

## Anthropogenic CO<sub>2</sub> in the Azores region

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**SUMMARY:** The AZORES-I cruise was conducted in August 1998, spanning the length of three latitudinal large-scale sections at 22, 28 and 32°W. The oceanic carbon system was oversampled by measuring total alkalinity, total inorganic carbon and pH. It is thus possible to estimate anthropogenic CO<sub>2</sub> (C<sub>ANT</sub>) and to investigate its relationship with the main water masses that are present. C<sub>ANT</sub> is calculated using the latest back-calculation techniques:  $\varphi C_T^\circ$  and TrOCA methods. Although the two approaches produce similar vertical distributions, the results of the TrOCA method show higher C<sub>ANT</sub> variability and produce higher inventories than those of the  $\varphi C_T^\circ$  method. The large proportion of Mediterranean Water found in the northern part of the study area is the main cause of the observed increase northwards of C<sub>ANT</sub> inventories. Changes in C<sub>ANT</sub> inventories between 1981 and 2004 are evaluated using data from the TTO-NAS, OACES-93 and METEOR-60/5 cruises. According to the  $\varphi C_T^\circ$  and TrOCA approaches, the average long-term rates of C<sub>ANT</sub> inventory change are 1.32±0.11 mol C m<sup>-2</sup> y<sup>-1</sup> (P=0.008) and 1.18±0.16 mol C m<sup>-2</sup> y<sup>-1</sup> (P=0.018), respectively. During the 1993-1998 a significant increase in the C<sub>ANT</sub> storage rate was detected by the  $\varphi C_T^\circ$  method. It is thought that this stems directly from the enhanced Labrador Seawater formation after the increased advection observed at the time.

**Keywords:** anthropogenic CO<sub>2</sub>, CO<sub>2</sub> uptake, water masses, Mediterranean Water, Labrador Seawater.

**RESUMEN:** CO<sub>2</sub> ANTROPOGÉNICO EN LA REGIÓN DE LAS AZORES. – La campaña de macro-escala Azores I se desarrolló durante el mes de agosto de 1998 y consta de tres secciones meridionales centradas en 22, 28 y 32°W. El sobre-muestreo realizado del sistema del carbónico, con medidas de alcalinidad total, carbono inorgánico total y pH, ha permitido el cálculo del CO<sub>2</sub> antropogénico (C<sub>ANT</sub>) e investigar su distribución en las masas de agua presentes. El C<sub>ANT</sub> se calculó mediante las últimas técnicas de retro-cálculo disponibles: los métodos  $\varphi C_T^\circ$  y TrOCA. A pesar de que ambos procedimientos producen distribuciones verticales similares, los resultados del método TrOCA indican mayores inventarios y variabilidad de C<sub>ANT</sub> que los estimados por el método  $\varphi C_T^\circ$ . La elevada proporción de agua mediterránea presente al norte de la región estudiada es la causa principal del aumento hacia el norte de los inventarios de C<sub>ANT</sub>. Las tasas de cambio en los inventarios de C<sub>ANT</sub> entre 1981 y 2004 se han evaluado utilizando datos de las campañas TTO-NAS, OACES-93 y METEOR-60/5. Según los métodos  $\varphi C_T^\circ$  y TrOCA, las tasas de cambio promedio a largo plazo del inventario de C<sub>ANT</sub> en esta zona son de 1.32±0.11 mol C m<sup>-2</sup> y<sup>-1</sup> (p-valor=0.008) y de 1.18±0.16 mol C m<sup>-2</sup> y<sup>-1</sup> (p-valor=0.018), respectivamente. Durante el periodo 1993-1998 el método  $\varphi C_T^\circ$  detecta un aumento significativo de la tasa de acumulación de C<sub>ANT</sub> provocado posiblemente por las elevadas tasas de formación de agua de Labrador, derivadas del aumento de la advección observada en dicho periodo.

**Palabras clave:** CO<sub>2</sub> antropogénico, captación de CO<sub>2</sub>, masas de agua, Agua Mediterránea, Agua de Labrador.

### 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 of 8.0±0.5 Pg yr<sup>-1</sup> of anthropogenic carbon (C<sub>ANT</sub>)

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 38% of the oceanic C<sub>ANT</sub> storage, though it only represents 29% of the

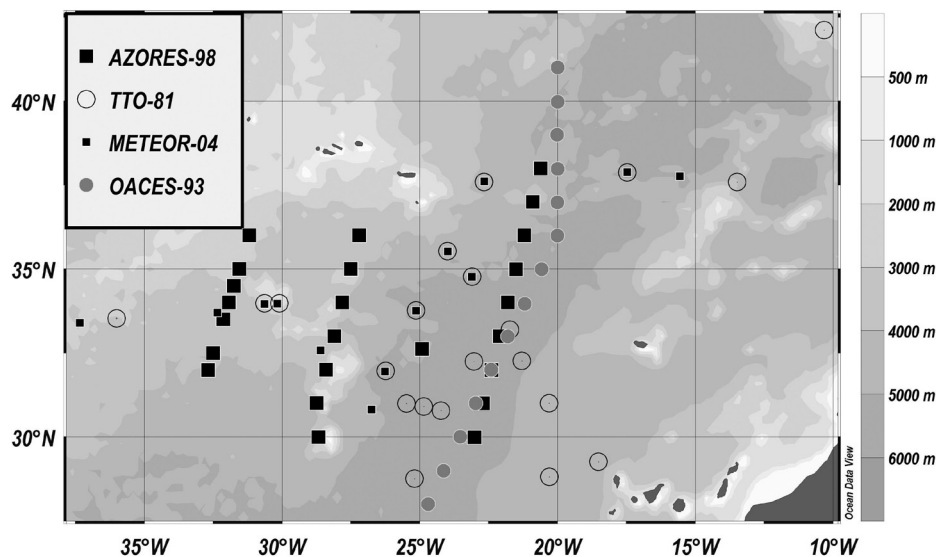


FIG. 1. – Map of the Azores Region showing the stations that were full-depth sampled during the AZORES I cruise (1998). The stations from the other three cruises considered are also shown: the TTO-NAS (1981), OACES (1993), and METEOR-60/5 (2004) cruises.

global ocean surface area (Sabine *et al.*, 2004). Quantifying the concentration and distribution of  $C_{ANT}$  in the oceans has therefore become a crucial issue for understanding the global carbon cycle and its future evolution in a world of high  $CO_2$ . Accordingly, considerable efforts have been devoted over the past decade to assessing the capacity of the ocean to sequester  $CO_2$  and the predicted changes brought about by the associated ocean acidification.  $C_{ANT}$  represents 3%, at most, of the total dissolved inorganic carbon ( $C_T$ ) pool, and its estimation has a considerable associated constraint: it is impossible to cross-check the estimates with direct in situ measurements since  $C_{ANT}$  cannot be chemically discriminated within the bulk of the oceanic  $C_T$ . In order to overcome this limitation, several methods for estimating  $C_{ANT}$  indirectly have been developed, based on different tracers.

Backup-calculation techniques were formulated to tackle the issue of  $C_{ANT}$  estimation. They were first described and applied in the pioneering works by Brewer (1978) and Chen and Millero (1979), who took the measured  $C_T$  and, through several estimations and assumptions, “stripped” from it the individual contributions or background signals from the processes affecting  $C_T$ , namely: organic matter remineralization (ROM) and dissolution of calcium carbonate ( $CaCO_3$ ) species that had occurred since the water mass had been last in contact with the atmosphere. Following the earlier concept of preformed nutrient defined by Redfield *et al.* (1963), the preformed total inorganic carbon ( $C_T^o$ ) was analogously defined: it is the  $C_T$  that the water mass had right upon formation. The  $C_T^o$  term has not remained constant since the Industrial Revolution because the water masses had gradually started to form in contact with an atmosphere continuously altered by human activities (Wallace, 2001). Therefore,

$C_T^o$  hosts the  $C_{ANT}$  imprint, which could be retrieved by subtracting a “zero- $C_{ANT}$ ” reference from it. Two different  $C_{ANT}$  reconstruction methods have been recently developed: the TrOCA method (Touratier *et al.*, 2007) and the  $\varphi C_T^o$  method (Vázquez-Rodríguez *et al.*, 2009). The TrOCA parameter is a quasi-conservative tracer calculated from  $O_2$ , total alkalinity ( $A_T$ ), and  $C_T$ , similarly to other classical conservative tracers such as “NO” (Broecker, 1974; Ríos *et al.*, 1989). The  $\varphi C_T^o$  method is an upgrade of the classical  $\Delta C^*$  approach (Gruber *et al.*, 1996) and proposes different parameterizations of the preformed  $A_T$  ( $A_T^o$ ) and air-sea  $CO_2$  disequilibrium ( $\Delta C_{dis}$ ) estimated from subsurface data (between 100 and 200 dbar).

The importance of quantifying accurately how much  $C_{ANT}$  is stored in the ocean has recently increased even further as several authors have observed a weakening in the strength of the North Atlantic  $CO_2$  sink over the last decade. Canadell *et al.* (2007) suggest that around 10% of the recent (2000–2006) increase in atmospheric  $CO_2$  concentrations can be attributed to the weakening of the ocean  $CO_2$  sink. The decline has been considerable (loss of ~40% in the  $CO_2$  uptake capacity) in the northern Atlantic basin (Schuster and Watson, 2007; Corbière *et al.*, 2007; Olsen *et al.*, 2008; Pérez *et al.*, 2008, Steinfeldt *et al.*, 2009). This change translates into an increasing fraction of the anthropogenic emissions remaining in the atmosphere, consistently with recent outputs from several Ocean Global Circulation Models (Orr *et al.*, 2001). The interannual decrease in the convection activity and the associated water mass formation events is mainly driven by the fluctuating phase of the North Atlantic Oscillation (NAO) (Schuster and Watson, 2007, Pérez *et al.*, 2008). The more feeble convection observed, together with the known decrease in the ocean’s natural buffering capacity (trig-

gered by the  $C_{ANT}$  increase), are strong candidates to account for the weakening of the North Atlantic sink. In particular, a strong decrease in  $C_{ANT}$  storage rates has been observed in the Irminger Sea occurring from the early 1990s to early 2000s (otherwise corroborated by chlorofluorocarbon-12 inventories). These periods of low convection, associated with two opposite NAO phases, have greatly helped to reduce the Labrador Seawater formation events in the North Atlantic Subpolar Gyre (NASPG). Ultimately, this has lowered the efficiency of the northern North Atlantic CO<sub>2</sub> sink (Pérez *et al.*, 2008; Kieke *et al.*, 2006). Contrastingly, Schuster and Watson (2007) found that the CO<sub>2</sub> air-sea exchange rate has kept nearly constant over the last decade in the North Atlantic Subtropical Gyre (NASTG). The present study will evaluate the  $C_{ANT}$  storage in the NASTG by applying the most recent back-calculation techniques to the data from four cruises spanning the eastern subtropical gyre from 1981 to 2004 (Fig. 1). The aim is two-fold: 1) to determine whether the oceanic  $C_{ANT}$  storage follows the expected rates of increase (assuming that winter mixed layers keep up with the increasing atmospheric CO<sub>2</sub> levels; and 2) to determine how the choice of the back-calculation method affects the results obtained.

## MATERIALS AND METHODS

### Data

The AZORES I cruise was performed in August 1998 on board the *BIO Hesperides* (Pérez *et al.*, 2003). The survey comprised three latitudinal large-scale sections at nominal longitudes of 22°W, 28°W, and 32°W (Fig. 1). A General Oceanic CTD (Mark III WOCE Single) was down-hauled along with a rosette mounted with 24 12-L Niskin bottles. Water samples for  $C_T$ ,  $A_T$ , pH, O<sub>2</sub> and nutrient analyses were taken at different levels of the water column.

The  $C_T$  analyses were performed by gas extraction with a SOMMA (Single Operator Multiparameter Metabolic Analyzer) apparatus. The CO<sub>2</sub> is carried in this equipment by a free-CO<sub>2</sub> gas (N<sub>2</sub>) into a coulometric cell, where it is quantitatively absorbed after reacting with methanolamine (Johnson *et al.*, 1993). Surface and deep replicate bottles for  $C_T$  measurements were collected at each station. The precision of these replicates ranged from <0.5 to 1  $\mu\text{mol kg}^{-1}$ . Regular calibrations were performed every 20-30 samples with Certified Reference Material (CRM) of CO<sub>2</sub>, supplied by Andrew Dickson (Scripps Institution of Oceanography, University of California), to check for the accuracy of the measurements. Overall, 72 CRM bottles were analyzed and a standard deviation of 1.2  $\mu\text{mol kg}^{-1}$  was obtained.

The  $A_T$  samples were analyzed by automatic potentiometric titration with HCl to an endpoint pH of 4.44 (Pérez and Fraga, 1987; Mintrop *et al.*, 2000). The accuracy and consistency of the  $A_T$  measurements were

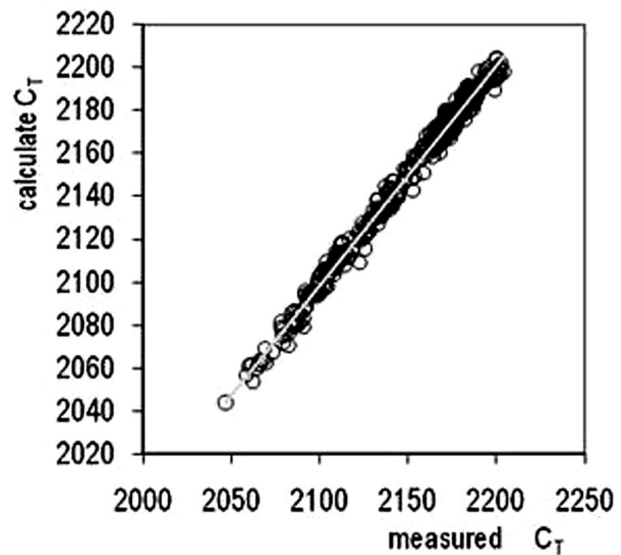


FIG. 2. – Relationship between the calculated and measured  $C_T$ . Units are in  $\mu\text{mol}\cdot\text{kg}^{-1}$ . The equation of the linear fit is:  $y=1.024x - 52.1$  ( $R^2=0.992$ ).

checked by  $A_T$  analytical determination of CRM bottles (batch 43). A total of 74 CRM analyses yielded an average  $A_T$  of  $2202.9 \pm 1.7 \mu\text{mol kg}^{-1}$ , coincident with the certified reference value. The average absolute difference (error) in duplicates of 445 different samples was 1.8  $\mu\text{mol kg}^{-1}$ . Seawater pH was measured using a double wavelength spectrophotometric procedure (Clayton and Byrne, 1993). Absorbance measurements were performed with a Cecil 3041 spectrophotometer. Temperature was controlled during the measurement sessions using a recirculating thermostatic bath at 25°C. The accuracy of the pH measurements was determined using the same CRM batch, and yielded a value of  $\pm 0.002$ . Where no measurement of  $C_T$  was available, this was calculated from  $A_T$  and  $\text{pH}_T$  using the inorganic carbon system thermodynamic equations and the acid constants from Mehrbach *et al.* (1973) fitted by Dickson and Millero (1987). The total error for these calculated  $C_T$  values is  $\pm 3 \mu\text{mol kg}^{-1}$ , considering the average values of pH,  $A_T$ , salinity and temperature during the cruise as well as the associated errors of pH and  $A_T$ . The regression between the measured and calculated  $C_T$  was very high (Fig. 2). The average difference between calculated and measured  $C_T$  during the cruise was  $-0.2 \mu\text{mol kg}^{-1}$ , with an average error of  $\pm 3.6 \mu\text{mol kg}^{-1}$ . The results of these calibrations prove the high internal consistency of the carbonic system data produced. The outstanding precision, accuracy and internal consistency of the shipboard CO<sub>2</sub> measurements during the Azores I cruise make the data highly reliable for the purposes of oceanic carbon studies.

In addition to the Azores I cruise, the data available from three other cruises (the TTO, OACES-93 and METEOR-04) was used to evaluate the temporal trends of  $C_{ANT}$  storage. The “Transient Tracers in the Ocean-

North Atlantic Study” (TTO-NAS) was performed in 1981 (TTO, 1986; Takahashi and Brewer, 1986). Tanhua *et al.* (2005) recently evaluated the quality of the carbon measurements made during this cruise using modern measurements based on CRM tests. After the corrections had been applied, the analytical error determined for  $C_T$  and  $A_T$  was  $\pm 3.7$  and  $\pm 3.5 \mu\text{mol kg}^{-1}$ , respectively. A revision of the TTO cruise in the area of the subtropical gyre was conducted in 2004 on board the R/V *Meteor* (Tanhua *et al.*, 2007) to get a direct comparison and compute decadal changes in  $C_{\text{ANT}}$  in comparison with the original TTO cruise. The  $C_T$  and  $A_T$  measurements during the METEOR 60/5 were made using the same methodologies as in the Azores I, and the analytical errors obtained for  $C_T$  and  $A_T$  were 1.5 and  $4.3 \mu\text{mol kg}^{-1}$ , respectively (Tanhua *et al.*, 2005). The  $C_T$  and  $A_T$  calibrations were performed by analyzing four different CRM batches (#58, #60, #63 and #64).

Finally, one meridional section along  $20^\circ\text{N}$  (Fig. 1) was occupied as part of the Ocean-Atmosphere Carbon Exchange Study (OACES). For the OACES-93 cruise the  $A_T$  and  $C_T$  measurements were performed using titration and coulometric techniques, respectively, just as in the METEOR-04 and AZORES I cruises (Wanninkhof *et al.*, 1999). The CRM Batch #16 was used for  $A_T$  and  $C_T$  measurement calibration. The corrections for  $C_T$  measurements typically did not exceed  $2 \mu\text{mol kg}^{-1}$ , while the mean standard deviation from all CRMs analyzed during the cruise was less than  $1.5 \mu\text{mol kg}^{-1}$ . The precision for  $A_T$  measurements throughout OACES-93 was  $\pm 2 \mu\text{mol kg}^{-1}$  (Castle *et al.*, 1998). Altogether, the three selected cruises performed in the Azores area allow the long and short-term trends of  $C_{\text{ANT}}$  storage to be studied during a 23-year time period.

### $C_{\text{ANT}}$ estimation methods

Two recently developed  $C_{\text{ANT}}$  back-calculation methods (the TrOCA and the  $\varphi C_T^\circ$  methods) were selected to determine  $C_{\text{ANT}}$  in the present study. The principles of the two methods are based on separating the contributions to  $C_T$  from ROM and  $\text{CaCO}_3$  dissolution in a similar manner. However, there are characteristic distinctions. The TrOCA approach uses a constant  $R_C$  value of 1.35 (after Körtzinger *et al.*, 2001), while the  $\varphi C_T^\circ$  method, following the  $\Delta C^*$  method, uses the constant  $R_C$  ratio of 1.45 proposed by Anderson and Sarmiento (1994). The most important difference between the two methods, however, lies in the way the reference for  $C_{\text{ANT}}$ -free waters is obtained. The TrOCA method estimates  $C_{\text{ANT}}$  using the following simple relationship:

$$C_{\text{ANT}} = \frac{(\text{TrOCA} - \text{TrOCA}^0)}{a} \quad (1)$$

where TrOCA represents a quasi-conservative tracer calculated from  $\text{O}_2$ ,  $C_T$  and  $A_T$  as follows:

$$\text{TrOCA} = \text{O}_2 + a(C_T - 0.5 \cdot A_T) \quad (2)$$

The  $\text{TrOCA}^0$  reference represents the TrOCA tracer without any anthropogenic carbon influence, i.e. the pre-industrial TrOCA:

$$\text{TrOCA}^0 = e^{\left(\frac{b-c\theta-d}{A_T^2}\right)} \quad (3)$$

The coefficients “a, b, c and d” in the above equations are properly defined and established in Touratier *et al.* (2007). The  $\text{TrOCA}^0$  equation is obtained from  $\Delta^{14}\text{C}$  and CFC-11 data in the global ocean. The  $\Delta^{14}\text{C}$  data are used to establish which water parcels can be assumed to be free of  $C_{\text{ANT}}$ . When the concentration of  $\Delta^{14}\text{C} < 175$  per mille, the age of the corresponding water mass is greater than 1400 years, long before the massive emissions of  $\text{CO}_2$  by humans had begun. The samples with maximum CFC-11 concentrations, typically between 262.9 and 271.3 pptv, corresponding to surface waters in 1992-1995 (maximum atmospheric  $p\text{CFC-11}$ ), were also selected as part of the dataset to obtain the  $\text{TrOCA}^0$  expression. Touratier *et al.* (2007) estimated an uncertainty of  $\pm 6.2 \mu\text{mol kg}^{-1}$  in  $C_{\text{ANT}}$  determination for the TrOCA approach, using an error propagation technique as in numerous previous works (Gruber *et al.*, 1996; Sabine *et al.*, 1999).

The  $\varphi C_T^\circ$  method shares similar fundamentals with the  $\Delta C^*$  back-calculation method (Vázquez-Rodríguez *et al.*, 2009). Differently though, the sub-surface layer (100-200 m) is taken in the  $\varphi C_T^\circ$  method as a reference for characterizing water mass properties at the moment of their formation (Pérez *et al.*, 2002). The air-sea  $\text{CO}_2$  disequilibrium ( $\Delta C_{\text{dis}}$ ) is parameterized at the sub-surface layer first using a short-cut method (Thomas and Ittekkot, 2001) to estimate  $C_{\text{ANT}}$ . Since the average age of the water masses in the 100-200 m depth domain, and most importantly in outcropping regions, is under 25 years, the use of the short-cut method to estimate  $C_{\text{ANT}}$  is appropriate (Matear *et al.*, 2003). The  $A_T^\circ$  and  $\Delta C_{\text{dis}}$  parameterizations (in terms of conservative tracers) obtained from sub-surface data are applied directly to calculate  $C_{\text{ANT}}$  in the water column for waters above the  $5^\circ\text{C}$  isotherm and via an OMP analysis for waters with  $\theta < 5^\circ\text{C}$ . This procedure especially improves the estimates in cold deep waters that are subject to strong and complex mixing processes between Arctic and Antarctic water masses. Waters below the  $5^\circ\text{C}$  isotherm also represent an enormous volume of the global ocean (~86%). One important aspect of the  $\varphi C_T^\circ$  approach is that none of the  $A_T^\circ$  or  $\Delta C_{\text{dis}}$  parameterizations are CFC-reliant. In addition, the  $\varphi C_T^\circ$  method proposes an approximation to the temporal and spatial variability of  $\Delta C_{\text{dis}}$  ( $\Delta\Delta C_{\text{dis}}$ ) in the Atlantic Ocean in terms of  $C_{\text{ANT}}$  and  $\Delta C_{\text{dis}}$  itself. Also, the small increase in  $A_T^\circ$  since the Industrial Revolution due to  $\text{CaCO}_3$  dissolution changes (as projected from models; Heinze, 2004) and the effect of rising sea surface temperatures on the parameterized  $A_T^\circ$  are accounted for in the parameterizations. These two last corrections are minor but should still be considered if one wishes to avoid a maximum  $4 \mu\text{mol kg}^{-1}$  bias ( $2 \mu\text{mol kg}^{-1}$  on average) in  $C_{\text{ANT}}$  esti-

mates. The  $\varphi C_T^\circ$  method expression for the calculation of  $C_{ANT}$  is as follows:

$$C_{ANT} = \frac{\Delta C^* - \Delta C_{dis}^t}{1 + \varphi |\Delta C_{dis}^t| / C_{ANT}^{sat}} \quad (4)$$

The  $\Delta C^*$  is defined after Gruber *et al.*, (1996) as:

$$\Delta C^* = C_T - AOU/R_C - 0.5 (PA_T - PA_T^\circ) - C_T^\pi \quad (5)$$

The constant term  $\varphi$  is a proportionality factor that stands for the  $\Delta C_{dis} / \Delta C_{dis}^t$  ratio and its value (0.55) is properly discussed in Vázquez-Rodríguez *et al.* (2009). The  $\Delta C_{dis}^t$  and  $PA_T^\circ$  terms are parameterized as a function of conservative parameters exclusively (Vázquez-Rodríguez *et al.*, 2009). The  $C_{ANT}^{sat}$  stands for the theoretical  $C_{ANT}$  saturation concentration depending on the  $pCO_2$  at the time of WMF and is defined as  $C_{ANT}^{sat} = S/35 (0.85\theta + 46.0)$  (at present  $xCO_{2,air}$ ). Based on earlier uncertainty and error evaluations (Gruber *et al.*, 1996; Sabine *et al.*, 1999; Lee *et al.*, 2003; Touratier *et al.*, 2007), an estimated overall uncertainty of  $\pm 5.2$  mmol kg<sup>-1</sup> is obtained for the  $\varphi C_T^\circ$  method. This is in agreement with the average uncertainty of 5.6 mmol kg<sup>-1</sup> for  $\Delta C_{dis}$  (Vázquez-Rodríguez *et al.*, 2009). For comparison, the overall estimated uncertainty of  $C_{ANT}$  using the  $\Delta C^*$  approach is  $\pm 6$  mmol kg<sup>-1</sup> in Sabine *et al.* (1999) and  $\pm 9$  mmol kg<sup>-1</sup> in Gruber *et al.* (1996).

The specific inventories of  $C_{ANT}$  were calculated by vertical integration down to 4500 m. The uncertainties of these estimates were obtained by means of random propagation with depth of the  $C_{ANT}$  standard errors of the estimate ( $\pm 5.2$  and  $\pm 6.2$   $\mu\text{mol kg}^{-1}$  for the  $\varphi C_T^\circ$  and TrOCA methods, respectively) over 100 perturbation iterations. It has been assumed that the uncertainties associated with the  $C_{ANT}$  estimation methods are purely random and do not introduce any biases. Therefore, they consider both measurement and parameterization errors. For the Azores region (between [10°W, 35°W] and [26°N, 42°N], and with an average depth of 4500 m) the final error in the  $C_{ANT}$  storage is obtained as the root mean square of the mean uncertainties from the vertical integrals at every station ( $\sim 1.5$  mol C m<sup>-2</sup>). The error of the averaged  $C_{ANT}$  storage in Table 1 is expressed as a standard deviation. The error bars shown in the corresponding graphs represent the confidence intervals of the mean.

## RESULTS

The most noteworthy thermohaline feature observed in the latitudinal variability of the Azores I cruise is the presence of the core of Mediterranean Water at about 1000 dbar (Ríos *et al.*, 1992). The vertical thermohaline structure is dominated in the upper layers of the main thermocline by the presence of North Atlantic Central Water (NACW, Fig. 3) and the influence of the Antarctic Intermediate Water (AAIW), which is well characterized by the maximum of AOU located

TABLE 1. – Specific inventories of  $C_{ANT}$  and  $C_{bio} = AOU/R_C$  term in the Azores region (10-35°W and 26-42°N). The error of the averaged  $C_{ANT}$  storage is expressed as a standard deviation.

| Cruise   | Year | $xCO_2$<br>ppm | $C_{ANT}^{sat}$<br>$\mu\text{mol kg}^{-1}$ | $C_{bio}$<br>$\mu\text{mol kg}^{-1}$ | $C_{ANT}$<br>( $\varphi C_T^\circ$ )<br>mol C·m <sup>-2</sup> | $C_{ANT}$<br>(TrOCA)<br>mol C·m <sup>-2</sup> | MPD<br>m |
|----------|------|----------------|--|--------------------------------------|---|---|----------|
| TTO-NAS  | 1981 | 339            | 40.0                                       | 213.5±2.5                            | 57±2  | 65±2  | 1390±51  |
| OACES    | 1993 | 357            | 49.3                                       | 210.3±3.3                            | 70±1  | 74±2  | 1388±28  |
| Azores I | 1998 | 367            | 54.6                                       | 217.2±2.0                            | 81±1  | 83±1  | 1439±13  |
| METEOR   | 2004 | 378            | 60.0                                       | 210.0±3.5                            | 87±1  | 92±1  | 1409±23  |

in the south. The upper North Atlantic Deep Water (*u*NADW) is located at  $\sim 2000$  dbar and is well characterized by the minimum of AOU towards the northern end of the section, indicating that the major component in this level is the Labrador Sea Water (LSW). The relative minimum of  $A_T$  located at this depth-horizon is also one of the featured LSW imprints. From this level down to the bottom the lower NADW (*l*NADW) is found, characterized by the maximum of silicate (not shown) and by the increase in  $A_T$  and AOU (Castro *et al.*, 1998).

Both  $C_{ANT}$  fields show similar latitudinal patterns. The vertical gradient is clearly identified by both  $C_{ANT}$  reconstruction methods. However, this vertical gradient is slightly different at the northern end of the Azores I section for the TrOCA and  $\varphi C_T^\circ$  methods. This likely stems from the presence of the MW, which here causes a higher penetration of  $C_{ANT}$  (Ríos *et al.*, 2001). The minimum values of  $C_{ANT}$  from the TrOCA method are lower than those from the  $\varphi C_T^\circ$  method at the 4500 dbar horizon. It must also be noted that the maximum surface values were as well predicted by the TrOCA approach. Even so, the correlation between  $C_{ANT}$  estimates from the  $\varphi C_T^\circ$  and TrOCA methods (Fig. 4) is found to be very high ( $R^2=0.94$ ), with a mean difference of  $-1.5 \pm 3.6$  mmol kg<sup>-1</sup> (lower than the uncertainties from both methods). However, there are some differences in the estimated  $C_{ANT}$  fields, most noticeably with respect to the vertical gradients or the variability ranges from both methods. The results from the TrOCA method show the highest range of  $C_{ANT}$  values, spanning from -1.6 to 60.8 mmol kg<sup>-1</sup>, while the  $\varphi C_T^\circ$  method predictions span from 3.8 to 56.1 mmol kg<sup>-1</sup>. This is the result of a combined effect resulting from the different preindustrial “zero- $C_{ANT}$ ” references and the quantification of biological contributions. Considering the different  $R_C$  ratios used and the AOU values recorded in deep waters ( $\sim 80$  mol kg<sup>-1</sup>), the biological components for the TrOCA and  $\varphi C_T^\circ$  methods amounted to 54 and 59 mmol kg<sup>-1</sup>, respectively. In the upper layers, with lower AOU values, the differences in  $C_{ANT}$  estimates between the methods comes mainly from the different parameterizations of the pre-industrial and preformed properties (TrOCA° and  $A_T^\circ$ ) and also from the  $\Delta C_{dis}$  parameterizations in warm waters in the  $\varphi C_T^\circ$  method. The TrOCA° is affected exponentially by temperature and by the square of  $A_T$ . For  $\varphi C_T^\circ$  the “zero- $C_{ant}$ ” reference involves two terms: the  $\Delta C_{dis}$  and  $C_{ANT}^{sat}$ ,

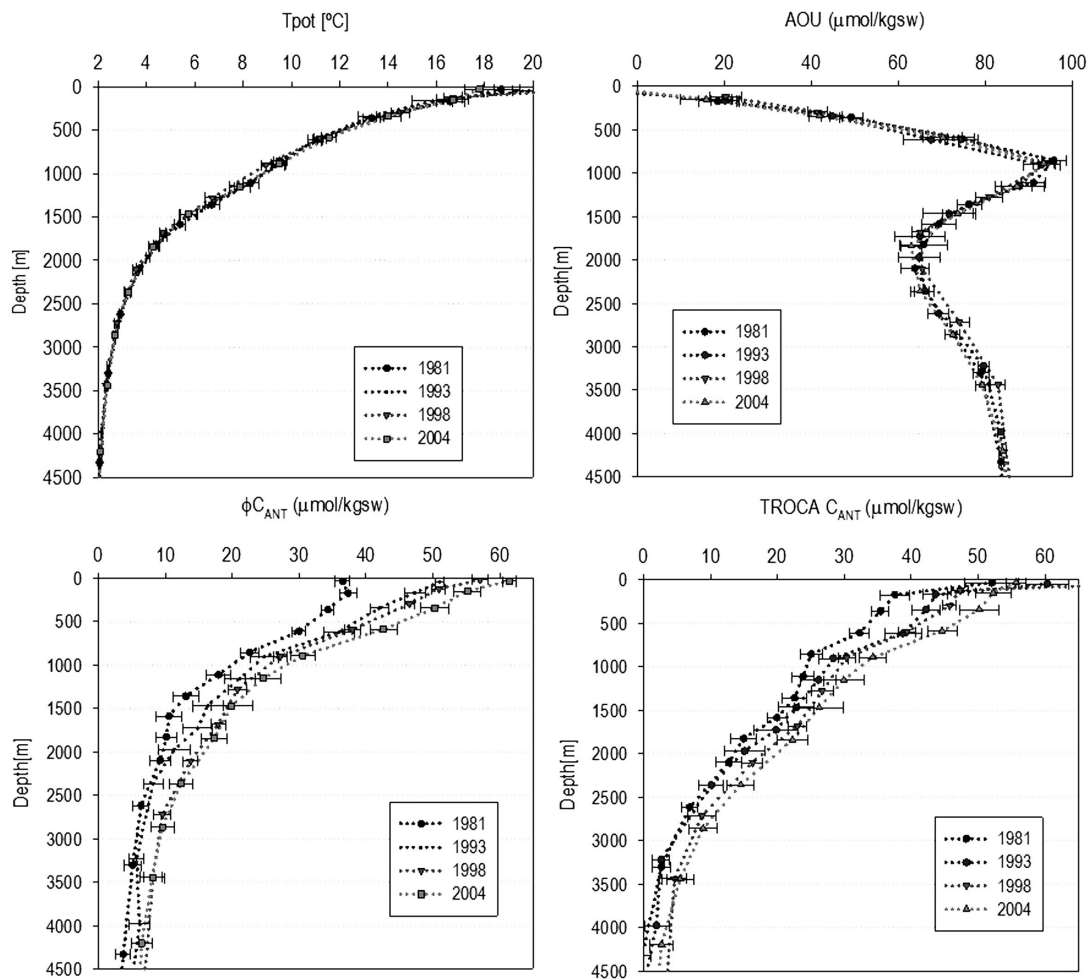


FIG. 3. – Averaged vertical profiles of potential temperature (°C), AOU ( $\mu\text{mol}\cdot\text{kg}^{-1}$ ) and  $C_{ANT}$  calculated with the TrOCA and  $\phi C_T^\circ$  methods (in  $\mu\text{mol}\cdot\text{kg}^{-1}$ ) for the cruises TTO-NAS (1981), OACES (1993), Azores I (1998) and METEOR-60/5 (2004).

which is affected linearly by  $A_T^\circ$  and temperature. The high alkalinity and high temperatures in the upper layer tend to produce low values for the reference TrOCA $^\circ$ , thus producing higher  $C_{ANT}$  estimates than  $\phi C_T^\circ$ . On other hand, in colder waters where AOU is high, the biological term is the main cause of the differences.

The vertical variability of the thermohaline properties, ventilation and  $C_{ANT}$  estimates in the Azores region is explored by plotting vertical profiles of potential temperature, AOU,  $C_{ANT}$  from the  $\phi C_T^\circ$  and TrOCA methods using data from the Azores I (1998) cruise, the previous TTO-NAS (1981) and OACES (1993), and the subsequent METEOR (2004) cruises (Fig. 5). It is thus attempted to compensate for the heterogeneous distribution of the stations in the cruises selected. This is possible partly due to the very low spatial variability of the water mass distribution in the Azores region. The vertical gradients of temperature are clearly coincident throughout the time span of selected years. The vertical variability of AOU is also quite consistent between cruises. During the OACES-93 cruise the NACW appears to be slightly more ventilated compared with the rest of the cruises, but within uncertainty ranges. This

ensures the representativeness of the stations studied in the Azores Region, and they can be regarded as reasonably equivalent in the four cruises.

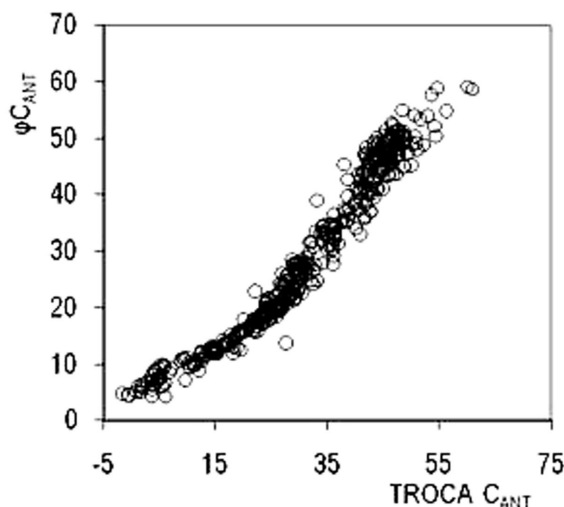


FIG. 4. – Relationship between  $C_{ANT}$  calculated with the TrOCA and  $\phi C_T^\circ$  methods (in  $\mu\text{mol}\cdot\text{kg}^{-1}$ ).

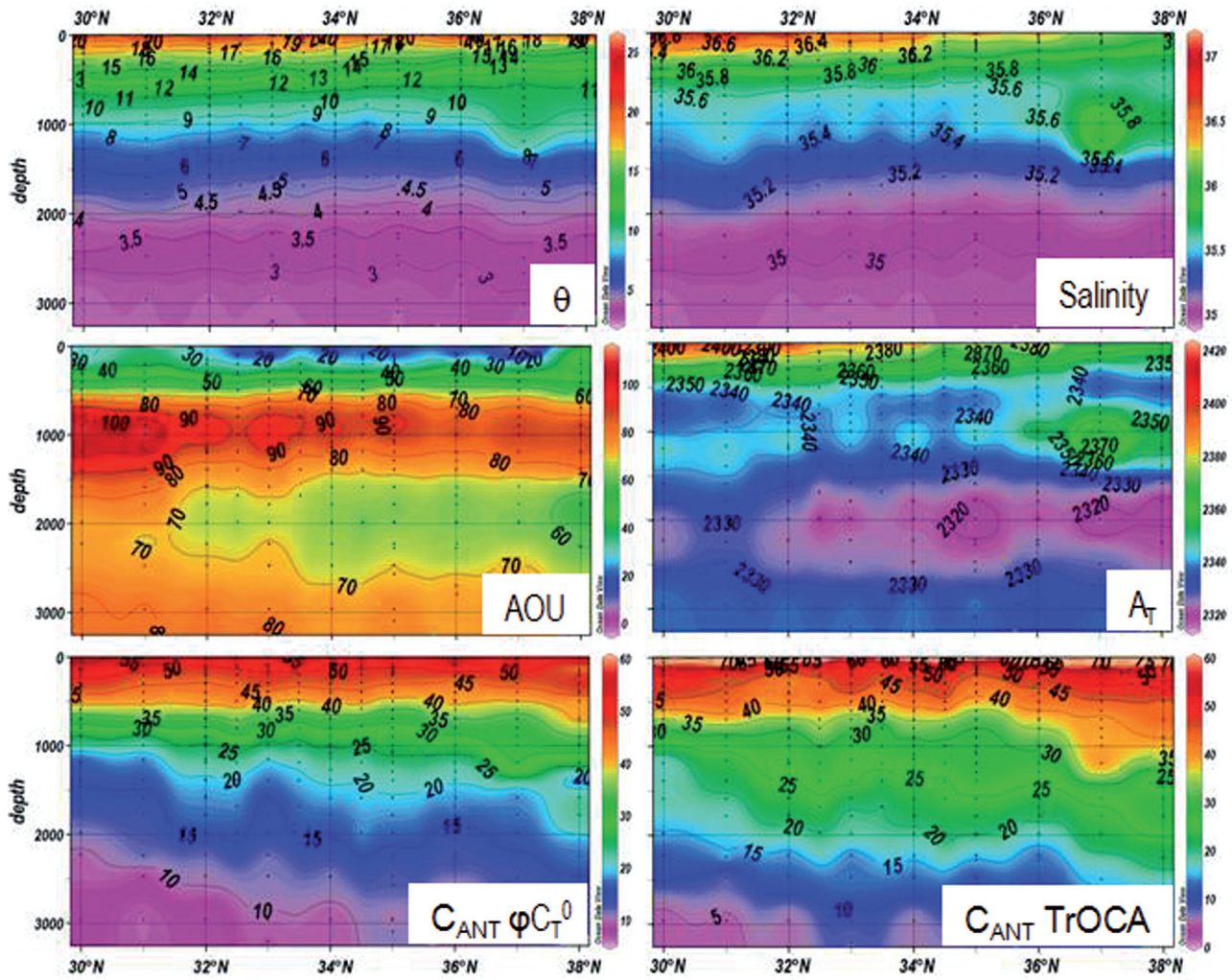


Fig. 5. – Latitudinal averaged distributions of potential temperature ( $^{\circ}\text{C}$ ), salinity (psu), AOU ( $\mu\text{mol kg}^{-1}$ ), total alkalinity ( $A_T$ ,  $\mu\text{mol kg}^{-1}$ ) and  $C_{\text{ANT}}$  ( $\mu\text{mol kg}^{-1}$ ) calculated by the  $\varphi C_T^0$  and TrOCA methods.

## DISCUSSION

The average vertical profiles of  $C_{\text{ANT}}$  provide clear evidence for the higher penetration of CO<sub>2</sub> in the uppermost layers of the ocean, regardless of the  $C_{\text{ANT}}$  reconstruction method applied. In the upper levels, a strong change in  $C_{\text{ANT}}$  observed between 1981 and 1993 was caused by a 5% increase in the atmospheric xCO<sub>2</sub> (from 339 to 357 ppm). There was also an increase in the penetration of the anthropogenic signal during this period of time. From 1993 to 2004 a clear change in  $C_{\text{ANT}}$  was again recorded in the upper layers, when the atmospheric xCO<sub>2</sub> underwent yet another 5% increase (Table 1). Differently though, subsurface values of  $C_{\text{ANT}}$  are higher when predicted with the TrOCA approach. Below the 2000 dbar level the vertical profiles of  $C_{\text{ANT}}$  are nearly coincident in all cases, although the ones from the older cruises (1981 and 1993) seem to be slightly lower than the ones from the modern ones (1998 and 2004).

The vertical integrations of  $C_{\text{ANT}}$  and the ROM contribution term to  $C_T$  ( $C_{\text{bio}} = \text{AOU}/R_C$ ) confirm that

there is a clear increase in  $C_{\text{ANT}}$  storage while the annual biological cycle remains close to steady state. The variability of the  $C_{\text{bio}}$  term is almost negligible (within uncertainties), but the average rate of increase of  $C_{\text{ANT}}$  storage is estimated as  $1.32 \pm 0.11 \text{ mol C m}^{-2} \text{ y}^{-1}$  (p-level=0.008) and  $1.18 \pm 0.16 \text{ mol C m}^{-2} \text{ y}^{-1}$  (p-level=0.018) using the  $\varphi C_T^0$  and TrOCA methods, respectively. There is no statistical significant difference between the two rates. The  $C_{\text{bio}}$  term is about three times higher than the  $C_{\text{ANT}}$  signal, meaning that small errors in this term, introduced via either AOU or  $R_C$ , would significantly affect  $C_{\text{ANT}}$  estimations. The uncertainties in the  $C_{\text{bio}}$  term estimation are included in the calculated uncertainties of  $C_{\text{ANT}}$  by using a perturbation iteration technique (Lee *et al.*, 2003). The  $C_{\text{ANT}}$  inventories in the Azores region turn out to be 5% to 13% higher for the TrOCA method than for the  $\varphi C_T^0$  approach. This result indicates that the higher  $C_{\text{ANT}}$  values obtained by TrOCA in the upper parts of the water column have a large predominance in the vertical integration. Lee *et al.* (2003) estimated a  $C_{\text{ANT}}$  specific inventory of

66.2 mol C m<sup>-2</sup> for the GLODAP canonical year of 1994, using the  $\Delta C^*$  method for the region between 30° and 40°N east from the Mid-Atlantic Ridge. This value is 5 to 9 mol C m<sup>-2</sup> lower than the estimates here obtained using the  $\varphi C_T^o$  and TrOCA methods. Using yet other  $C_{ANT}$  estimation approaches, Tanhua *et al.* (2007) obtained  $C_{ANT}$  specific inventories of 84±2 and 90±3 mol C m<sup>-2</sup> by applying to the METEOR-04 data the Transient Time Distribution (TTD) (Waugh *et al.*, 2006) and the extended Multilinear Regression (eMLR) methods, respectively. Their estimates are close to the ones computed here (Table 1).

The Mean Penetration Depth (MPD) is defined as the ratio of  $C_{ANT}$  specific inventory to the  $C_{ANT}$  concentration in the winter mixed layer (after Broecker *et al.*, 1979). It is assumed that the winter mixed layer is in equilibrium with the present atmosphere. Table 1 provides the MPDs calculated for each cruise using the results and estimates from the  $\varphi C_T^o$  method. The obtained averaged MPD is ~1406±24 m. The small variability of the MPD is of the same order of magnitude as the uncertainties. However, the slightly higher values obtained for 1998 could be related to the concomitant end of a strong water mass formation period in the North Atlantic (Kieke *et al.*, 2006; Pérez *et al.*, 2008; Steinfeldt *et al.*, 2009). This period of weak convection activity could have produced an anomalous increase in  $C_{ANT}$  specific inventories due to the rapid advection of the newly ventilated LSW. As a matter of fact, this positive anomaly in the  $C_{ANT}$  storage rate becomes unambiguous when the above increase in the mean slope in the specific inventory of  $C_{ANT}$  (1.32±0.11 mol C m<sup>-2</sup> y<sup>-1</sup>) is compared with its homologue for the 1993-1998 period. The specific inventory of  $C_{ANT}$  increased by 2.1±0.3 mol C m<sup>-2</sup> y<sup>-1</sup> from 1993 to 1998, which is significantly higher (by approx. 60%) than the mean rate of change in  $C_{ANT}$  specific inventories for 1981-2004 in the Azores region, according to  $C_{ANT}$  estimates from the  $\varphi C_T^o$  method. When the TrOCA method is used, the  $C_{ANT}$  storage change from 1993 to 1998 is ~56%, which is not statistically different at a 95% confidence interval. Álvarez *et al.* (2003) had previously estimated MPDs in the Azores region. For the eastern North Atlantic basin they reported MPDs of 1277±75 and 1473±75 m for the bands between 30-35°W and 35-40°N, respectively. The results obtained here are in good agreement with these MPD values and also confirm the northward increase in  $C_{ANT}$  penetration observed in Figure 3, caused by the advected  $C_{ANT}$  from the MW (Ríos *et al.*, 2001; Álvarez *et al.*, 2005).

In summary, the  $C_{ANT}$  reconstruction methods used have corroborated that the CO<sub>2</sub> has been increasingly penetrating the ocean through the uppermost layers, causing the overall inventories to increase over time in the Azores region. Though there is general agreement in the results, the different  $C_{ANT}$  methods produce singular scenarios that need to be checked, most importantly at inventory levels. The existing discrepancies, especially between the widely used  $\Delta C^*$  and the rest

of the methods considered here, makes it advisable to further extend this type of comparative study to larger ocean extensions in order to obtain more confident state-of-the-art  $C_{ANT}$  inventories.

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