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Anthropogenic carbon and water masses in the Bay of Biscay

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Abstract

As part of the VACLAN (Climatic Variability in the North Atlantic) project a section covering the Bay of Biscay was sampled on board R/V Thalassa in September 2005. This work estimates the distribution of the different water masses using an extended optimum multiparametric method and it studies water mass distribution of anthropogenic carbon as calculated with two different approaches. Regarding water masses present in this region, the Eastern North Atlantic Central Water layer is mainly constituted by its subpolar component and the Mediterranean Water appears very diluted, increasing its dilution towards Northeast. In relation to the anthropogenic carbon inventory there are small differences between two different methods used, 95 vs 87 mol C m⁻², both with the same distribution pattern where the concentration decreases with the depth. Eastern North Atlantic Central Water presents the highest anthropogenic carbon inventory, supporting more than 50% of the total column (52%). This work confirms the relevant role of the Bay of Biscay as a sink zone in the oceanic circulation.

1. Introduction

The Bay of Biscay is located in the north coast of the Iberian Peninsula and covers a region limited to the west by the line connecting Galicia (northwest limit of the Iberian Peninsula) with the western limit of the Celtic Sea shelf (south coast of Ireland) and by the French coast to the east (Fig. 1). The shelf width has high variability, being about 150 km width with smooth slopes in the west French shelf and decreasing to 30 km width off southwest corner. The shelf width is reduced until 12 km off the north coast of the Iberian Peninsula.
The oceanography of the Bay of Biscay is to some extent peculiar. This region is located in the limit of two North Atlantic gyres, the subtropical anticyclonic gyre associated to the Azores Current and the subpolar cyclonic gyre associated to the North Atlantic Current (Lavín et al. 2006). Besides the existence of a weak anticyclonic circulation in the centre of the Bay, the geomorphologic irregularities of the zone cause the circulation to become cyclonic close to the continental margin (Koutsikopoulos and Le Cann 1996). The interaction between them and a variety of coastal features determines the hydrodynamic characteristics of the Bay of Biscay. These characteristics are important in order to understand the distribution of variables such as the carbon cycle in the water column.

Most of the water masses characterizing the Bay of Biscay have their origin in the North Atlantic Ocean except for the Mediterranean Water (MW) which enters the Bay from the southwest and disappears gradually towards the east through mixing processes. During winter, in the northern part of the Bay of Biscay (French/Armorican shelf), large vertical convection leads to water mass formation while salty and warm waters come from the south as a poleward current (Pingree and Le Cann 1992) with characteristics of subtropical Eastern North Atlantic Central Water (ENACWT). Cold and low salty water sinks and spreads through the Bay in the isobath of 400 m with characteristics close to the subpolar ENACW (ENACWP). On the contrary, in the Cantabrian shelf the winter water mass formation has less relevance due to, among other things, its shorter less extension compared to the French one (Fraga 1990, Borja and Collins 2004) as well as the thermal conditions over the shelf (Somavilla et al. 2009).

The oceanic circulation and the water mass mixing processes may be studied through the Optimum Multiparametric Analysis (OMP) a conceptually simple approximation based on
the analysis of real data (Thompson and Edwards 1981, Tomczak Matthias 1981, Mackas et al. 1987, Tomczak M and Large 1989). The OMP method requires to know the distribution of properties such as potential temperature ($T_{pot}$), salinity (S), nitrate ($NO_3$), silicate ($SiO_2$) and oxygen ($O_2$). Also carbonic systems variables may be incorporated in an extended optimum multiparametric analysis (eOMP), in order to obtain the percentages of the main water masses.

The Bay of Biscay accounts for a strong specific inventory (Lee et al. 2003) of anthropogenic carbon ($C_{ant}$) which can be related to the convergent circulation in the Bay (Paillet and Mercier 1997). The relevance of water formation areas in the uptake and storage of $C_{ant}$ has been put forward by Sabine (2004). Marginal seas and coastal bays have been traditionally considered as insignificant in this balance although recent data points to an underestimation in their contribution (Tanhua et al. 2009, Schneider et al. 2010). The Bay of Biscay is a marginal sea where convective processes are active and probably contribute to ameliorate the increase of $C_{ant}$ levels due to CO$_2$ emissions from the burning of fossil fuels. This study aims at estimating the $C_{ant}$ distribution within the water column, in particular the contributions by the main water masses present in the Bay of Biscay, together with the characterization of the physical and chemical properties of each of these water masses. Furthermore, a comparison between the $C_{ant}$ specific inventory of the Bay of Biscay and other regions of the North Atlantic will help assess the relative role of the Biscay Bay in the $C_{ant}$ uptake and storage.

2. Data set

Within the framework of the VACLAN (North Atlantic Climate Variability) project a cruise was made (Vaclan-05) from 30$^{th}$ August to 11$^{th}$ September 2005 on board the
oceanographic vessel R/V Thalassa. The vertical section (Fig. 1) cuts the Bay of Biscay basin from Cape of Ortegal (Spain) to Concarneau (France), 30 full-depth stations were sampled along the cruise. In every station a Seabird SBE9/11 CTD and 24 bottle rosette system General Oceanics were deployed, reducing the number of levels in the coastal stations.

Dissolved oxygen was measured on board according to the Winkler method by potentiometric titration (Grasshoff 1983). The precision of the measurements was determined by duplicate analysis of samples from different bottles closed at the same depth, being 1 μmol kg\(^{-1}\). The Apparent Oxygen Utilization (AOU), defined as the deficit of O\(_2\) relative to saturation conditions, is used to describe the oxygen distribution.

Samples for inorganic nutrient salts were taken and immediately frozen, and finally analyzed in the A Coruña Oceanographic Centre (IEO). The nutrients were determined by colorimetric method, using a continuous flow analyzer (Technicon Autoanalyzer AA III) following Grasshoff et al. (1999). The analysis follows quality control procedures, using certified reference material, verified in intercomparison programs and the QUASIMEME (Quality Assurance of Information for Marine Environment Monitoring in Europe) project (Wells et al. 1997). The accuracy of nitrate and phosphate was ±0.1 and ±0.01 μmol kg\(^{-1}\), respectively (Mouriño and Fraga 1985, Alvarez-Salgado et al. 1992).

The pH samples were measured following the spectrophotometric method by Clayton and Byrne (1993). The indicator dye was m-cresol purple solution in seawater. Samples are reported at 25 °C and in the total scale (pH\(_{25}\)). The accuracy and precision of the pH measurements were ±0.0018 and ±0.0015 pH units, respectively. Those results were
obtained after analysis of certified CO$_2$ reference material (CRM, Dr. Dickson lab, Scripps Institution of Oceanography), batch 70.

The total alkalinity concentration ($A_T$) was determined by potentiometric titration with HCl 0.1N to a final pH close to 4.42 (Pérez and Fraga 1987, Mintrop et al. 2000). The electrode was standardized with a 4.4 buffer made in CO$_2$ free seawater (Pérez et al. 2000). In order to check the accuracy of the $A_T$ measurements, CRM samples were analyzed during the cruise. The accuracy was $\pm 1.0$ µmol·kg$^{-1}$. Additionally, each sample of $A_T$ was analyzed twice, the average absolute difference of the 654 replicates was 1.2 µmol·kg$^{-1}$. The 99% of these differences were under 4 µmol·kg$^{-1}$.

The components of the carbonate system in natural waters can be defined by pH, $A_T$, total inorganic carbon ($C_T$), and CO$_2$ partial pressure (pCO$_2$). By measuring at least two of the measurable parameters, it is possible to calculate those components not measured. Here, the combination of pH and $A_T$ was selected because it gives the best estimates for the calculated parameters (Millero 2007, Hoppe et al. 2010). In this case, $C_T$ was estimated from $A_T$ and pH using thermodynamic equations in seawater and the constants described by Mehrbach et al. (1973) refitted by Dickson and Millero (1987) for carbonate, and Dickson (1990) for sulphate.

3. Methods

3.1. Extended Optimum Multiparameter analysis

The OMP method considers each sample of a water parcel as if they were the nodes of a grid (e.g., latitude vs. depth). In each one of the nodes some properties as $S$, Tpot, $O_2$, NO$_3$, and SiO$_2$ are measured. The value of each property is assumed to be the result of mixing
certain number of water masses present in the region (source water types, SWT) with
known characteristics. The value of each property can be expressed as a linear combination
of the SWT values of this property. If enough properties are measured the contribution of
each SWT can be estimated for each node when the mixing equations for all the properties
are altogether optimized. The OMP methods have two constrictions: the mass balance
equation has to be satisfied at any position or node and the mixing fractions (contributions)
of the SWT have to be always positive for obvious reasons of physical relevance.

The classical OMP assumes that mixing processes are lineal, that observed properties
(tracers) are conservative and that SWT characteristics are accurately known and constant
with time. Nevertheless, in the marine environment, except for S and Tpot, most of the
observed properties are not strictly conservative (e.g., O₂, inorganic nutrients) as are often
involved in biogeochemical reactive processes. The selected strategy here to introduce non-
conservative variables in an OMP analysis, is the one that includes a biogeochemical term
in the mixing equations based on Redfield ratios (Rₙ= ΔO₂ : ΔNO₃ and Rₙ= ΔO₂ : ΔC₅). Also
an additional biogeochemical unknown is introduced, ΔO₂ as, ≈ AOU, that quantifies the
mineralization of organic matter. This procedure is called extended OMP (eOMP) analysis
and includes a new assumption to compute the biogeochemical changes according to fixed
Redfield ratios which should be previously known. Nowadays, the improvement of the
OMP methods responds to a better understanding of the biogeochemical behaviour of the
tracers and a more precise knowledge of the Redfield ratios associated with them (de
Brauwere et al. 2007).

Besides the above approximations, and as a general rule for both OMP, classical and
extended, analysis, before the optimization process each property equation is weighted in
base of the accuracy and variability of the tracers. Those properties measured with more
accuracy in the marine environment (S, Tpot) and the mass balance equation account for
the greatest weights in order to assure that the errors associated to the equation of these
tracers are minimal. The SWT properties represent preformed variables which were initially
extrapolated from regression lines with salinity and temperature, as in Poole and Tomczak
(1999), and then subjected to an iterative process in OMP in order to obtain the types that
better fit the cruise data (Álvarez et al. 2004).

The main water masses in the studied section and the SWT to define them are summarized
in Table 1. The selected SWT properties, corresponding weight for each equation and the
reliability of the eOMP (determination coefficients and standard error) are shown in Table
2 and their distribution in a potential Temperature-Salinity (T/S) diagram in Fig. 2. Each
tracer has an estimation error obtained as in Poole and Tomczak (1999).

Consequently with the assumption of AOU represents the biogeochemical contribution in
the mixing model, O2 for all SWT equals to saturation and, inorganic nutrients refer to
preformed conditions. The Redfield ratios used in the eOMP for the non-conservative
variables in this study (NO3, C T and O2) are referenced to oxygen consumption (ΔO2) and
have values of RM=9.3 (Fraga et al. 1998, Pérez et al. 2001) and RC=1.45 (Anderson and
Sarmiento 1994) for NO3 and C T, respectively.

3.2. Anthropogenic carbon estimation

Two approaches are used to estimate C ant: TrOCA and φC T. Both are data-based requiring
measurements of C T, A T, O2, Tpot, S and inorganic nutrients. The approach TrOCA, is
based on the semiconservative tracer TrOCA (Tracer combining O2, C T and A T) defined by
Touratier and Goyet (2004) and improved by Touratier et al. (2007).
\[ C_{\text{ant}} (\text{TrOCA}) = (\text{TrOCA} - \text{TrOCA}^0) / a \]  
\[ \text{TrOCA} = O_2 + a (C_T - 0.5 A_T) \]  
\[ \text{TrOCA}^0 = e^{(b + c \theta + d / A_T^2)} \]

where \( C_{\text{ant}} \) is calculated as the difference between current (equation 1b) and pre-industrial \( \text{TrOCA} \) (\( \text{TrOCA}^0 \), equation 1c) divided by a stoichiometric coefficient, \( a \). \( \text{TrOCA}^0 \) and the coefficient \( a \) were adjusted using \( \Delta^{14}C \) and CFC-11 data to identify water masses with particular ages. \( \Delta^{14}C \) and CFC-11 were taken from the database GLODAP (Global Ocean Data Analysis Project). When \( \Delta^{14}C<175\% \) then \( C_{\text{ant}} \) is taken to be zero, the age of this water mass was estimated about 1400 years (Matsumoto and Key 2004). On the other hand, \( C_{\text{ant}} \) saturation corresponded to the maximum concentration of CFC11, which was attributed to surface water in 1992-1995. The parameter values used are \( a = 1.279 \pm 7.3 \cdot 10^{-3}, b = 7.511 \pm 5.2 \cdot 10^{-3}, c = -1.087 \cdot 10^{-2} \pm 2.5 \cdot 10^{-5} \, ^\circ C^{-1} \) and \( d = -7.81 \cdot 10^5 \pm 2.9 \cdot 10^4 \, (\mu mol \, kg^{-1})^2 \). The values of \( C_{\text{ant}} \) estimated by the TrOCA method have an associated uncertainty of \( \pm 6.2 \mu mol \, kg^{-1} \) (Touratier et al. 2007).

Following the back-calculation method by Gruber et al. (1996), the \( \varphi C_T^0 \) method is a process-oriented geochemical approach that attempts to account for the nature and anthropogenic phenomena that ultimately have affected carbon cycle since 1750 (Pérez et al. 2008, Vázquez-Rodríguez et al. 2009b, Pérez et al. 2010, Ríos et al. 2010). The method considers processes that control the uptake and storage of \( C_{\text{ant}} \) by the ocean, from the biogeochemistry of the marine carbon cycle to mixing and air-sea exchange. It also considers the spatio-temporal variability of preformed \( A_T \) and the air-sea \( CO_2 \) disequilibrium (\( \Delta C_{\text{dis}} \)) terms since the pre-industrial era. The subsurface layer is used as a
reference for water mass formation, which characterizes the parameterization of preformed 
A_T and ΔC_dis. A random propagation error analysis associated with the input variables 
necessary to calculate C_{ant} yielded an overall uncertainty of ±5.2 μmol kg^{-1}.

Similarities and differences can be found between both methods. Among the differences, 
the TrOCA method uses for the Redfield ratio, R_C = 1.35 (Kortzinger et al. 2001), whereas 
the φC_T^0, uses the constant R_C with a value of 1.45 (Anderson and Sarmiento 1994). The 
most remarkable difference between both methods is the way they define water with no 
C_{ant}. TrOCA uses old deep seawater to fix TrOCA^0 as C_{ant} free-seawater whereas φC_T^0 does 
not fix any C_{ant}-free seawater when computing A_T and ΔC_dis from the subsurface 80-180 m 
deep layer.

4. Results

The main water masses in the studied section were obtained as a result of using the eOMP 
method and they are summarized in Table 1. In surface appears ENACW (Eastern North 
Atlantic Central Water), comprises two mode waters of different origins: ENACW_p and 
ENACW_T. The subpolar variety of ENACW is characterized by a weak salinity minimum 
(~35.58) as about 500 dbar (Harvey 1982, Ríos et al. 1992, Pérez et al. 1993, Fiúza et al. 
1998) which is detected along our section (Figs. 2 and 3b), this salinity minimum is due to 
mixing processes and affected by zonal variability (González-Pola et al. 2005). The water 
type H splits ENACW in the subtropical and subpolar branches (Fig. 2). According to our 
OMP analysis there are few points (<5%) with both Tpot and S higher than those of water 
type H (Fig. 3a, b). These values are located to south of the section, this means that 
practically all water column above 500 m depth is quite homogeneous and belongs to
subpolar ENACW, the presence of ENACW$_T$ being almost negligible (Fig 2). ENACW$_T$ has been observed as saline water intrusions in winter and spring by others authors (González-Pola et al. 2005), but it was not observed here.

Below ENACW$_P$, MW is clearly identified by a saline maximum signal (35.8-35.9) around 1000 dbar (Fig. 3b). Along the VACLAN transect, the salinity maximum decreases northward reaching 35.7 near the French coast (del Río et al. 1998, van Aken 2000). MW also presents high values of AOU (>80 μmol kg$^{-1}$, Fig. 3c) indicating a high organic matter mineralization. The maximum percentage of MW (50%) was observed near the Spanish coast (Fig. 4a) around 1200 dbar and is slightly diluted northward at this horizon (40% at the French coast). Iorga and Lozier (1999) described the route of MW from the Strait of Gibraltar: from its sinking zone at the Strait of Gibraltar at 400 m depth, S~38.3 with AOU~65 μmol kg$^{-1}$ (Huertas et al. 2009). At the Northwest corner of the Iberian Peninsula, it reaches the Galician Bank with AOU values of 80 μmol kg$^{-1}$ (Pérez et al. 1993), as a result of this meeting, MW bifurcates (Ruiz-Villarreal et al. 2006). After crossing Galician Bank MW converges again, and moves towards the Bay of Biscay, in this area MW presents a local cyclonic recirculation. Throughout this path MW loses slowly its high salinity signal by mixing with ENACW$_P$ and LSW achieving the observed salinity when it reaches the Bay of Biscay. Furthermore, the fact that the percentage of MW is higher in the southwest part of the Bay than in the northeast corroborates the cyclonic gyre of MW inside the Bay (Paillet and Mercier 1997).

Below MW, the core of LSW (Labrador Sea Water) is found at 2000 dbar. This water mass is associated with an AOU minimum (60 μmol kg$^{-1}$, Fig. 3c) caused by the strong ventilation during the winter deep-convection when LSW is formed in the Labrador Sea.
The LSW is also characterized by a salinity (Fig. 3b) and $A_T$ minima which are traces of the large freshwater input into the Labrador Sea (Paillet and Mercier 1997). The maximum percentage of LSW was 60% (Fig. 4b), located at the same depth that the AOU minimum (2000 dbar), and decreased slightly towards the French coasts. The entrance of LSW inside the Bay occurs mainly through the Armorican slope (North east of the Bay) and it is supposed to mix completely inside (Paillet et al. 1998). Also the entrance of LSW is shown in the central and southern part of the section, coherent with the circulation given by Fraile-Nuez et al. (2008). Once inside the Bay the LSW circulation accompanies that of MW above entering in a cyclonic gyre (Paillet and Mercier 1997, Paillet et al. 1998). From the results obtained here, the evidence of this circulation pattern is shown as higher percentages of LSW off the Spanish coast than off the French coast, but strong recirculation and high mesoscale activity are important in the area (Fraile-Nuez et al. 2008).

The deepest water mass found in this section is NEADW (North Eastern Atlantic Deep Water) at depths from 2500 dbar down to the sea bottom. NEADW is partially originated in the Southern Ocean and when it reaches the North Atlantic region it receives the cold and less saline inputs from the Nordic Seas overflows in the Iceland basin. Despite this mixing process it is detected by the high silicate concentration in NEADW (Fig. 3f) derived from its Antarctic origin (Arhan et al. 1994, Castro et al. 1998). These latter mixing processes are the cause for differentiating an upper component, $\text{NEADW}_U$ (upper Northeast Atlantic Deep Water), and a lower one, $\text{NEADW}_L$ (lower Northeast Atlantic Deep Water), which delimits the line of NEADW in the T/S profile. The presence of $\text{NEADW}_L$ is represented in Fig. 4c. From 2000 dbar down a progressive increase in $\text{NEADW}_L$ is observed, with an 80% contribution at 4000-5000 dbar. The $\text{NEADW}_L$ enters the Eastern North Atlantic basin through the Vema and Romanche Fractures (Broecker and Peng 1982, Broecker et al. 1985).
and at the Bay of Biscay it extends through the bottom (Paillet and Mercier 1997). NEADW_U has stronger interaction with LSW and MW than the lower one. In fact, Álvarez et al. (2005) decomposed NEADW_U in four source water types MW, LSW, NEADW_L, and the Iceland Scotland Overflow Water (ISOW) which are the components of NEADW_U according to Broecker and Peng (1982) and van Aken (2000). The NEADW_L presents higher percentages of abundance in the middle and towards the north of the VACLAN transect (Fig 4c), corroborating again the circulation scheme proposed by Paillet and Mercier (1997).

For each layer, Table 3 summarizes the averaged contribution of each water source used by the eOMP. The error of the mean given in table 3 is computed from the standard deviation divided by the square root of N (std : \sqrt{N}). The ENACW layer is defined by density (\sigma_1) less than 31.8, it has a thickness of 656 m and is mainly constituted by ENACW_P (93%), it also contains 7% of MW. The MW core layer is defined as 32.25 > \sigma_1 > 31.8, it has an averaged thickness of 548 m and is essentially dominated by ENACW_P (52%) and MW (42%), showing a strong dilution of MW type. Below this layer, MW and LSW suffer strong mixing, conforming the Mixed Mediterranean and Labrador Layer (MMLL), this layer, 36.89 > \sigma_1 > 32.25, has an average thickness of 367 m. Here, LSW is the most important component (average 41%) along with MW (average 26%). The core of LSW, 36.95 > \sigma_1 > 36.89, has a thickness about 300 m reaching the highest percentage of LSW (61%). Also LSW is the most important component of NEADW_U layer with an average percentage of 42%. This layer, with a thickness of 593 m, has also important contribution of NEADW_L and ISOW. Finally the thicker and deeper layer (~1550 m) corresponds with NEADW_L, contributing with an average of 66%.
Besides the water mass distribution and the variables used to characterize them, the rest of measured variables along VACLAN give more information on the characteristics of the water column in this zone of the Bay of Biscay. The normalized total alkalinity (NTA, Fig. 3d) is obtained from total alkalinity (i.e., NTA=AT 35/S) and its distribution shows a similar pattern to SiO₂ (Fig. 3f) with a high correlation between them (r²=0.98). Both variables present high gradients below 2000 dbar caused by the dissolution of carbonate and opal denoting the presence of water from Antarctic regions. The distributions of pH (Fig. 3e) and NO₃ have also similar patterns and high correlation between them (r²=0.90), in agreement with results obtained by Ríos et al. (1995). Both variables present an almost homogeneous vertical profile in deep waters (>2000 dbar) and a relatively large gradients towards the surface due to remineralization processes in the upper layer and down to 1000 dbar approximately. These latter processes together with the carbonate and opal dissolution mark the natural carbonic cycle so, the main variables implicated are pH, NO₃, AOU, SiO₂ and NTA.

The vertical distributions of C_{ant} estimated with both TrOCA and φC_T⁰ methods (Fig. 3g, h), is quite homogeneous along the section due to C_{ant} transport occurring mainly along isopycnals (Lee et al. 2003). The distribution of C_{ant} and its uncertainties were analyzed based on a division of the water column in six layers (Table 3). These selected layers take into account the density of the most representative water masses in the region (Fajar et al. 2010 - this issue). Usually, the C_{ant} values are high at subsurface levels, about 54 μmol kg⁻¹ using the TrOCA method and 50 μmol kg⁻¹ using the φC_T⁰ method (Fig. 3g, h). The C_{ant} decreases towards the bottom because it enters the ocean through gas exchange at the atmosphere-ocean interface. Around 1000 dbar a concentration of C_{ant} about 37 and 31 μmol kg⁻¹ was estimated using TrOCA and φC_T⁰ respectively. The C_{ant} values decrease
gradually below 2000 dbar where values of 21 and 16 μmol kg$^{-1}$ were estimated with TrOCA and φC$_T^0$ methods respectively. At depths greater than 3000 dbar the C$_{ant}$ values are homogeneous and minima (~ 5 μmol kg$^{-1}$). C$_{ant}$ inventories were obtained by integrating the C$_{ant}$ within the water column from surface down to the bottom. The obtained C$_{ant}$ inventories in the water column are 87±5 mol C m$^{-2}$ for the case of the φC$_T^0$ method and 95±5 mol C m$^{-2}$ for the TrOCA method.

5. Discussion

The concentrations of C$_{ant}$ estimated with TrOCA are higher than those computed by φC$_T^0$ from the surface layer down to 2000 dbar (Table 3, Fig 3g, h), while the φC$_T^0$ method estimates higher C$_{ant}$ values compared to TrOCA in waters below 2000 dbar. These differences between methods are due to the inherent formulation of each method, because the temporal variability of ΔC$_{dis}$ is assumed to be zero in the TrOCA method whereas it is negative in the φC$_T^0$ method (Vázquez-Rodríguez et al. 2009a). Nevertheless, the differences between methods are small (-0.7±4.4 μmol kg$^{-1}$, n=301), and both have the same pattern with C$_{ant}$ concentration decreasing with depth. C$_{ant}$ inventories obtained with both methods in the water column of the VACLAN transect (95±5 mol C m$^{-2}$ and 87±5 mol C m$^{-2}$ for TrOCA and φC$_T^0$ respectively) are similar to those obtained by Fajar et al. (2010 - this issue) in the Iberian basin for 2003 (93±4 mol C m$^{-2}$ with TrOCA and 89±4 mol C m$^{-2}$ with φC$_T^0$). The relevance of each water mass in the storage C$_{ant}$ can be evaluated by taking into account the percentage of each water masses in each level and the layer thickness. ENACW is the water mass storing more anthropogenic carbon (53 and 51% with TrOCA and φC$_T^0$...
respectively). The rest of water masses have very similar contribution to the total inventory. MW shows a contribution of 17% and 16% using TrOCA and $\theta C^0_T$ respectively. Similar values are obtained for LSW (15 and 13% with TrOCA and $\theta C^0_T$ methods respectively). For ISOW and NEADW$_L$, the contributions are higher when the $\theta C^0_T$ method is used in relation to the TrOCA approach. The $C_{ant}$ accumulated in the ISOW is 6% (4%) using the $\theta C^0_T$ (TrOCA) approach. The deeper mass with low levels of $C_{ant}$, NEADW$_L$ accumulated about a 10% following TrOCA, and 14% $\theta C^0_T$, which is mainly due its thickness (1548 m) that represents about 40% of water column.

Lee et al. (2003) evaluated the $C_{ant}$ inventory in the Atlantic Ocean obtaining a value of ~75 mol C m$^{-2}$ for 1994. Comparing the result from Lee et al. (2003) with those obtained here, an increased trend in $C_{ant}$ accumulation in the Bay of Biscay of ~20% can be deduced in agreement with the atmospheric CO$_2$ increase rate. This conclusion indicates that the Bay of Biscay is an important sink for $C_{ant}$ because of winter mass formation, a behavior very similar to the northern North Atlantic region. These results are in agreement with Padin et al. (2008), who showed that the Bay of Biscay is a strong sink for CO$_2$ in an annual basis. According to them the Bay of Biscay takes up between 3 and 5 TgCyr$^{-1}$ of CO$_2$. This uptake is approximately between 6% and 10% of the estimated uptake for the North Atlantic ocean between 45$^\circ$ and 55$^\circ$N (Telszewski et al. 2009). Furthermore, the distributions of $C_{ant}$ in the water column are also in agreement with the circulation pattern proposed by Paillet and Mercier (1997) from an inverse model results. According to these authors the velocity of the deep layers (>2000 dbar) of the Bay is around 0.1-0.2 cm s$^{-1}$ so it takes of the order of one decade for the deep waters to complete the cyclonic circulation. This could explain the small differences of $C_{ant}$ concentration between the south and the
north part of the VACLAN transect, with a slightly higher penetration of $C_{\text{aut}}$ in the water column in the southern part of the section off Spanish coast.

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References


Table 1: Main water masses crossed by the VACLAN-05 section in the Bay of Biscay, brief description of their characteristics and some references where more information about their origin and circulation may be found.

<table>
<thead>
<tr>
<th>Name and acronym</th>
<th>Source</th>
<th>Characteristics</th>
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<td>Subtropical Eastern North Atlantic Central Water (Subtropical ENACW)</td>
<td>Subtropical gyre</td>
<td>Mode water formed in the area of the Azores Current, $\theta&gt;13^\circ$C and $S&gt;36$, very low nutrient concentration</td>
<td>Pollard &amp; Pu, 1985; Ríos et al. 1992.</td>
</tr>
<tr>
<td>Subpolar Eastern North Atlantic Central Water (Subpolar ENACW)</td>
<td>Subpolar gyre</td>
<td>Mode water formed north of 42°N and east of 20°W, $\theta&lt;12^\circ$C and $S&lt;35.5$, higher concentration of nutrients than subtropical ENACW.</td>
<td>Harvey, 1982; McCartney &amp; Talley, 1982; Pollard et al. 1996.</td>
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<td>Mediterranean Water (MW)</td>
<td>Gulf of Cadiz</td>
<td>Formed by entrainment of central waters on the high salinity outflow from the Mediterranean Sea, spreads at 800-1300 m, $S&gt;36$ and $\theta \sim 11^\circ$-12°C</td>
<td>Wüst &amp; Defant, 1936; Zenk, 1975; Ambar &amp; Howe, 1979; Pérez et al. (1993)</td>
</tr>
<tr>
<td>Labrador Sea Water (LSW)</td>
<td>Labrador Sea &amp; Irminger Sea</td>
<td>Formed by winter convection, spreads between 1500-2000m, $\theta \sim 3^\circ$C, $S \sim 34.8$ and, high oxygen content.</td>
<td>Talley &amp; McCartney, 1982; Harvey &amp; Arhan, 1988; Pickart et al. 2003.</td>
</tr>
</tbody>
</table>
Table 2: Physical and chemical characteristics and errors of the seven source water types (SWT) used in the eOMP. Correlation coefficient ($r^2$) and standard error (Std. Err.) of the regression between the measured and predicted variable are also shown. The units are $\mu$mol kg$^{-1}$ except for salinity and potential temperature (°C).

<table>
<thead>
<tr>
<th></th>
<th>Tpot</th>
<th>S</th>
<th>SiO$_2$</th>
<th>NO$_3$</th>
<th>A$_T$</th>
<th>O$_2$</th>
<th>C$_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ENACW$_T$</td>
<td>15.30±0.15</td>
<td>36.100±0.02</td>
<td>2.0±1.7</td>
<td>1.2±0.3</td>
<td>2369±3</td>
<td>244±3</td>
<td>2097±4</td>
</tr>
<tr>
<td>H</td>
<td>12.20±0.13</td>
<td>35.660±0.02</td>
<td>3.8±1.8</td>
<td>6.1±0.3</td>
<td>2342±3</td>
<td>256±3</td>
<td>2116±4</td>
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<tr>
<td>ENACW$_P$</td>
<td>8.30±0.15</td>
<td>35.230±0.01</td>
<td>9.8±0.6</td>
<td>11.1±0.2</td>
<td>2334±1</td>
<td>304±2.5</td>
<td>2095±2</td>
</tr>
<tr>
<td>MW</td>
<td>11.74±0.03</td>
<td>36.500±0.005</td>
<td>9.1±0.8</td>
<td>4.0±0.2</td>
<td>2412±3</td>
<td>261±2</td>
<td>2155±3</td>
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<tr>
<td>LSW</td>
<td>3.40±0.15</td>
<td>34.890±0.01</td>
<td>9.1±2.5</td>
<td>12.5±0.2</td>
<td>2304±1</td>
<td>325±2.5</td>
<td>2112±2</td>
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<tr>
<td>NEADW$_U$</td>
<td>2.60±0.03</td>
<td>34.960±0.003</td>
<td>35±6</td>
<td>11.9±0.2</td>
<td>2359±2</td>
<td>327±1.2</td>
<td>2139±2</td>
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<tr>
<td>NEADW$_L$</td>
<td>1.90±0.03</td>
<td>34.885±0.003</td>
<td>50±5</td>
<td>13.6±0.2</td>
<td>2362±2</td>
<td>337±1.2</td>
<td>2144±2</td>
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<tr>
<td></td>
<td>W r$^2$</td>
<td>Std. Err.</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>5 6</td>
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<td>0.968</td>
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<td>0.985</td>
<td>0.96</td>
<td>0.995</td>
<td>0.02</td>
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<tr>
<td></td>
<td></td>
<td>0.80</td>
<td>0.54</td>
<td>2.5</td>
<td>1.6</td>
<td>3.3</td>
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</table>
Table 3: Physical and chemical mean and standard deviation characteristics for the layers corresponding to the main water masses along VACLAN-05. The $C_{\text{ant}}$ units are $\mu$mol kg$^{-1}$. Mean and standard deviation of the percentage of water types in each layer, except for ENACW$\rho$ that represents the sum of the water types: H and ENACW$\rho$.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thick (m)</th>
<th>Limits</th>
<th>S</th>
<th>$T_{\text{pot}}$ (°C)</th>
<th>AOU $\mu$mol kg$^{-1}$</th>
<th>$C_{\text{ant}}$ $\varphi C_{\text{r}}$</th>
<th>$C_{\text{ant TrOCA}}$</th>
<th>ENACW$\rho$</th>
<th>MW</th>
<th>LSW</th>
<th>ISOW</th>
<th>NEADW$\text{L}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ENACW</td>
<td>656</td>
<td>$\sigma_1&lt;31.8$</td>
<td>35.637±0.003</td>
<td>11.39±0.1</td>
<td>40.4±1.6</td>
<td>50.0±0.6</td>
<td>54.3±0.6</td>
<td>93±0.5</td>
<td>7±0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW</td>
<td>548</td>
<td>$32.25&lt;\sigma_1\sigma_1&gt;31.8$</td>
<td>35.790±0.016</td>
<td>9.79±0.10</td>
<td>84.1±0.4</td>
<td>31.2±0.5</td>
<td>37.0±0.5</td>
<td>52±2</td>
<td>42±1</td>
<td>42±1</td>
<td></td>
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<tr>
<td>MMLL</td>
<td>367</td>
<td>$\sigma_1&gt;32.25\sigma_2&lt;36.89$</td>
<td>35.383±0.027</td>
<td>6.36±0.18</td>
<td>72.3±1.0</td>
<td>22.1±0.5</td>
<td>29.5±0.5</td>
<td>20±2</td>
<td>26±1.5</td>
<td>41±2</td>
<td>4±0.5</td>
<td>10±0.6</td>
</tr>
<tr>
<td>LSW</td>
<td>299</td>
<td>$36.95&lt;\sigma_2\sigma_2&lt;36.89$</td>
<td>35.080±0.01</td>
<td>4.11±0.07</td>
<td>63.5±0.9</td>
<td>16.2±0.5</td>
<td>21.9±0.6</td>
<td>3±1</td>
<td>11±1</td>
<td>61±2</td>
<td>7±2</td>
<td>18±1</td>
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<tr>
<td>NEADW$\text{U}$</td>
<td>593</td>
<td>$37.05&lt;\sigma_2\sigma_2&gt;36.95$</td>
<td>35.003±0.004</td>
<td>3.15±0.05</td>
<td>69.5±0.8</td>
<td>10.6±0.6</td>
<td>12.6±0.8</td>
<td>5±0.5</td>
<td>42±3</td>
<td>21±2</td>
<td>32±2</td>
<td></td>
</tr>
<tr>
<td>NEADW$\text{L}$</td>
<td>1548</td>
<td>$\sigma_2&gt;37.05$</td>
<td>34.939±0.002</td>
<td>2.28±0.02</td>
<td>81.8±0.5</td>
<td>6.7±0.3</td>
<td>3.5±0.4</td>
<td>1±0.2</td>
<td>10±1</td>
<td>23±1</td>
<td>66±1</td>
<td></td>
</tr>
</tbody>
</table>
Figure legends:

Figure 1: VACLAN-05 cruise positions.

Figure 2: Potential temperature – salinity diagram for samples collected during the cruise (sea surface samples excluded). The solid symbols represent the characteristics of the source water types.

Figure 3: Vertical distribution of (a) potential temperature (°C), (b) salinity, (c) apparent oxygen utilization (μmol kg\(^{-1}\)), (d) normalized total alkalinity (μmol kg\(^{-1}\)), (e) pH\(_{25}\), (f) silicate (μmol kg\(^{-1}\)), (g) and (h) distribution of anthropogenic CO\(_2\) (μmol kg\(^{-1}\)) estimated with TROCA and φ\(_{C_T}\), respectively.

Figure 4: Percentages of the water mass obtained after the eOMP, (a) Mediterranean water (MW), (b) Labrador Sea Water (LSW), (c) North East Atlantic Deep Water lower (NEADWL).
Figures:

Figure 1:
Figure 2:
Figure 3:

Distance (km)

Pressure (db)
Figure 4:

![Graph showing distance (km) vs pressure (db) with labels S, N, MW, LSW, and NEADW.](image)