The subsurface layer reference to calculate preformed alkalinity and air-sea CO₂ disequilibrium in the Atlantic Ocean.

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Abstract

The subsurface ocean layer (100-200 m deep) is suggested as a reference to parameterize preformed alkalinity (A_T°) and air-sea CO₂ disequilibrium (ΔC_{dis}) in the Atlantic. Results suggest that this domain retains the memory of water mass formation (WMF) conditions over annual periods and avoids the large, short-term variability of the uppermost layers. Its thermohaline variability also encompasses and represents all water masses that outcrop in the Atlantic. Subsurface data also avoids the scarcity of late wintertime surface observations and benefit from the larger availability of year-round measurements, thus enhancing their representativeness and application coverage. This last feature is most relevant in high Atlantic latitudes, where WMF typically occurs and the widespread ice sheets often preclude surface pCO₂ sampling during wintertime. The obtained A_T° and ΔC_{dis} parameterizations achieve uncertainties of ± 4.6 and ± 5.6 $\mu\text{mol kg}^{-1}$, respectively, improving significantly the estimates in previous works, particularly in the high latitudes. The A_T° parameterization is well correlated with observations and is coherent with the latitudinal subsurface distribution of silicate, particularly in the northern subpolar region, where previous studies showed discrepancies. The ΔC_{dis} estimates in the upper layers are coherent with air-sea $\Delta p\text{CO}_2$ data from Takahashi's climatology, thus tackling known important shortcomings and biases of anthropogenic CO₂ estimates in Atlantic waters.

Keywords

Preformed total alkalinity, air-sea CO₂ disequilibrium, carbon cycle, anthropogenic CO₂, Atlantic Ocean, subsurface layer, parameterization.

1. Introduction

In recent years, a good deal of coordinated international research programs, like WOCE, JGOFS or CARBOOCEAN, have focused on tackling and minimising the uncertainties of the global carbon budget. These uncertainties stem from the difficulty of estimating accurately the air-sea CO₂ fluxes and carbon storage in some environmental compartments like the land and the ocean. A fundamental piece for solving the intricate puzzle of global carbon content is estimating the anthropogenic CO₂ (C_{ant}) that dissolves into the ocean.

The C_{ant} has built up and added to the natural fraction of the total inorganic carbon (C_T) pool in the ocean since the Industrial Revolution, when the zero-baseline for C_{ant} is set by definition. The molecules of C_{ant} and natural CO₂ are indistinguishable, and there is no analytical procedure at present that is able to quantify C_{ant} directly. Therefore, this has to be estimated indirectly from other measurable physical-chemical tracers, under certain assumptions. Back-calculation methods to estimate C_{ant} are based on the fact that preformed C_T (C_T[°], the C_T stored in a given water mass when it is formed) has changed since the Industrial revolution due to the increasing partial pressures of atmospheric CO₂ (pCO₂^{atm}), which forces more of this gas to dissolve in the ocean (Brewer, 1978).

The C_{ant} added to the naturally occurring fraction of C_T[°] in a water mass can be reckoned by subtracting from it (back-calculating) a preindustrial “zero-C_{ant}” reference: C_{ant} = C_T[°] - C_T^{°π} (superscript “π” denotes “Pre-Industrial”). The estimates of back-calculated C_{ant} improved over the years from many contributions (Gruber et al., 1996; Wallace, 2001; Pérez et al., 2002; Waugh et al., 2006; Touratier et al., 2007). The first formal definition and estimation of the CO₂ air-sea disequilibrium term (ΔC_{dis}) by Gruber et al. (1996) meant a leap forward in the back-calculation technique, albeit with certain caveats (Matsumoto and Gruber, 2005). The C_{ant} was re-expressed as the difference between the quasi-conservative tracer ΔC* and DC_{dis}^ρ, namely: C_{ant} = ΔC* - DC_{dis}^ρ = (C_T[°] - C_{T_{Teq}}^ρ) - DC_{dis}^ρ, where C_{T_{Teq}}^ρ is the C_T in equilibrium with the preindustrial

atmospheric CO₂ level of 280 ppm (calculated from thermodynamic equations) and ΔC_{dis}^p is the ΔC_{dis} during the pre-industrial era.

When water masses upwell to the surface from lower layers the air-sea gas exchanges lead them to reach different degrees of equilibrium with the atmospheric partial pressure CO₂ ($p\text{CO}_2^{\text{atm}}$), depending on the existing air-sea $p\text{CO}_2$ gradient ($\Delta p\text{CO}_2$) during water mass ventilation. Afterwards, the water masses lose contact with the atmosphere as they sink (water mass formation; WMF) and air-sea exchanges cease. A certain amount of CO₂ gets stored in seawater, where it can remain in the inorganic phase or be incorporated through photosynthetic activity to the organic carbon pool. From this mechanism of water mass ventilation follows that one of the most crucial aspects for back-calculating C_{ant} from C_T° -based techniques relies essentially in being able to reconstruct accurately WMF conditions from the available observations.

Unfortunately, cruises are usually unable to record WMF conditions as they do not normally coincide with that particular moment, and this leaves the representativeness of WMF conditions from the available datasets as a pending issue that limits the quality of parameterizations for preformed total alkalinity (A_T° ; the A_T of a water mass when it outcrops and loses contact with the atmosphere) and ΔC_{dis} . The use of the available data should therefore be optimised in order to compensate for the spatiotemporal sparseness of observations and attain the best results possible. Recently, the work from Pardo et al. (2010) addressed this issue in the Pacific and Indian basins by proposing the use of subsurface data as a reference to parameterize A_T° and ΔC_{dis} .

The complexity of the numerous deep-water mass formation processes hosted by the Atlantic Ocean represents an added difficulty for finding an analogous reference layer. The present study has a two-fold purpose: *a)* find and provide supporting evidence for a reference region in the Atlantic that retains the memory of WMF conditions and; *b)* use data from the Atlantic to obtain optimum estimates of A_T° and ΔC_{dis} and compare them with previous estimates from different authors in order to evaluate the results.

2. Dataset

The current work uses a combination of three different datasets to study the Atlantic reference layer for A_T° and ΔC_{dis} , namely: *a*) bottle data from eleven different cruises; *b*) A subset of selected surface and subsurface data (potential temperature, salinity, nitrate and phosphate) from the World Ocean Atlas 2005 (WOA05) for three $5^\circ \times 5^\circ$ regions; *c*) Means of wintertime ΔC_{dis} calculated from $\Delta p\text{CO}_2$ values in the latest available $p\text{CO}_2$ climatology from Takahashi et al. (2009).

The selected cruises (Fig. 1; Table 1) include the WOCE tracks A02, A14, A16, A17, A20, AR01, I06-Sa and I06-Sb, the CLIVAR A16N legs 1 and 2, the WOCE/CLIVAR OVIDE 2002 and 2004 cruises and the NSeas-Knorr cruise (Bellerby et al., 2005; Olsen et al., 2006). The availability of high-quality, carbon system measurements, calibrated with Certified Reference Materials (CRMs) and quality-controlled were the main cruise selection criteria. All of the above cruises are part of the Atlantic Synthesis effort made within the CARBOOCEAN Integrated Project framework (<http://www.carbon-synthesis.org/>). The data are available from the Global Ocean Data Analysis Project (GLODAP; http://cdiac.ornl.gov/oceans/glodap/Glodap_home.htm, the Climate Variability and Predictability (CLIVAR; <http://www.clivar.org>) and the Carbon In the Atlantic (CARINA; <http://store.pangaea.de/Projects/CARBOOCEAN/carina/index.htm>) data portals.

For the vast majority of the samples, pressure and temperature data come from filtered CTD measurements. Salinity and nutrient data come from analysis of individual Niskin bottles collected with a rosette. All WOCE C_T samples in the dataset used were analyzed with the coulometric titration technique described in Johnson et al., 1993. For the OVIDE cruise, C_T data was obtained from the thermodynamic equations of the carbon system using direct measurements of pH and A_T , and the carbon dioxide dissociation constants from Dickson and Millero (1987). The shipboard A_T measurements were analyzed by potentiometric titration using a titration system and a potentiometer, and further determined by either developing a full titration curve (Millero et al., 1993; DOE, 1994; Ono et al., 1998) or by single point titration (Pérez and Fraga, 1987; Mintrop et al., 2000). The pH measurements were performed with pH

electrodes or, more commonly, with a spectrophotometric method (Clayton and Byrne, 1993) adding *m*-cresol purple as the indicator in either scanning or diode array spectrophotometers.

The analytical accuracies for C_T , A_T and pH were typically assessed within $\pm 2 \mu\text{mol kg}^{-1}$, $\pm 4 \mu\text{mol kg}^{-1}$ and ± 0.003 pH units, respectively. A downward adjustment of $8 \mu\text{mol kg}^{-1}$ in the A_T values from WOCE A17 (Table 1) has been suggested by Ríos et al. (2005) after comparing A_T data from that cruise with other measurements. Otherwise, the preliminary results from a crossover analysis exercise performed by the CARBOOCEAN Atlantic Synthesis group sustain that no further corrections are needed for the carbon system parameters of the selected cruises.

The WOA05 data is a set of objectively analysed climatological fields and provides excellent spatial resolution ($1^\circ \times 1^\circ$ grid of lon. x lat.) to make a thorough examination of different Atlantic layers and to assess how suitably they represent the bulk Atlantic waters. It includes the following variables: *in situ* temperature, salinity (S), dissolved oxygen, Apparent Oxygen Utilization (AOU), percent oxygen saturation, phosphate, silicate, and nitrate at 33 standard depth levels for annual, seasonal, and monthly compositing periods for the World Ocean. The WOA05 data product was accessed from http://www.nodc.noaa.gov/OC5/WOA05/pr_woa05.html.

The $p\text{CO}_2$ climatology from Takahashi et al. (2009) provides the mean distribution for the atmospheric and sea-surface $p\text{CO}_2$ over the global oceans in non-El Niño conditions. Takahashi's climatology provides data of $\Delta p\text{CO}_2 = p\text{CO}_2^{\text{sea}} - p\text{CO}_2^{\text{air}}$ i.e., an air-sea disequilibrium term that involves CO_2 exclusively. Takahashi's $\Delta p\text{CO}_2$ disequilibrium can be defined as the difference between the surface C_T that, in theory, would have been in equilibrium with the atmospheric $p\text{CO}_2$ at time "*t*" (i.e., $C_{T\text{eq}}^{p\text{CO}_2^t}$) and the theoretical C_T of the water saturated with a $p\text{CO}_2^{\text{atm}} = p\text{CO}_2^t + \Delta p\text{CO}_2^t$, i.e., the $C_{T\text{eq}}^{p\text{CO}_2^t + \Delta p\text{CO}_2^t}$. Both of these terms can be calculated theoretically from the set of thermodynamic equations of the marine inorganic carbon system. The climatological air-sea $\Delta p\text{CO}_2$ data from Takahashi et al. (2009; http://www.ldeo.columbia.edu/res/pi/CO2/carbondioxide/air_sea_flux/sumflux_2006.tx

t) are originally presented in a 4° (latitude) x 5° (longitude) grid for a reference year 2000 and is based on about 3 million measurements of sea-surface pCO₂ obtained between 1970 and 2007. In the present work we have considered exclusively winter data of air-sea ΔpCO₂ from Takahashi's climatology as follows: In the Northern Hemisphere (latitude >25°N) the months from January through March were assumed for the boreal winter; In the Southern Hemisphere (latitude < -25°S) the months from July through September were contemplated for the austral winter, and for the Equatorial region (latitude=[-25°S ; 25°N]), annual averages were taken as representative of wintertime conditions.

3. Methodology

3.1. The Atlantic subsurface layer.

The fact that air-sea gas exchanges are indeed surface events can easily lead to the wrong conception that surface observations make up for an optimal set of data to parameterize ΔC_{dis} or any other air-sea disequilibrium. However, the degrees of CO₂ and O₂ disequilibria, and preformed properties are not established until the moment of WMF, after the water masses loose contact with the atmosphere and are rapidly capped by the seasonal thermocline. If these WMF moments could be forecasted precisely and sampling was planned accordingly, then the collected surface data would have incontrovertible value in the context of C_{ant} back-calculation, particularly for A_T^o, C_T^o and ΔC_{dis} estimation.

The variability of the seasonal cycle in surface waters is quite large in terms of non-conservative tracers like C_T or pCO₂ (Bates et al., 1996; Corbière et al., 2007), and even for conservative ones like potential temperature (θ), salinity (S), NO or PO (Broecker, 1974). Typical sea surface temperature (SST) oscillations can reach up to 10 °C (Pond & Pickard, 1978) in temperate waters and up to 6 °C in subpolar regions where WMF processes abound (Lab Sea Group, 1998). In the case of pCO₂, the amplitude of variations ranges between 80 and 160 ppm that eventually translate into significant changes of surface C_T (Bates et al., 1996; Lefèvre et al., 2004; Lüger, 2004; Corbière et al., 2007). The seawater pCO₂ (pCO₂^{sw}) depends on thermodynamics, biological

activity, physical mixing and air-sea gas exchanges. While the thermodynamic relationship between $p\text{CO}_2^{\text{sw}}$ and temperature is well known (Takahashi et al., 1981; Weiss et al., 1985) the effects of biological production and mixing are more difficult to resolve and explain (Lüger et al. 2004). In the light of this rather large variability, using surface data to estimate preformed properties or ΔC_{dis} in the upper ocean layers becomes dubious, at best. Surface data would yield a manifold of plausible but inaccurate reconstructions of WMF biogeochemical scenarios and the coefficients of preformed property parameterizations would depend ultimately on the date of sampling (Lo Monaco et al., 2005).

The surface outcropping of water masses abounds in the high latitudes of the Atlantic and occurs typically towards the end of the boreal and austral winter seasons in the northern and southern hemispheres, respectively. At this point in time, minimum seasonal values of θ and air-sea $\Delta p\text{CO}_2$ are reached together with minimum vertical gradients of $p\text{CO}_2^{\text{sw}}$ due to the wind-driven homogenization of the winter mixed layer (Pond and Pickard, 1978; Marshall and Schott, 1999). According to Lüger et al. (2007), the winter mixed layer depth (WMLD) is a parameter of critical importance for studying changes in the upper water column. Deep WMLs have associated important vertical transports of high concentrations of nutrients and C_T that increase the $p\text{CO}_2^{\text{sw}}$ in the upper layer. On the contrary, more stratified regions hamper this kind of vertical transports. Based on this WMLD concept, the physical-chemical properties of the surface layers would only be comparable or actually equal to those of lower layers in late wintertime, during the maximum WMLD occurrence (Pond and Pickard, 1978; Woods, 1985). Unluckily, the harsh meteorological conditions and the extension of ice covers in the high latitudes reduce the number of cruises that can be conducted there during the winter season.

As an alternative to the often unavailable surface late-wintertime data Pérez et al. (2002) and Ríos et al. (2003) used regional data from the 50-200 m layer as a first approximation to the winter mixed layer preformed conditions. They calculated preformed silicate concentrations (Si°) and then estimated the change in A_T ($\Delta A_T = A_T - A_T^\circ$) as a function of Si° and θ for the North Atlantic, based on data from one single cruise (OacesNatlIIB-93). Although this last approach was conceptually asserted, no

formal proof for the *modus operandi* was provided in those works and their results are only applicable at a regional scale.

An exploratory analysis was performed with a subset of WOA05 data to find a depth range that can be used as a reference for estimating WMF conditions. The elective depth range must be sufficiently separated from the surface's influence so that it is not affected directly by the large seasonal and circadian variability (Pardo et al., 2010). At the same time, the region needs to be able to “register” the biogeochemical evolution of the upper layers, particularly the one due to the atmospheric CO₂ anthropogenic forcing. In other words, it has to be susceptible of sensing the longer-term variability influence of the upper layers, which in the Atlantic is greatly influenced by the North Atlantic Oscillation (NAO) (Pérez et al., 2008; Pérez et al., 2010). Three meridionally distant Atlantic areas of 5°x5°, where important water masses form and WMLDs are locally largest, were selected (Fig. 1): the Rockall Plateau (formation area of Subpolar Mode Water -SPMW), the Labrador Sea (formation area of Labrador Seawater -LSW) and the Sargasso Sea (formation area of Subtropical Mode Water -STMW). Monthly averages of subsurface data from conservative parameters θ , S, $\text{NO} = 9 \text{ NO}_3 + \text{O}_2$ and $\text{PO} = 135 \text{ PO}_4 + \text{O}_2$ (Broecker, 1974), typically used in back-calculation parameterizations, were calculated for the three regions and plotted in Fig. 2.

Different subsurface domains spanning 100 meters were attempted: from 50 m to 300 m depths at 50 m intervals, namely: 50-150, 100-200, 150-250 and 200-300 m. Fig. 2 shows the 100-200 m averages, which turned out to be the interval that fulfilled best the above listed subsurface requirements: it showed the least seasonal variability and, concomitantly, had the closest monthly average tracer concentrations to those in the upper layers (0-20 m) during late wintertime (generally from January through April), independently of the considered Atlantic WMF region. Furthermore, Fig. 2 clearly shows that the variability of physical properties and biological forcing in the subsurface layer is at least one order of magnitude weaker than in the surface layer. This means that WMF biogeochemical properties are longer preserved throughout the annual cycle in the 100-200 m domain. In other words, the subsurface layer retains a memory of the WMF conditions up to sixth months after their wintertime formation periods. Interesting and useful enough, it is over those months, during the milder meteorological

spring and summer conditions, when more cruises are conducted and more data will be available for parameterizations.

Like CO_2 , oxygen is actively being exchanged between the atmosphere and the ocean and gives even a better idea of how the surface and subsurface layers behave when dealing with dissolved gases (Fig. 2e). Even though dissolved oxygen is not a conservative tracer (it is being actively produced and consumed by organic matter) its annual variability at the subsurface layer is actually comparable to that of conservative tracers like NO or PO (Figs. 2c and 2d, respectively) in all three considered regions. Contrarily, the dissolved oxygen concentration in the surface layer is subject to large seasonal variability due to events like the spring and autumn blooms or differential heating over the seasonal cycle.

Adding to the above results, the TS diagram in Fig. 3 shows how the thermohaline variability of the subsurface layer and the rest of the Atlantic's water column are very much alike. The latter tightly encloses and represents the assortment of water masses in the bulk of the Atlantic Ocean, unlike surface waters in the uppermost 25 meters. It must be noted that the wedge of high salinity waters in the water column (depth >200 m) not enclosed by the subsurface cluster in Fig. 3 corresponds to water masses under the influence of Mediterranean Water (MW). In spite of its bulky appearance in the TS diagram (like that of fresh surface waters), it only affects to a reduced subset of North Atlantic samples compared to the full dataset. Nevertheless, its influence can be easily estimated and corrected by solving the triangular mix defined by the TS signatures of the following end-members: Labrador Seawater (LSW), Subpolar Mode Water (SPMW) and MW (Fig. 3) from the TS signatures of the three end-members.

3.2. Estimating A_T° in the Atlantic from subsurface data.

Among the several A_T° parameterizations proposed in the past the ones from Gruber et al. (1996), Millero et al. (1998), and Lee et al. (2003) have been widely used. The A_T° parameterization from Millero et al. (1998) has separate quadratic equations of the term (0-20) for the North Atlantic (30°N – 80°N) and the Southern Ocean (70°S –

30°S). In the Equator (30°S – 30°N), they assign all waters a constant A_T° of 2291 $\mu\text{mol kg}^{-1}$. The parameterizations from Gruber et al. (1996) and Lee et al. (2003) are very much alike consisting both of multiple linear regressions (MLR) of the form “ $A_T^\circ = \alpha + \beta \cdot S + \gamma \cdot \text{Tr}$ ”, where $\text{Tr} = \text{NO}$ in the case of Lee et al. (2003) and $\text{Tr} = \text{PO}$ in Gruber et al. (1996). Another difference between them is that Gruber et al.’s can be applied globally, while Lee et al.’s can only be applied south from 60°N. All three mentioned A_T° parameterizations are based on surface A_T measurements collected year-round. It has been shown by other authors (Broecker and Peng, 1982; Ríos et al., 1995; Pérez et al., 2002) that these parameterizations yield systematic negative $\Delta A_T = A_T - A_T^\circ$ values despite of the net increases of silicate (ΔSi) that suggest no net CaCO_3 precipitation in the regions where the equations were applied (see section 4.2.1).

Here, we used subsurface bottle data from cruises in Table 1 and Fig. 1 to obtain an improved A_T° parameterization for the Atlantic. The stationary state for subsurface A_T is assumed in the decadal timescale covered, that is, A_T can actually change during the different WMF stages and further evolution of the water mass, but A_T will be the same at any given stage of the successive formation and ventilation cycles in the decadal timescale.

Also, we considered normalized potential A_T (NPA_T). The traditional normalization of A_T ($\text{NA}_T = A_T^{35/S}$) to $S=35$ has been used (Poisson and Chen, 1987). The normalization to a common $S=35$ removes the A_T - S co-variation, compensates for freshwater balance effects and brings all surface waters close to subsurface conditions. Although this normalization scheme (“zero alkalinity at zero salinity”) comes with certain caveats (Friis et al., 2003), the errors arising from its use are not large when intended for back-calculating C_{ant} , because it would affect equally industrial and preindustrial values. Moreover, the recommendations of alternative alkalinity normalizations in the work from Friis et al. (2003) refer to surface (upper 50 meter) rather than subsurface waters. Alternatively, the potential A_T (PA_T) term is defined as $\text{PA}_T = A_T + \text{NO}_3 + \text{PO}_4$, after Brewer et al. (1975) and Fraga and Álvarez-Salgado (2005). The main advantage of parameterizing PA_T instead of A_T is that organic matter remineralization has no effect on PA_T , but CaCO_3 dissolution does (by a factor of two), thus making PA_T a valid parameter subject to alkalinity shifts.

An exploratory analysis of the data was performed in order to study the latitudinal variability of the subsurface layer properties, some of which are plotted in Fig. 4. The high correlation observed between subsurface θ and S responds to the direct link between average zonal temperatures and the evaporation-precipitation rates (Fig. 4a). Figure 4b shows the strong correlation between all considered NPA_T parameterizations and the silicate gradient, particularly north from $50^\circ S$. 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 ($R^2=0.88$) stems from the relationship between the dissolution of opal and calcium carbonate. Silicate was therefore included in the following MLR fit of PA_T^{SSL} (“SSL” stands for “subsurface layer”):

$$PA_T^{SSL} \pm 4.6 = 585.7 \pm 13 + (46.2 \pm 0.4) S + (3.27 \pm 0.07) \theta + (0.240 \pm 0.005) NO + (0.73 \pm 0.01) Si \quad (1)$$

$$(R^2=0.97, N=1951)$$

Where $NO = 9 NO_3 + O_2$ ($\mu mol \text{ kg}^{-1}$) is the conservative tracer defined by Broecker (1974), and Si is the silicate concentration ($\mu mol \text{ kg}^{-1}$). Most importantly, since this PA_T equation has been obtained using subsurface data, which represent WMF conditions, it can be assumed that PA_T estimates obtained from equation (1) are actually PA_T° (i.e., $PA_T^{SSL} \approx PA_T^\circ$). Thus, from (1): $A_T^\circ = PA_T^{SSL} - (NO_3^\circ + PO_4^\circ)$, where $NO_3^\circ = NO_3 - AOU/9$ and $PO_4^\circ = PO_4 - AOU/135$ (AOU stands for Apparent Oxygen Utilization). The $O_2:N=9$ and $O_2:P=135$ Redfield remineralization ratios (Redfield et al., 1963) here used were proposed by Broecker (1974) and satisfactorily applied previously in the North Atlantic by Pérez et al. (2002) for C_{ant} estimation purposes.

The uncertainty of the A_T° estimates obtained from equation (1) is $\pm 4.6 \mu mol \text{ kg}^{-1}$, which is lower than the ones reported in Gruber et al. (1996) and in Lee et al. (2003). Compared to the rest of considered A_T° parameterizations (Fig. 4b), the obtained A_T° fit has the closest match with the latitudinal subsurface distribution patterns of measured subsurface NPA_T ($\approx NPA_T^\circ$) and silicate, particularly in the high latitudes (south from $50^\circ S$ and north from $60^\circ N$) and in the Equator ($25^\circ S - 25^\circ N$), where large

discrepancies are observed (Fig. 4b). On a general basis, the A_T° parameterizations from Gruber et al. (1996), Millero et al. (1998), and Lee et al. (2003) are significantly lower than the measured subsurface NPA_T in the southern hemisphere and systematically higher in the North Atlantic.

3.3. ΔC_{dis} parameterization in the Atlantic from subsurface data.

The ΔC_{dis} cannot be measured directly like A_T and must therefore be defined theoretically from observable parameters. The ΔC_{dis} at the time “t” of WMF (ΔC_{dis}^t) was first defined (Gruber et al., 1996) as the difference between the C_T in the mixed layer at the time of WMF (C_T^{ot}) and the theoretical C_T in equilibrium (C_{Teq}^t) with the corresponding pCO_2^{atm} as follows:

$$\Delta C_{dis}^t = C_T^{ot} - C_{Teq}^t = C_T - (AOU/R_C + 1/2 (PA_T - PA_T^\circ)) - C_{Teq}^t(xCO_2(t), A_T^\circ, S, \theta) \quad (2)$$

To obtain C_T^{ot} , the measured C_T in the 100-200 m layer has to be corrected for the organic matter remineralization (AOU/R_C term) and $\Delta CaCO_3 = 1/2 (PA_T - PA_T^\circ)$ contributions (first parenthesis in equation 2). The subsurface C_{Teq}^t is obtained from the thermodynamic equations of the inorganic carbon system using S , θ , AOU , A_T° , nitrate, phosphate and age (t) estimated from CFC12 concentrations as input parameters. The water pressure and fugacity terms have been also taken into account in the calculation of C_{Teq}^t (Pérez et al., 2002). The A_T° terms were calculated from equation (1). In equation (2), positive values indicate sea outgassing of C_{ant} and negative values indicate C_{ant} uptake by the ocean.

One important shortcoming of the ΔC_{dis}^t definition in (2) is that it depends on non-conservative tracers, which is something to be avoided in robust parameterizations. Hence, we used the subsurface ΔC_{dis} results from equation (2) as input data for an MLR fit that is based on conservative tracers (equation 3). The parametric coefficients of equation (3) for different temperature and latitude intervals are summarised in Table 2, together with the error estimates of the fit.

$$\Delta C_{\text{dis}}^t = a + b (\theta - 10) + c (S - 35) + d (\text{NO} - 300) + e (\text{PO} - 300) \quad (3)$$

The temperature and latitude intervals considered for equation (3) intend to improve the accuracy of ΔC_{dis}^t by means of regionalized equations (Pardo et al., 2010). For the case of central waters ($8 \leq \theta \leq 18$ °C) a distinction between hemispheres has been made. This is because no mixing between Arctic and Antarctic waters takes place in this oceanographic region. Similarly, a thermal boundary between warm ($\theta > 18$ °C) subsurface waters and colder waters has been established in the Equatorial upwelling region. The fitted ΔC_{dis}^t from (3) has a high correlation with the original ΔC_{dis}^t values from (2) ($R^2=0.72$; $n=1934$). The standard error of the estimates for equation (3) is between 4 and 7 $\mu\text{mol kg}^{-1}$ (average 5.6 $\mu\text{mol kg}^{-1}$; Table 2).

3.4 Calculating A_T^0 and ΔC_{dis} at depth in the Atlantic.

To obtain the profiles of A_T^0 and ΔC_{dis} in the entire water column, the subsurface calculations from equations (1) and (3) have to be conveyed into the ocean interior. This should be done differently depending on the θ of the sample. When water samples are found above the 5 °C isotherm, where preformed properties and ΔC_{dis} are established, and no mixing between Arctic and Antarctic origin waters occurs, then equations (1) and (3) can be applied directly.

Parameterizations (1) and (3) were obtained from subsurface waters ranging from 0 to 20 °C (Fig. 4a) and represent the assortment of water masses in the Atlantic Ocean (Fig. 3). Based on this 0-20°C temperature range equations (1) and (3) could be applied directly in the entire water column, however, this practice is not recommended for waters with $\theta < 5$ °C for two reasons. On the one hand, below the 5 °C isotherm there are complex, non-linear mixing processes of water masses that are formed in the Arctic and the Antarctic regions. On the other hand, A_T^0 and ΔC_{dis} are established near the surface, where water masses are formed and where these properties can be ideally calculated. Away from this region, typically below the 5°C isotherm, the A_T^0 and ΔC_{dis} of a given water parcel depends on the A_T^0 and ΔC_{dis} values and specific mixing

proportions from its source water masses. From a pragmatic point of view there is also an added interest to optimising the A_T° and ΔC_{dis} estimates in this region: waters below the 5 °C isotherm represent an enormous volume of the global ocean (~86%) and can therefore affect C_{ant} inventories quite significantly even from small uncertainties in A_T° and ΔC_{dis} estimates (Vázquez-Rodríguez et al., 2009).

Consequently, the determination of A_T° and ΔC_{dis} where $\theta < 5$ °C should be ideally estimated via an extended OMP (eOMP) analysis (Poole and Tomczak, 1999; Álvarez et al., 2004) to avoid important biases. The eOMP analysis is a method used to estimate the mixing proportions (and thus tracer concentrations) from a set of end-members that make up a particular water sample (Poole and Tomczak, 1999). Unlike the classical OMP, it accounts for the biogeochemical changes that cannot be disregarded in large scale mixing processes and have to be included in the analysis. The eOMP consists of a system of linear equations built from relationships of conservative and non-conservative tracers that is solved by minimizing the residuals using a non-negative least square routine. The OMP has been used successfully in previous studies with similar needs for solving water mass mixing (Karstensen and Tomczak, 1998; Sabine et al., 2002; Lee et al., 2003; Álvarez et al., 2004).

4. Results and discussion

4.1 Comparison of ΔC_{dis} estimates in the subsurface layer

As introduced in section 2 when describing Takahashi's ΔpCO_2 climatology, the ΔC_{dis} term of C_{ant} back-calculation equations and de ΔpCO_2 disequilibrium are not equally defined. The ΔC_{dis} considers CO_2 disequilibrium, oxygen disequilibrium (through the AOU/R_C term in equation (2)) and CFC disequilibrium when estimating water mass ages and formation times " t " for the theoretical calculation of the C_{Teq}^t term. On the contrary, Takahashi's ΔpCO_2 strictly considers CO_2 disequilibrium ($^{Taro}DC_{dis}^t = C_{Teq}^{pCO_2^t} - C_{Teq}^{pCO_2^t + DpCO_2^t}$). Therefore, the term denoted in Fig. 4c as $^{Taro}DC_{dis}^t$ is not directly comparable with the rest of ΔC_{dis} in that plot. The latitudinal distribution of surface AOU is thus included to account for oxygen disequilibrium ($AOU = [O_2]_{measured} - [O_2]_{saturation}$), make $^{Taro}DC_{dis}^t$ and the rest of ΔC_{dis} directly comparable and, therefore, get

rid of the differences that derive directly from the theoretical definitions of these two terms. Subtracting AOU/R_C from $^{Taro}\Delta C_{dis}^t$ to make it comparable to the rest of ΔC_{dis} is particularly appropriate and explains most of the differences in regions where WMF occurs, like in the Nordic Seas or the Southern Ocean.

The original ΔC_{dis}^t definition in equation (2) ($^{Classic}DC_{dis}^t$) was applied to subsurface data from all cruises in Fig. 1. The plot of $^{Classic}DC_{dis}^t$ in Fig. 4c shows slightly positive values (between 0 and 5 $\mu\text{mol kg}^{-1}$) in the tropical areas, especially on the southern hemisphere ($[-20^\circ\text{S} ; -15^\circ\text{S}]$). The North Atlantic subpolar region has ΔC_{dis}^t values ranging from -5 to 5 $\mu\text{mol kg}^{-1}$. In the rest of subpolar domains and in the subtropical regions the ΔC_{dis}^t values are very similar (-15 to 0 $\mu\text{mol kg}^{-1}$). The strongest disequilibria are found in the Southern Ocean (south from 50°S) and in the Nordic Seas, with values in the interval of -10 to -35 $\mu\text{mol kg}^{-1}$ for the former and 0 to -25 $\mu\text{mol kg}^{-1}$ for the latter region.

The subsurface ΔC_{dis} distribution from equation (3) ($^{SSL}DC_{dis}^t$, where “SSL” stands for “subsurface layer”) in Fig. 4c has an excellent correlation with $^{Classic}\Delta C_{dis}^t$ since it was originally fitted after ΔC_{dis} estimates from equation (2) ($R^2=0.72$; $n=1934$). Most importantly, $^{SSL}DC_{dis}^t$ is well correlated with the ΔC_{dis} distribution derived from the pCO_2 climatology of Takahashi et al. (2009) ($^{Taro}\Delta C_{dis}^t$). Exceptionally, some discrepancies between $^{SSL}DC_{dis}^t$ and $^{Taro}\Delta C_{dis}^t$ arise in the Equatorial and southern subtropical regions ($[-30^\circ\text{S} ; 5^\circ\text{N}]$) and in the Southern Ocean, where Takahashi’s climatology lacks data (particularly during wintertime).

Comparatively, $^{Classic}\Delta C_{dis}^t$ and $^{SSL}DC_{dis}^t$ have lower values than $^{Taro}\Delta C_{dis}^t$ throughout the studied latitudinal interval of the Atlantic. Such differences with respect to $^{Taro}\Delta C_{dis}^t$ are largest in the Southern Ocean and in the tropical region, where AOI can largely account for them, as commented above. Besides AOI, two other factors can explain the observed differences between $^{Taro}\Delta C_{dis}^t$ and $^{Classic}\Delta C_{dis}^t$ or $^{SSL}DC_{dis}^t$: a) the Antarctic upwelling of North Atlantic Deep Water (NADW) occurs in a region that has been classified as a High-Nutrient-Low-Chlorophyll (HNLC) biogeochemical province (Longhurst et al., 1995). These regions have limited photosynthetic activity and

therefore lower uptake of dissolved CO₂ and O₂ production, which leaves signs of apparent aging in tracer data that are accounted for in $^{Classic}\Delta C_{dis}^t$ and $^{SSL}DC_{dis}^t$ but not in $^{Taro}\Delta C_{dis}^t$ and; b) the ice cap hindrance of air-sea gas exchanges in the Southern Ocean constraints the oceanic uptake of O₂ from the atmosphere by the old, C_T rich and oxygen undersaturated upwelled NADW (Lo Monaco et al., 2005). Concurrently, the ice sheets encumber CO₂ outgasing in this region that has been catalogued as a CO₂ source to the atmosphere ($^{Taro}\Delta C_{dis}^t > 0$; Takahashi et al., 2009).

On the other hand, previous literature (Gruber, 1998; Matsumoto and Gruber, 2005) had acknowledged that the $^{Lee}\Delta C_{dis}^t$ estimated with the ΔC^* method (Gruber et al., 1996; Lee et al., 2003; Olsen et al., 2008) has differences in the high latitudes and in the Equator with Takahashi's climatology, as shown in Fig. 4c. These differences are also observed with respect to $^{SSL}DC_{dis}^t$. Lee et al. (2003) give the lowest and less varying average ΔC_{dis} ($-16.1 \pm 3.3 \mu\text{mol kg}^{-1}$) for the whole studied extension of the Atlantic subsurface layer compared with the rest of estimates in Fig. 4c (-8.6 ± 7.9 and $-1.7 \pm 14.4 \mu\text{mol kg}^{-1}$ for $^{SSL}DC_{dis}^t$ and $^{Taro}\Delta C_{dis}^t$, respectively).

The $^{Lee}\Delta C_{dis}^t$ and $^{Classic}\Delta C_{dis}^t$ are conceptually defined equally, however, the way the definition is applied in Lee et al. (2003) make the two results diverge (Fig. 4c). The $^{Lee}\Delta C_{dis}^t$ values come from an A_T^0 parameterization based on surface data and from CFC-based age estimates in old Antarctic waters (ages >25 years), where this practice is not recommended (Doney et al., 1988, 1997).

4.2 Sensitivity of C_{ant} estimates to different A_T⁰ and ΔC_{dis} parameterizations

The expression to calculate C_{ant} given below in equation (4) is the one used by the ΔC^* method (Gruber et al., 1996) and it summarizes well the main biogeochemical processes that need to be considered when back-calculating C_{ant}. Since we will be discussing the results here obtained with those in Lee et al. (2003), who applied the ΔC^* method, this equation is provided for reference.

$$C_{ant} = \Delta C^* - \Delta C_{dis} = (C_T^0 - C_{T_{eq}}^\pi) - \Delta C_{dis} = [(C_T - \text{AOU}/R_C - \Delta \text{CaCO}_3) - C_{T_{eq}}^\pi] - \Delta C_{dis} \quad (4)$$

where the ΔCaCO_3 term accounts for the dissolution / precipitation of CaCO_3 in the water column according to the expression $\Delta\text{CaCO}_3 = \frac{1}{2}(\Delta\text{PA}_T) = \frac{1}{2}(\text{PA}_T - \text{PA}_T^0)$ (Gruber et al., 1996; Lee et al., 2003). This expression takes into account the effects of organic matter remineralization on A_T (Fraga and Álvarez-Salgado 2005). The cycling of carbonate minerals is the major biogeochemical process affecting seawater alkalinity (Friis et al., 2003), which is the reason why ΔCaCO_3 can be expressed as a function of A_T . In fact, alkalinity was historically explained as ‘being a measure of its potential carbonate of lime’ (Dittmar, 1884). The ΔCaCO_3 is the one term in the context of C_{ant} back-calculation where the importance of solid A_T^0 parameterizations and estimates comes in place.

4.2.1 Influence of A_T^0 parameterizations on C_{ant} estimates

The different parameterizations of A_T^0 affect the back-calculation of C_{ant} through the term $\Delta\text{CaCO}_3 = \frac{1}{2}(\text{PA}_T - \text{PA}_T^0)$ (Gruber et al., 1996; Lee et al., 2003). According to equation (4) the uncertainties in the determination of A_T^0 (δA_T^0) affect C_{ant} estimates by $0.4 \delta A_T^0$, i.e., $1 \mu\text{mol kg}^{-1}$ of δA_T^0 translates into a $0.4 \mu\text{mol kg}^{-1}$ difference of C_{ant} in any given water sample. In this aspect, the lower uncertainties here obtained for A_T^0 ($\pm 4.6 \mu\text{mol kg}^{-1}$; equation 1) compared to previous parameterizations are expected to reduce some biases in C_{ant} back-calculation estimates.

The dissolution of CaCO_3 is thermodynamically and kinetically favoured below the lysocline, at the high pressure (>2300 dbar on average for the Atlantic) and low temperature conditions of the deep ocean (Feely et al., 2004; Royal Society, 2005). The water column distributions of ΔCaCO_3 derived from the A_T^0 parameterizations in equation (1) and in Lee et al. (2003) shown in Fig. 5 are in good general agreement in this sense: there is a tendency for calcium carbonate dissolution to increase in deep waters (where A_T is also larger than in the upper layers), mainly in the Deep South Atlantic where the oldest, C_T -enriched water masses are found.

The most important discrepancies are found in the subpolar North Atlantic, where $^{Lee}\Delta\text{CaCO}_3$ yields ample negative values (as much as $-6 \mu\text{mol kg}^{-1}$), and in the

Southern Ocean, where the highest overall ΔCaCO_3 values are found ($^{Lee}\text{DCaCO}_3$ estimates are $\sim 25 \mu\text{mol kg}^{-1}$ on average; Fig. 5b). Such differences between $^{SSL}\text{DCaCO}_3$ (this study) and $^{Lee}\text{DCaCO}_3$ stem mainly from the ability of each A_T^0 parameterization to reconstruct preformed conditions in the Atlantic and from how A_T^0 and ΔCaCO_3 are calculated in the lower layers of the water column, i.e., via isopycnal propagation of surface estimates (Gruber et al., 1996; Lee et al., 2003) or by using eOMP results (this study).

Very little CaCO_3 dissolution ($\Delta\text{CaCO}_3 > 0$) occurs in the upper layers of the northern and southern subpolar regions. Actually, both A_T^0 parameterizations in Fig. 5 predict even some CaCO_3 precipitation ($\Delta\text{CaCO}_3 < 0$) at varying extents above ~ 700 meters, particularly north from 30°N . Nonetheless, the large negative values of $^{Lee}\text{DCaCO}_3$ (Fig. 5b) in most of the North Atlantic deep layers is an improbable result. Even though the upper ocean is supersaturated with CaCO_3 there is a downward increase of the CaCO_3 dissolution (Broecker and Peng, 1982; Doney et al., 2009). There is no evidence that such net precipitation of CaCO_3 predominates over dissolution in the uppermost layers of the subpolar North Atlantic. The review of the global carbonate budget (Milliman et al., 1999; Berelson et al., 2007) shows that a considerable portion of surface-produced calcite (as much as 60-80%) actually dissolves above the lysocline, in the upper 1000 m, as a result of biological mediation. This finding was further corroborated from sediment trap records in the North Atlantic (Honjo and Manganini, 1993; Martin et al., 1993).

Regarding the ΔCaCO_3 values obtained for the Southern Ocean, the $^{SSL}\text{DCaCO}_3$ fields show average values of $\sim 15 \pm 2 \mu\text{mol kg}^{-1}$ for this region while $^{Lee}\text{DCaCO}_3$ estimates are $\sim 25 \mu\text{mol kg}^{-1}$, on average. This average $7 \mu\text{mol kg}^{-1}$ difference would translate into almost $3 \mu\text{mol kg}^{-1}$ less in terms of C_{ant} concentration whenever the A_T^0 parameterization from Lee et al. (2003) is applied in back-calculation techniques. This result partly explains the low inventories of C_{ant} predicted by the ΔC^* method (Gruber et al., 1996; Lee et al., 2003) in the Southern Ocean when compared to other C_{ant} calculation approaches (Vázquez-Rodríguez et al., 2009). The residence time of waters under the lysocline in the Southern Ocean rarely exceeds 40 years on average (Vázquez-

Rodríguez et al., 2009) due to the rapid sinking of the Antarctic Bottom Water Plume (AABW). According to Milliman et al. (1999) the residence time under the lysocline can largely determine, besides temperature and pressure, the saturation state of CaCO_3 (Feely et al., 2004), and 40 years is a relatively short time for as much CaCO_3 dissolution to occur as suggested by $^{Lee}\text{DCaCO}_3$ (Fig. 5b).

4.2.2 Influence of ΔC_{dis} on C_{ant}

The estimates of ΔC_{dis} have a 1:1 repercussion on C_{ant} estimates according to the classic back-calculation equation (Gruber et al., 1996), since ΔC_{dis} is directly subtracted from the measured C_T concentration (equation 4). Thus their effect on C_{ant} calculations is 60% larger than the ones derived from A_T^0 parameterizations: uncertainties of $\pm 1 \mu\text{mol kg}^{-1}$ in A_T^0 and $\pm 1 \mu\text{mol kg}^{-1}$ ΔC_{dis} translate into ± 0.4 and $\pm 1 \mu\text{mol kg}^{-1}$ in terms of C_{ant} , respectively.

The water column average $^{SSL}\text{DC}_{\text{dis}}^t$ for the composite transect of cruises denoted by star symbols in Fig. 1 were plotted vs. the average θ of the isopycnal surfaces given by Lee et al. (2003). Compared to $^{SSL}\text{DC}_{\text{dis}}^t$, the magnitude of $^{Lee}\text{DC}_{\text{dis}}^t$ in the North Atlantic is systematically lower ($10 \pm 6 \mu\text{mol kg}^{-1}$ on average; Fig. 6a). A similar scenario occurs in the intertropical zone (average offset of $9 \pm 5 \mu\text{mol kg}^{-1}$; Fig. 6b). In the South Atlantic $^{SSL}\text{DC}_{\text{dis}}^t$ and $^{Lee}\text{DC}_{\text{dis}}^t$ estimates are opposite in trend and have an average offset of $5 \pm 9 \mu\text{mol kg}^{-1}$. The differences between the minimum estimates from $^{SSL}\text{DC}_{\text{dis}}^t$ ($-25 \pm 4 \mu\text{mol kg}^{-1}$) and $^{Lee}\text{DC}_{\text{dis}}^t$ ($-9 \pm 3 \mu\text{mol kg}^{-1}$) for this region (isopycnal level $\sigma_4 = 46.05 \text{ kg m}^{-3}$) are remarkably large and represent a major source of bias in the C_{ant} inventory estimates of the Southern Ocean (Vázquez-Rodríguez et al., 2009). Although C_{ant} concentrations are moderate in this region, its large volume make even small uncertainties in C_{ant} concentration estimates translate into large biases of water column inventories. Part of these differences between $^{SSL}\text{DC}_{\text{dis}}^t$ and $^{Lee}\text{DC}_{\text{dis}}^t$ can be explained from the differences in the respective A_T^0 parameterizations. The low $^{Lee}\text{DCaCO}_3$ estimates (Fig. 5b) derived from $^{Lee}A_T^0$ introduce systematic biases in $^{Lee}\text{DC}_{\text{dis}}^t$ of about $-8 \mu\text{mol kg}^{-1}$.

The $C_{T\text{eq}}^\pi$ linearization and the effects of water pressure on $f\text{CO}_2$ calculations (Pérez et al., 2002) not contemplated in $^{Lee}DC_{\text{dis}}^t$ represent additional minor sources of discrepancy between $^{SSL}DC_{\text{dis}}^t$ and $^{Lee}DC_{\text{dis}}^t$. Also, the different set of thermodynamic constants for the carbon system used in this study and in Lee et al. (2003) can be easily reconciled for a more direct and objective comparison of these two sets of ΔC_{dis} estimates. Considering the latter and also the influence of the $^{Lee}A_T^0$ parameterization on $^{Lee}DC^*$ this term was expressed and refitted in terms of $^{SSL}DC^*$ (the ΔC^* obtained after applying the here proposed $^{SSL}A_T^0$ estimates), namely:

$$^{Lee}_{refit}DC^* \pm 0.8 = ^{SSL}DC^* - 0.377 (^{Lee}A_T^0 - ^{SSL}A_T^0) - (0.0721 \theta^2 - 1.36 \theta + 5.0) \quad (5)$$

($R^2=0.999$)

After applying the correction in (5) we obtain a set of refitted estimates ($^{Lee*}DC_{\text{dis}}^t$) that make the differences between $^{SSL}DC_{\text{dis}}^t$ and $^{Lee}DC_{\text{dis}}^t$ in the North Atlantic to drop noticeably to $0 \pm 7 \mu\text{mol kg}^{-1}$ (Fig. 6a). However, the standard deviation of this average difference is still significantly higher than the average uncertainty for $^{SSL}DC_{\text{dis}}^t$ in the North Atlantic ($\pm 6.0 \mu\text{mol kg}^{-1}$; Table 2). Conversely, both sets of ΔC_{dis} estimates are in better agreement in the tropical region (Fig. 6b) after the refit (average difference of $0 \pm 3 \mu\text{mol kg}^{-1}$).

Overall, the $^{SSL}DC_{\text{dis}}^t$ estimates are still less negative than $^{Lee*}DC_{\text{dis}}^t$ in deep and subtropical waters, while the opposite occurs in subpolar waters ($5 < \theta < 10^\circ\text{C}$). In the South Atlantic the refit of Lee's results produces larger differences with $^{SSL}DC_{\text{dis}}^t$ (average $-10 \pm 9 \mu\text{mol kg}^{-1}$; Fig. 6b) and, importantly, $^{SSL}DC_{\text{dis}}^t$ and $^{Lee*}DC_{\text{dis}}^t$ remain opposite in trend: $^{Lee*}DC_{\text{dis}}^t$ yields less negative values than $^{SSL}DC_{\text{dis}}^t$ in the Southern Ocean and in southern subtropical waters (Fig. 6b). In terms of C_{ant} , the less negative values from $^{Lee*}DC_{\text{dis}}^t$ translate into lower concentrations and therefore lower estimates of column inventory of C_{ant} . This is most important in the Southern Ocean because it

considerably lowers the overall C_{ant} inventory estimates in Lee et al. (2003) for the Atlantic and global oceans (Vázquez-Rodríguez et al., 2009).

Lee et al. (2003) claim that the systematic biases in A_T^0 parameterizations largely cancel out when applying the ΔC^* method to estimate C_{ant} because it affects $\Delta C^* = (C_T^o - C_{\text{Teq}}^o)$ and ΔC_{dis} by the same token. However, this argument does not prove or give credit to the solidness of their ΔC^* or ΔC_{dis} estimates. The ΔC^* method combines a “shortcut method” (Thomas and Ittekkot, 2001; Matear and McNeil, 2003) to estimate C_{ant} in the upper young waters with the classic back-calculation approach in deeper layers, where $\Delta C^* \approx \Delta C_{\text{dis}}$ is assumed (as $C_{\text{ant}} \rightarrow 0$). The shortcut method calculates C_{ant} indirectly from CFC12-derived age estimates. Therefore, A_T^0 parameterizations have an inconsequential relevance in upper layers for the ΔC^* method. However, the uncertainties in CFC12 ventilation ages derived from non-linear mixing processes (Sonnerup, 2001; Matear and McNeil, 2003; Matsumoto and Gruber, 2005) lead to an overestimation of C_{ant} and, consequently, to underestimating ΔC_{dis} in upper ocean layers.

On the other hand, the approximation $\Delta C^* \approx \Delta C_{\text{dis}}$ in deep and very old isopycnals where C_{ant} invasion can be reasonably assumed to be negligible (according to ancillary tracer concentration data like CCl_4 , tritium, ^3He or CFCs) is not straightforward and has been challenged (Doney et al., 1997; Mecking et al., 2004). Such practice has misleadingly prone researchers in the past to consider C_{ant} -void waters where there were actually low concentrations of this tracer, above determination uncertainties (Orsi et al., 2002; Lo Monaco et al., 2005; Waugh et al., 2006; Vázquez-Rodríguez et al., 2009). In sum, setting inappropriate $C_{\text{ant}}=0$ references in the ΔC^* method for old water masses yields less negative ΔC_{dis} estimates that introduce positive systematic biases in $^{Lee}\Delta C_{\text{dis}}^t$ (Coatanoan et al., 2001). Hence, the low $^{Lee}\Delta C_{\text{dis}}^t$ estimates in the upper ocean and high values in deep waters (Fig. 6) might in fact be artefacts of the ΔC^* method itself.

5. Conclusions

The proposed subsurface layer of 100-200 m as a reference to estimate A_T^0 and ΔC_{dis} in the Atlantic has proved to be a region that represents well WMF conditions and preserves them year-through after late wintertime outcropping events. The A_T^0 estimates here obtained from subsurface data have reported lower uncertainties ($\pm 4.6 \mu\text{mol kg}^{-1}$) than the parameterizations in previous works (Millero et al., 1998; Gruber et al., 1996; Lee et al., 2003) and avoids the systematic negative $\Delta A_T = A_T - A_T^0$ values from the latter that suggested excessive net CaCO_3 precipitation above the lysocline in the Atlantic (Broecker and Peng, 1982; Ríos et al., 1995; Pérez et al., 2002). Albeit all A_T^0 parameterizations are in good general agreement (Fig. 4b) there are important differences in the high latitudes (Southern Ocean and Nordic Seas) and in the Equator. On the other hand, the results of ΔC_{dis}^t here obtained in the upper layers are in good agreement with the CO_2 disequilibria estimated from Takahashi's climatology of $\Delta p\text{CO}_2$ (Takahashi et al., 2009). Altogether, the A_T^0 and ΔC_{dis} parameterizations here proposed minimise the large biases in C_{ant} calculations from back-calculation methods known to occur particularly at high Atlantic latitudes (Lo Monaco et al., 2005; Waugh et al., 2006; Vázquez-Rodríguez et al., 2009; Khatiwala et al., 2009).

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Table captions

Table 1. List of selected Atlantic cruises (Fig. 1). Surface layer data (depth <100 m) has been discarded to avoid the influence of seasonal variability on the long-term trends. Acronyms and superscripts denote the following: ^aY= measured values available; ^bN= measured values unavailable; ^cNA= no adjustment made; ^dY+Calc= When direct measurements were unavailable, A_T was calculated from C_T and pH measurements, using the thermodynamic relationships of the carbon system; ^e = Correction in $\mu\text{mol kg}^{-1}$, after ORNL/CDIAC 148 report.

Table 2. Coefficients and statistics for the multi-linear regression (MLR) of ΔC_{dis}^t vs conservative parameters (equation 3). Except for θ ($^{\circ}\text{C}$) and S, all other variables and standard errors are given in $\mu\text{mol kg}^{-1}$. N stands for the number of valid points used for the fit, and R^2 is the correlation coefficient of the adjustment. The standard error of the estimate (Std. error) was calculated as $S/\sqrt{N}$.

Figure captions

Figure 1. Atlantic cruises used to test the adequacy of different reference layers for A_T° and ΔC_{dis} parameterizations. Ancillary information for these cruises is given in Table 1. The Sargasso Seawater (SSW) formation area [(55.5°W-60.5°W);(28.5°N-33.5°N)], the Subpolar Mode Water (SPMW) formation area [(17.5°W, 22.5° W);(49.5°N, 54.5°N)] and the Labrador Seawater (LSW) formation area [(55.5°W, 60.5°W);(28.5° N, 33.5°N)], are framed by the blue, red and green squares, respectively. These regions are used as references to explore the annual variability of tracers in the surface and subsurface layers (Fig.2).

Figure 2. Annual variability of conservative tracers (θ , S, NO and PO) in the surface (0-20m) and subsurface (100-200 m) layers of $5^\circ \times 5^\circ$ areas in the Sargasso Sea, Rockall Plateau and Labrador Sea boxed in Fig. 1. Monthly averages were taken from WOA05. The constant stoichiometric ratios used to calculate NO and PO are $R_N=O_2:N=10.4$ and $R_P=O_2:P=175$, respectively (after Broecker, 1974).

Figure 3. TS diagram from WOA05 data showing the thermohaline variability in the Atlantic Ocean. The star symbols stand for subsurface layer measurements from cruises in Fig. 1, which encompass those from WOA05 data. The cold and low-salinity surface samples (light-grey circles) falling outside the main body of the TS (conformed by the blue and red circles) correspond to Arctic waters subject to high freshwater inputs from rivers and sea-ice melting. Water mass acronyms denote the following: AABW= Antarctic Bottom Water; WSDW=Weddell Sea Deep Water; CDW=Circumpolar Deep Water; AAIW= Antarctic Intermediate Water; SAMW=Subantarctic Mode Water; ISW= Ice Shelf Water; WW= Winter Water; ISOW= Iceland-Scotland Overflow Water; DSOW= Denmark Strait Overflow Water; MW= Mediterranean Water; SPMW= Subpolar Mode Water; LSW= Labrador Sea Water; MOW= Mediterranean Overflow Water; ENACW= Eastern North Atlantic Central Water.

Figure 4. Latitudinal distributions of various tracers in the Atlantic subsurface layer (100-200 m): θ and S (Fig. 4a); silicate and NPA_T^0 (Fig. 4b); ΔC_{dis} and AOU (Fig. 4c). The data here plotted were obtained by vertically averaging subsurface bottle data from the cruises in Fig. 1, and then bringing them to the same horizontal grid resolution as in Takahashi's climatology ($4^\circ \times 5^\circ$) to make results comparable, especially in Fig. 4c. The pink circles in Fig. 4b are NPA_T values from direct subsurface layer observations (cruises in Fig. 1). The green circles in Fig. 4b are the NPA_T^0 estimates from equation (1). Fig. 4c shows a comparison of subsurface estimates for $^{Classic} \Delta C_{dis}^t$ and $^{SSL} DC_{dis}^t$ (equations (2) and (3)),

$^{Lee}\Delta C_{dis}^t$ (Lee et al., 2003) and $^{Taro}\Delta C_{dis}^t$ (Takahashi et al., 2009). The plotted Takahashi's $\Delta pCO_2 = pCO_2^{sea} - pCO_2^{air}$ data in Fig. 4c corresponds to winter data only. Average surface AOU (red circles) is included as a water mass ventilation proxy.

Figure 5 Water column distribution of the term $\Delta CaCO_3 = \frac{1}{2}(PA_T - PA_T^0)$ that represents the $CaCO_3$ dissolution/precipitation processes in the context of C_{ant} back-calculation. The contour plots correspond to the composite transect of cruises denoted by star symbols in Fig. 1, extending north to south in the eastern Atlantic basin. Fig. 5a shows the $\Delta CaCO_3$ fields obtained after applying the A_T^0 expression in equation (1) ($^{SSL}DCaCO_3$, this study). In Fig. 5b ($^{Lee}DCaCO_3$) the A_T^0 parameterization from Lee et al. (2003) was used, which is only defined for waters south from 60°N.

Figure 6 Comparison of $^{SSL}DC_{dis}^t$ and $^{Lee}DC_{dis}^t$ estimates in the water column vs. θ in a) the North Atlantic (lat. >20°N) and; b) the South Atlantic (lat. <20°S) and Intertropical Atlantic (20°S < lat. <20°N). To make a more objective and direct comparison with $^{SSL}DC_{dis}^t$, the original $^{Lee}DC_{dis}^t$ (Lee et al., 2003) was refitted ($^{Lee*}DC_{dis}^t$) considering the differences caused by the distinctive A_T^0 parameterizations and use thermodynamic constants of the carbon system.

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Cruise Information			Parameters Analyzed									Adjustments	
Section	Date	P.I.	C _T	A _T	fC O ₂	p H	Fre ons	N	P	S i	O	C _T	A _T
A02	6/11 - 7/3/1997	P. Koltermann	Y _a	Y	N ^b	N	Y	Y	Y	Y	Y	NA ^c	NA
AR01	23/1 - 24/2/1998	K. Lee	Y	Y	Y	Y	Y	Y	Y	Y	Y	NA	NA
A14	1/11 - 2/11/1995	H. Mercier	Y	Y+C ^d alc	N	N	Y	Y	Y	Y	Y	NA	NA
A16	4/7 - 29/8/1993	R. Wanninkhof	Y	Y	Y	Y	Y	Y	Y	Y	Y	NA	NA
A16N	4/6 - 11/8/2003	J. Bullister	Y	Y	Y	Y	Y	Y	Y	Y	Y	NA	NA
A17	1/4 - 21/3/1994	L. Memery	Y	Y+C ^d alc	N	Y	Y	Y	Y	Y	Y	NA	-8 ^e
A20	17/7 - 10/8/1997	R. Pickart	Y	Y	Y	N	Y	Y	Y	Y	Y	NA	NA
A25 (OVI DE)	6/6 - 5/7/2002	H. Mercier	N	Y	Y	Y	Y	Y	Y	Y	Y	NA	NA
I06- Sa	23/1 - 9/3/1993	A. Poisson	Y	Y	Y	N	Y	Y	Y	Y	Y	NA	NA
I06- Sb	20/2 - 22/3/1996	A. Poisson	Y	Y	Y	N	Y	Y	Y	Y	Y	NA	NA
NSeas	1/6 - 7/6/2002	R. Bellerby	Y	Y	N	N	Y	Y	Y	Y	Y	NA	NA

Table 1

Region	Latitude Band	θ Interval [°C]	a	b (θ - 10)	c (S- 35)	d (NO - 300)	e (PO - 300)	N	R ²	Std. error
Atlantic	[70° S – 70° N]	5 ≤ θ < 8	-7.1 ±1.0	1.29 ±0.3 2	11. 1 ±1.0	*	*	13 8	0.6 2	4.1
N. Atl.	(20° N – 70° N]	8 ≤ θ < 18	- 13. 4 ±1.5	1.18 ±0.4 6	*	*	0.17 ±0.0 3	45 4	0.4 0	5.7
N. Atl.	(20° N – 70° N]	18 ≤ θ ≤ 25	- 38. 6 ±3.0	1.67 ±0.3 9	16. 3 ±1.4	- 0.32 ±0.07	0.52 ±0.0 5	27 2	0.5 5	6.7
Intertrop.	[20° S – 20° N]	8 ≤ θ < 18	- 14. 4 ±0.6	2.39 ±0.1 3	*	*	*	44 1	0.4 3	5.0
Intertrop.	[20° S – 20° N]	18 ≤ θ ≤ 25	-3.9 ±3.5	2.55 ±0.4 8	11. 3 ±2.4	*	*	12 5	0.1 8	7.1
S. Atl.	[70° S – 20° S)	8 ≤ θ < 18	- 10. 7 ±2.6	- 1.82 ±0.6 5	9.7 ±2.4	- 0.12 ±0.04	- 0.13 ±0.0 4	23 2	0.3 1	4.0
S. Atl.	[70° S – 20° S)	18 ≤ θ ≤ 25	- 38. 6 ±3.0	1.67 ±0.3 9	16. 3 ±1.4	- 0.32 ±0.07	0.52 ±0.0 5	27 2	0.5 5	6.7

Table 2