\(^{-2}\) from latitude 10\(^o\)S to 50\(^o\)S (Orr et al., 2001). The above evidences support the \(C_{\text{ANT}}\) specific inventory results here obtained by the \(\varphi C_T^o\), TTD and TrOCA methods, especially south of 30\(^o\)S. This suggests revising the Atlantic and global \(C_{\text{ANT}}\) inventories based on much larger, updated and high-quality data collections with different calculation methods.

On average, the western Atlantic basin shows \(C_{\text{ANT}}\) specific inventories that are \(\sim 35\%\) larger than those in the eastern basin between the Equator and 45\(^o\)S, compared with the work from Vázquez-Rodríguez et al. (2009b). This is congruent with the fact that the deep waters of the West Atlantic basin, i.e., NADW and AABW, are more ventilated and therefore have higher \(C_{\text{ANT}}\) burdens than those in the East Atlantic basin. As mentioned in the introductory section, the WOCE A17 tracks adequately the deep-water-bearing DWBC and facilitates making this inter-basin comparison.

5. Conclusions

This work examines the \(C_{\text{ANT}}\) distribution and inventories in the South Atlantic western basin calculated with data from the WOCE A17 cruise. The \(C_{\text{ANT}}\) estimates obtained with the \(\Delta C^*, \varphi C_T^o\), TrOCA (all three corrected for the \(A_T\) offset reported in Rios et al, 2005) and TTD methods show different concentration distributions depending on the water masses and
circulation. All methods reported the maximum values of $C_{ANT}$ (50-60 µmol kg$^{-1}$) in the upper warm waters from the tropical gyres, where the SACW predominates. The TrOCA method gives the highest [$C_{ANT}$] values. In the upper layers, concentrations reach even over the theoretical limit of the $C_{ANT}$ saturation for 1994. The minimum $C_{ANT}$ values (~5 µmol kg$^{-1}$) from all methods are found in the oldest waters flowing northwards, at about 1000 dbar ($\mu$CDW) and around 3500 dbar (lCDW). The TTD and $\varphi C_{T^o}$ methods show similar distributions of these minimum values. The TrOCA and GLODAP-$\Delta C^*$ methods both show the minima associated to the $\mu$CDW, but the minimum associated to the lCDW reaches the bottom in the case of TrOCA (unlike the TTD and $\varphi C_{T^o}$ methods) and it disappears in the case of the $\Delta C^*$. North of 15ºS the relative maxima are associated to the slightly more ventilated and younger $\mu$NADW and lNADW. The TrOCA approach gives the highest relative maximum in the $\mu$NADW of all four methods, being three times higher than the TTD method and two times higher than $\Delta C^*$ and $\varphi C_{T^o}$ methods. The main overall discrepancies between the four methods correspond to the relative $C_{ANT}$ maximum of the lNADW: this structure is well identified in the $\varphi C_{T^o}$ and TTD methods but seems to disappear in the case of TrOCA and GLODAP-$\Delta C^*$. South of 40ºS there is a slight increase of $C_{ANT}$ below 4000 dbar originated by the penetration northwards of the AABW that is detected by the $\varphi C_{T^o}$, TrOCA and TTD methods. The $\Delta C^*$ approach consistently yielded negative estimates of $C_{ANT}$ below ~2800 db (Fig. 3) that were not considered when computing column inventories of $C_{ANT}$.

In terms of specific inventories of the western Atlantic basin, the $\varphi C_{T^o}$, TrOCA and TTD $C_{ANT}$ estimation methods confirm an increasing tendency south from the Equator. Contrarily, the $\Delta C^*$ method shows a decreasing trend south from 35ºS. South of 40ºS the average $C_{ANT}$ inventory obtained from $\varphi C_{T^o}$, TrOCA and TTD methods is significantly higher (~45%) than those in the GLODAP database calculated from the $\Delta C^*$ method.
ACKNOWLEDGEMENTS

We would like to thank the captain, officers and crew of the R/V Maurice Ewing and all the participants of the CITHER–2 cruise. We are also very grateful to G. Rosón for his pH and alkalinity measurements. Special thanks go to M. Arhan (coordinator of the WOCE–France program CITHER) and L. Mémery (chief scientist of cruise CITHER-2). This work was developed and funded by the European Commission within the 6th Framework Programme (EU FP6 CARBOOCAN Integrated Project, Contract no. 511176) and by the Xunta de Galicia within the INCITE framework (M4AO project PGIDIT07PXIB402153PR). Marcos Vázquez-Rodríguez was funded by the Consejo Superior de Investigaciones Científicas (CSIC) I3P predoctoral grant program REF.: I3P-BPD2005.

References


Figure captions

Figure 1 Map of the eastern South Atlantic Ocean showing the position of the 107 full–depth stations surveyed during the CITHER-2 (WOCE A17) cruise.
Figure 2  Vertical profiles of measured $\theta$ ($^\circ$C), salinity, [Si(OH)$_3$] ($\mu$mol kg$^{-1}$), calculated Apparent Oxygen Utilisation (AOU; $\mu$mol kg$^{-1}$), CaCO$_3$ dissolution ($\Delta$Ca; $\mu$mol kg$^{-1}$) and water mass age (years) from CFC12 data. The acronyms of the main water masses present along the WOCE A17 line are labeled on the $\theta$ (SACW, uNADW, lNADW, uCDW, lCDW and AABW) and salinity (AAIW) plots.

Figure 3  Vertical profiles of C$_{ANT}$ along the WOCE A17 line according to four different estimation approaches: the $\varphi$C$_T^\circ$, the GLODAP-$\Delta$C*, the TrOCA and the TTD methods. All concentrations are in $\mu$mol kg$^{-1}$. The reported -8 $\mu$mol kg$^{-1}$ A$_T$ offset (Rios et al., 2005) has been considered and corrected for in all three C$_{ANT}$ back-calculation approaches, i.e., $\varphi$C$_T^\circ$, GLODAP-$\Delta$C* and TrOCA. The spots where negative C$_{ANT}$ estimates were predicted by the $\Delta$C* method have been automatically set to zero and filled with a light purple color. They are located below the C$_{ANT}$=0 isopleth (pressures > ~2800 dbar).

Figure 4  C$_{ANT}$ specific inventories were estimated by vertical integration. The uncertainties of these estimates were calculated by means of random propagation with depth of an average 5.2 $\mu$mol kg$^{-1}$ standard error of the C$_{ANT}$ estimate over 100 perturbation iterations. Assuming that the uncertainties attached to the C$_{ANT}$ estimation method are purely random and do not introduce biases, the final error is calculated by propagating the individual errors associated to the samples. They reflect both measurement and parameterization errors. For each of the considered latitude belts the mean of the integrated values at each station was calculated. The error bars here shown were computed as the confidence intervals of the mean.
Figure 2
Figure 3