Author Contributions:

Conceptualization: M. López-Mozos, F. F. Pérez, A. Velo
Data curation: M. López-Mozos, G. Gebbie, A. Velo
Formal analysis: M. López-Mozos, F. F. Pérez, L. I. Carracedo, A. Velo
Funding acquisition: F. F. Pérez, A. Velo
Investigation: M. López-Mozos, F. F. Pérez, L. I. Carracedo

A Novel Back-Calculation Approach to Estimate Ocean Anthropogenic Carbon Using Carbon-Based Data and a Total Matrix Intercomparison Method

M. López-Mozos[1,2] [ID], **F. F. Pérez[1]** [ID], **L. I. Carracedo[3]** [ID], **G. Gebbie[4]** [ID], **and A. Velo[1]** [ID]

[1]Instituto de Investigaciones Marinas (IIM-CSIC), Vigo, Spain, [2]Facultad de Ciencias del Mar, Universidade de Vigo, Vigo, Spain, [3]University Brest, CNRS, Ifremer, IRD, Laboratoire d'Océanographie Physique et Spatiale (LOPS), IUEM, Plouzané, France, [4]Department of Physical Oceanography, Woods Hole Oceanographic Institution, Woods Hole, MA, USA

Abstract Over the last decades, back-calculation (BC) techniques for ocean anthropogenic carbon (C_{ant}) estimation have improved and evolved into different methodologies that are not exempt from various assumptions and limitations. No single optimal BC method exists to date for computing C_{ant}; therefore, it is necessary to continue advancing the broad range of approaches. Here, we present a novel method based on the BC fundamentals that combines marine-carbonate-system (MCS) data and the Total Matrix Intercomparison (TMI) framework. This MCS-TMI approach differs from other BC methods by using the TMI to reconstruct deep-ocean biogeochemical properties and their preformed conditions. It also incorporates a global sea-air oxygen disequilibrium term, and a dynamic stoichiometric carbon-to-oxygen ratio that depends on the water-mass ideal time. The MCS-TMI yields a total C_{ant} inventory of 124 ± 7 Pg C (referred to 1995), in good agreement with previous global C_{ant} climatologies. The MCS-TMI method uncertainty (± 5.6 µmol kg^{-1}) is controlled by input-data errors that, nonetheless, have a minimal impact on the total C_{ant} inventory. In contrast, our total C_{ant} inventory uncertainty is governed by methodological errors, specifically those related to the TMI's boundary conditions. Our study demonstrates the effectiveness of MCS data-based climatologies in reconstructing a 3D gridded C_{ant} climatology, and the validity of ocean circulation transport operators for obtaining BC preformed conditions.

Plain Language Summary Since the industrial revolution, human-induced excess carbon dioxide (C_{ant}) has been disrupting the carbon cycle. The ocean absorbs part of it, reducing atmospheric excess but causing severe consequences for marine systems. Oceanic C_{ant} storage is uneven, and estimates rely on indirect methods due to the impossibility of an analytical procedure for discerning the signal. To date, there is no optimal method for calculating C_{ant}. Progress is essential, and advancements are needed across various approaches. Back-calculation methods differ from the rest by using marine-carbonate-system (MCS) data, and their results serve as observational references. In this study, we present a novel approach for estimating marine C_{ant} globally, which relies on an improved back-calculation formulation and is based exclusively on climatological MCS high-quality data. Our resulting C_{ant} climatology agrees with previous global studies, underscoring the feasibility of our approach and emphasizing the relevance of accurate MCS data for climate change related research.

1. Introduction

The ocean plays a key role in climate regulation, storing 40 times more carbon than the atmosphere (Friedlingstein et al., 2023). Since the industrial revolution, the carbon cycle has been altered by the excess of atmospheric carbon dioxide (CO_2) emissions from human activities (C_{ant}), leading the ocean to counteract such CO_2 increase by absorbing nearly a third of it (Gruber et al., 2019). The anthropogenic carbon (C_{ant}) invasion into the ocean is increasing ocean acidity and causing severe impacts on marine systems (Bednaršek et al., 2023; Feely et al., 2023; IGBP, IOC, SCOR, 2013). Therefore, it is crucial to understand and quantify the oceanic CO_2 uptake, storage, and distribution, particularly the anthropogenic component (Intergovernmental Panel on Climate Change IPCC, 2019). Nevertheless, both components of CO_2, that is, anthropogenic and natural, have high variability and uncertainties that are difficult to observe and quantify (Müller et al., 2023). This is particularly true for the C_{ant} signal, as it represents only a small fraction of the dissolved inorganic carbon pool (C_T). Moreover, the C_{ant} signal

Methodology: M. López-Mozos, F. F. Pérez, L. I. Carracedo, A. Velo
Project administration: F. F. Pérez, A. Velo
Resources: M. López-Mozos, F. F. Pérez, A. Velo
Software: M. López-Mozos, G. Gebbie, A. Velo
Supervision: F. F. Pérez, L. I. Carracedo, A. Velo
Validation: M. López-Mozos, F. F. Pérez
Visualization: M. López-Mozos, F. F. Pérez
Writing – original draft: M. López-Mozos
Writing – review & editing: M. López-Mozos, F. F. Pérez, L. I. Carracedo, G. Gebbie, A. Velo

is not directly distinguishable from the natural component (Brewer, 1978; Chen & Millero, 1979), which has led to the development of various techniques to derive it indirectly.

Significant progress has been made in ocean C_{ant} estimates over the last few decades, as evidenced by the within-uncertainty agreement between C_{ant} inventories derived from independent methods (Khatiwala et al., 2013). This highlights the importance of using multiple approaches, each with its own limitations and regional biases. C_{ant} methodologies can be categorized into (a) model-based and (b) observation-based approaches. The model-based category includes Global/Regional Ocean Biogeochemical Models (GOBMs/ROBMs) and data assimilation models (e.g., OCIMv2021, DeVries, 2022), which provide C_{ant} estimates and forecasts that are highly valuable for climate-related predictions and decisions. Observation-based approaches include methods that use transient tracers' data (e.g., Green Function methods) or marine-carbonate-system (MCS) data (i.e., back-calculation techniques or repeated observations to infer decadal changes, such as the eMLR* of Gruber et al., 2019; Müller et al., 2023). The synergy between model-based and observation-based approaches is fundamental. For instance, observational products are frequently used to assess GOBMs/ROBMs performance (e.g., DeVries et al., 2023; Fu et al., 2022), thereby emphasizing the importance of further advancement in observation-based C_{ant} estimates.

Marine data acquisition is advancing significantly by increasing the number, frequency and coverage of observations (e.g., https://www.glodap.info/), especially for MCS measurements. The quality standards implemented for MCS (e.g., https://www.go-ship.org/DatReq.html) are leading to the highest levels of accuracy in MCS data to date (Dickson et al., 2003). In addition, progress in BGC-Argo sensors (Johnson et al., 2017) supports the ongoing improvement of MCS data collection in the future. Therefore, the use of MCS data for C_{ant} estimation is becoming increasingly important, particularly given the limited lifespan of transient tracers, such as Chlorofluorocarbons (CFCs), and their uncertain long-term traceability.

Assessing C_{ant}-change rates (i.e., relative changes in C_{ant} storage) is fundamental (e.g., Müller et al., 2023) to fully understand how the ocean is storing the CO_2 excess since pre-industrial times. However, to quantify the storage in terms of absolute total C_{ant} inventories, year-referenced C_{ant} estimates are necessary (e.g., Sabine et al., 2004). This, combined with the growing efforts by the scientific community to improve the acquisition, quality and availability of MCS data, fosters the advancement of back-calculation techniques, which were previously limited by the lack of high-quality MCS data (Bockmon & Dickson, 2015).

The back-calculation techniques (Brewer, 1978; Chen & Millero, 1979) were the first C_{ant} methods proposed. They attempt to deduce the anthropogenic fraction from the total C_T pool, basing this partition on CO_2 observations. To do so, the biological activity is first subtracted from the C_T measurements, often inferred through changes in oxygen (O_2) and total alkalinity (A_T), to obtain its preformed condition, that is, the state at the time of last ventilation before biological activity had an impact. Subsequently, from the resulting preformed C_T, a pre-industrial reference value of preformed C_T is subtracted. Over time, back-calculation techniques have evolved, differing in their approaches while undergoing improvements that have resulted in methods for C_{ant} estimation at global (ΔC^* method, Gruber et al., 1996; TrOCA method, Touratier & Goyet, 2004a, 2004b; Touratier et al., 2007) and regional (C_{IPSL}°, Lo Monaco et al., 2005; φCt° method, Pardo et al., 2011; Vázquez-Rodríguez et al., 2009), scales. All of these methods have been extensively applied and validated (e.g., Pardo et al., 2014; Sabine et al., 1999, 2002, 2004; Vázquez-Rodríguez et al., 2012; see Khatiwala et al. (2013) for an extended review). However, some of their common assumptions are, to a certain extent, restrictive and could be addressed more realistically, such as O_2 saturation (ΔC^*, TrOCA, φCt°), the use of linear methods for mixing modeling based on conservative variables (as in ΔC^* or φCt°), the exclusion of denitrification (TrOCA), the computation of pre-industrial tracers through parametrizations (e.g., A_T, sea-air CO_2 disequilibrium, TrOCA), or the use of a fixed oxygen-to-carbon stoichiometric ratio ($r_{o:c}$).

The effect of organic matter (OM) remineralization on carbon is often estimated by a fixed ratio from oxygen consumption. $r_{o:c}$ is actually subject to differ from that expected from the Redfield composition (Redfield et al., 1963) depending on the nature of the OM, that is, in the percentage of proteins, lipids and carbohydrates (Anderson, 1995; Anderson & Sarmiento, 1994; Fraga et al., 1998; Körtzinger et al., 2001). In fact, below depths of 1,000 m, where the flow of particulate material decreases, dissolved organic material (DOM) becomes more prevalent (e.g., Middelburg, 2019), coinciding with the presence of older water masses. DOM has different compositions and lifetimes (Hansell, 2013; Hansell & Carlson, 2014) and its reactivity has been demonstrated to

decrease along the deep branch of conveyor circulation (Sulpis et al., 2023), so the $r_{o:c}$ could change depending on the age of the water masses. Additionally, back-calculation methods assume that during the formation of water masses they are in perfect equilibrium with the atmosphere, thus neglecting the sea-air oxygen disequilibrium that is frequently observed at the time of water mass formation and subduction (Duteil et al., 2013; Ito et al., 2004). This omission can lead to overestimations of oxygen consumption by up to 25% when calculated from Apparent Oxygen Utilization (AOU; Duteil et al., 2013). However, including the sea-air oxygen imbalance can be challenging because of the difficulty in obtaining the preformed oxygen content (Ito et al., 2004).

The behavior of the preformed variables matches that of the conservative tracers, and therefore they are not significantly altered as they circulate in the ocean, allowing for the tracking of the steady-state ocean circulation (Broecker, 1974). For variables that are subject to biological activity, and thus deviate from conservative behavior, back-calculation techniques have adopted different parameterizations as for the conservative tracers, even though they can exhibit non-conservative behavior in some regions (Matsumoto & Gruber, 2005). Additionally, preformed variables have also been estimated from surface parametrizations and later reconstructed in the deep ocean through an Optimum Multiparameter analysis (OMP; Tomczak & Large, 1989). However, the OMP mixing framework may neglect water masses with potential significance in the overall deep-ocean property distribution, which data-assimilated inversion models represent more accurately (Gebbie & Huybers, 2010). With higher resolution, and lower computational demand, such tools provide transport operators of a steady-state ocean circulation that have proven to be versatile for numerous applications, such as the modeling of preformed variables (Carter et al., 2021; Lauvset et al., 2020; Liang et al., 2023).

Here, we present a new approach for estimating the steady-state component of C_{ant} globally (see Text S1 in Supporting Information S1) that relies on a back-calculation formulation and input climatological data that are based on high-quality MCS data. Our approach includes: 1) a novel, $2° \times 2°$ grid resolution, water mass mixing framework (TMI: Total Matrix Intercomparison; Gebbie & Huybers, 2010), which 2) avoids the use of linear regressions to estimate preformed variables, 3) allow us to pioneering account for global oxygen disequilibrium, and 4) to propose a dynamic stoichiometric, carbon to oxygen, ratio depending on the ideal time of the water mass. This synthesis paper is structured as follows. Section 2 provides details of the data used, the back-calculation formulation followed, the procedure for deep-reconstruction of variables, the estimation of their preformed conditions with the TMI, and the uncertainties associated. Section 3 presents the results and their discussion by: 3.1 showing the biogeochemical processes and other back-calculation formulation terms representation, 3.2 the resulting C_{ant} distribution and total inventory, including a validation through comparison with other methodologies, 3.3 sensitivity analysis, and 3.4 C_{ant} distribution at depth to assess and validate C_{ant} results. Section 4 summarizes the main conclusions of the study and provides insights on remaining challenges and future work.

2. Materials and Methods

2.1. Back-Calculation Approach

Proposed by Brewer (1978) and Chen and Millero (1979), back-calculation techniques aim to separate the anthropogenic component from the total inorganic carbon pool by representing C_{ant} as the difference between the preformed total inorganic carbon content ($C_T°$) and the analogous in pre-industrial conditions ($C_T°^\pi$) (Equation 1). Note that preformed conditions (denoted as ° hereafter) are the water parcel properties at the time of last ventilation, deduced by correcting non-physical effects experienced since the parcel left the (sub)surface (Equation 2).

$$C_{ant} = C_T° - C_T°^\pi \qquad (1)$$

$$C_T° = C_T - \text{biogeochemical (bgc) effect} \qquad (2)$$

In a back-calculation approach, the removal of the biogeochemical effect to obtain the preformed total inorganic carbon is based on the representation of the remineralization and the carbonate pump through changes in oxygen (ΔO_2) and total alkalinity (ΔA_T), respectively. Constant stoichiometric ratios are assumed, despite relationships that sometimes deviate from a fixed pattern of behavior (Anderson, 1995; Fraga et al., 1998; Körtzinger et al., 2001). For A_T changes ($\Delta A_T = A_T - A_T°$), no preformed alkalinity change over time is considered, this assumption being reasonably acceptable (Feely et al., 2004; Matsumoto & Gruber, 2005). However, how to

compute its preformed condition is subject to more debate. So far, all back-calculation methods assume that during water masses formation they are in perfect oxygen equilibrium with the atmosphere. Oxygen changes are often derived from Apparent Oxygen Utilization ($\Delta O_2 = AOU = O_{2,sat} - O_{2,measured}$) assuming that AOU is equal to zero at surface, neglecting significant oxygen disequilibrium regions (Duteil et al., 2013; Ito et al., 2004).

The recognized ΔC^* method (Gruber et al., 1996) does contemplate the pre-industrial CO_2 drift compared to saturation at the time of water mass formation and subduction when obtaining the preformed condition of the pre-industrial C_T. This step introduced the pre-industrial sea-air CO_2 disequilibrium term ($\Delta C_{dis}{}^\pi$) in the $C_T{}^{\circ\pi}$ calculation (Equation 3; Equation 4), expressed as the difference between the ocean-atmosphere partial pressure of CO_2, converted to carbon concentrations.

$$C_T{}^{\circ\pi} = C_T{}^{\pi SAT} + \Delta C_{dis}{}^\pi \tag{3}$$

Based on the original back-calculation framework by Brewer (1978) and Chen and Millero (1979) (Equation 1), including the preindustrial sea-air CO_2 disequilibrium term proposed by Gruber et al. (1996) (Equation 3) leads to the expression:

$$C_{ant} = C_T - \text{bgc effect} - C_T{}^{\pi SAT} - \Delta C_{dis}{}^\pi \tag{4a}$$

where C_T is the total inorganic carbon content of a sample; *bgc effect* is the biogeochemical effect; $C_T{}^{\pi SAT}$ is the pre-industrial C_T in saturation; and $\Delta C_{dis}{}^\pi$ is the pre-industrial sea-air CO_2 disequilibrium. Replacing the biogeochemical effect:

$$C_{ant} = C_T - \frac{1}{r_{o:c}} \cdot AOU - \frac{1}{2} \cdot \left[A_T - A_T^{\circ} + AOU \cdot \left(\frac{1}{r_{o:n}} + \frac{1}{r_{o:p}} \right) \right] - C_T{}^{\pi SAT} - \Delta C_{dis}{}^\pi \tag{4b}$$

where A_T is the Total Alkalinity; A_T° is the preformed Total Alkalinity; and $r_{o:c}$, $r_{o:n}$ and $r_{o:p}$ are the oxygen to carbon, oxygen to nitrogen and oxygen to phosphorus stoichiometric ratios. According to Gruber et al. (1996), this leads to:

$$C_{ant} = \Delta C^* - \Delta C_{dis}{}^\pi \tag{4c}$$

where ΔC^* includes the first three terms of (Equation 4a).

As a novelty in this study, we considered a (i) preformed AOU term to capture the oxygen disequilibrium, and a (ii) denitrification correction, as proposed by Gruber and Sarmiento (1997), but following Carter et al. (2021):

$$C_{ant} = \underbrace{C_T - \frac{1}{r_{o:c}} \cdot (AOU - AOU^{\circ}) + r_{c:n} \cdot \Delta N*}_{\text{Remineralization}} \overbrace{- \frac{1}{2} \cdot \left[A_T - A_T^{\circ} + (AOU - AOU^{\circ}) \cdot \left(\frac{1}{r_{o:n}} + \frac{1}{r_{o:p}} \right) \right]}^{\text{Carbonate pump}} - C_T{}^{\pi SAT} - \Delta C_{dis}{}^\pi \tag{5}$$

$$\underbrace{}_{\text{Preformed } C_T}$$

where AOU° is the preformed Apparent Oxygen Utilization (see Section 2.3); $r_{c:n}$ is the carbon to nitrogen denitrification ratio; and $\Delta N*$ is equal to $= (NO_3^- - NO_3^{-\circ}) - 16\ (PO_4^{3-} - PO_4^{3-\circ})$, where $NO_3^{-\circ}$ and $PO_4^{3-\circ}$ are the preformed nitrate and phosphate (see Section 2.3), respectively.

2.2. Data

We used the observation-based gridded products from Broullón et al. (2019, 2020), which provide global 3D monthly climatologies of Total Alkalinity (A_T) and total inorganic carbon (C_T) at $1° \times 1°$ resolution. Both

products are centered in 1995 and encompass 102 surface-to-bottom vertical levels. A_T and C_T are the outputs from neural networks (NN) trained with data from Global Ocean Data Analysis Project version 2.2016 (GLO-DAPv2. 2016; Olsen et al., 2016) and applied to World Ocean Atlas 2013 V2 (WOA13 V2, here on WOA13; Locarnini et al., 2013; Zweng et al., 2013) monthly climatologies of temperature (T), salinity (S) and dissolved oxygen (O_2). Nutrient fields were derived by applying CANYON-B NN (Bittig et al., 2018) to WOA13 T, S and O_2 as input data, getting nitrate (NO_3^-), phosphate (PO_4^{3-}) and silicate (SiO_4^{4-}). In our study, we used these same T, S, O_2 and nutrients fields. Monthly climatological data were averaged to obtain a unique annual climatological value and interpolated to a $2° \times 2°$ and 33 vertical levels resolution grid to match the TMI grid (see Section 2.3), using the Data-Interpolating Variational Analysis (DIVA; Troupin et al., 2012). Potential temperature (θ) and Apparent Oxygen Utilization (AOU) were calculated with the *Gibbs Seawater (GSW) Oceanographic* MATLAB Toolbox, by McDougall and Barker (2011). The pre-industrial C_T in saturation ($C_T^{\pi SAT}$) was calculated with CO2SYS for MATLAB (Lewis & Wallace, 1998; Sharp et al., 2021; van Heuven et al., 2011) with a pre-industrial CO_2 partial pressure (pCO_2^π) set to 280 μatm, an input pressure of 0 dbar, and using θ and preformed A_T, PO_4^{3-}, SiO_4^{4-} (see Section 2.3) along with the K_1 and K_2 from Sulpis et al. (2020), as they cover a wide range of low temperatures, K_{SO4} from Dickson (1990), K_F from Pérez and Fraga (1987) and T_B of Uppström (1974).

Stoichiometric carbon to nitrogen denitrification ratio ($r_{c:n}$) was adopted from Gruber and Sarmiento (1997). Different relationships have been proposed for oxygen to carbon, oxygen to nitrogen and oxygen to phosphorus stoichiometric ratios (Anderson, 1995; Anderson & Sarmiento, 1994; Fraga et al., 1998). We used the ratios proposed by Anderson and Sarmiento (1994) for oxygen to nitrogen and phosphorus. For oxygen to carbon ratio, the ratio proposed by Anderson (1995) is a better fit for older water masses that present more resistant DOM (Hansell, 2013), so we tested both Anderson and Sarmiento's (1994) and Anderson's (1995) and finally used an average of the two weighted by the TMI ideal age, that is, the average time since a water parcel was last in contact with the surface, according to:

$$r_{o:c}^{\ T} = r_{o:c\ (S\&A\ 1994)} \cdot (1 + \alpha_{o:c} \cdot T), \text{where}$$

$$\alpha_{o:c} = (r_{o:c\ (A\ 1995)} - r_{o:c\ (S\&A\ 1994)})/(r_{o:c\ (S\&A\ 1994)} \cdot 1000)$$

where $r_{o:c}^{\ T}$ is an age-based oxygen to carbon stoichiometric ratio; $r_{o:c\ (S\&A\ 1994)}$ is the ratio proposed by Anderson and Sarmiento (1994) of 117/170; $r_{o:c\ (A\ 1995)}$ is the ratio proposed by Anderson (1995) of 106/150; and T is the mean or ideal age in years, at grid level, provided by the TMI (Gebbie & Huybers, 2012). Note that we adopt 1000 years as the maximum average age.

2.3. TMI and Estimate of Preformed Variables

The preformed variables refer to the properties of a water mass parcel that remain unchanged from the time of its last ventilation. In the case of conservative properties, their off-(sub)surface value is equivalent to that of the last ventilation, together with the result of mixing processes acting on the tracer (Broullón et al., 2019; Vázquez-Rodríguez et al., 2012). In contrast, the observed value of non-conservative properties is equal to the sum of its value if it were conservative (mixing) along with the biogeochemical effect.

Rather than relying on preformed (sub)surface-properties parametrization, and their subsequent deep ocean reconstruction through a classical OMP (Gruber et al., 1996; Pardo et al., 2011; Vázquez-Rodríguez et al., 2009), we assumed that winter surface properties represent the preformed conditions. This assumption is based on the fact that subduction primarily occurs during the respective winters of each hemisphere (Qiu & Huang, 1995; Williams et al., 1995), and thus the conditions of these months influence the preformed state of the variables (Iselin, 1939; Stommel, 1979). Therefore, we can reconstruct deep-ocean conditions from winter surface properties by using the geometry of water masses pathways provided by an ocean transport model (Transport Matrix Intercomparison, TMI hereafter; Gebbie & Huybers, 2010; Gebbie et al., 2023). The TMI is a data-assimilation inverse model constrained almost entirely from observations, since it is based on the inversion of modern-day climatologies of temperature, salinity, phosphate, nitrate, oxygen, and oxygen-18/oxygen-16 isotope ratios and provides a steady-state circulation in a 2°-by-2° horizontal resolution with a vertical discretization of 33 levels. A wider description of the TMI and its applications can be found in Gebbie and Huybers (2010, 2011, 2012).
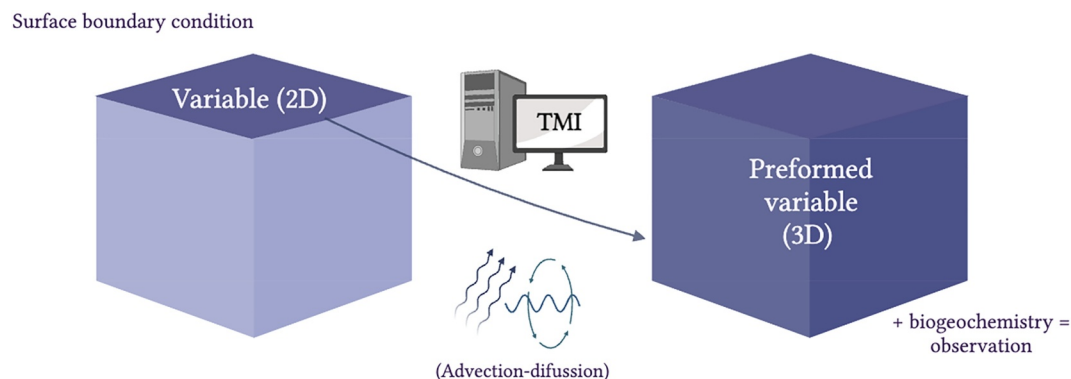
Figure 1. Simplified propagation scheme from a surface 2D variable to its 3D reconstruction at depth through the Total Matrix Intercomparison (TMI): imposing a surface boundary condition that best represents the surface preformed condition, this 2D layer propagates into the ocean interior through a steady-state inversion (no sink-sources considered). The 3D output provides a reconstruction of the ocean interior preformed property that is only affected by mixing, since the model does not account for non-physical effects. Thus, the difference between the observed property and the propagated one can be attributed to biogeochemistry; if it is a conservative tracer the difference must be equal to zero, if there are no residuals in the propagation.

We forced the surface boundary condition of the TMI with two types of data, that is, conservative and non-conservative tracers, and reconstruct their interior ocean distribution: for each ocean grid point the TMI provides the mixing fraction contribution that comes from the surface grid points. The three-dimensional (3D) field obtained only represents physical effects, as we excluded any sink-source processes in the deep ocean reconstruction. This results in preformed values for non-conservative properties or a deep reconstruction for conservative tracers. Then, we assume that differences between the observed properties and the analogous TMI-reconstructed properties (Figure 1), if any, can be attributed to biogeochemical processes.

Surface-boundary TMI input layers were estimated as the average of the monthly climatologies that best represent the water masses formation conditions according to latitude, that is: north of 20°N (south of 20°S) the average of January, February and March winter-months (July, August, September), and between 20°N and 20°S annual-average. The resulting winter-surface nitrate, phosphate and silicate layers were directly propagated, along with winter-AOU and ΔC_{dis}^{π}, obtaining their preformed conditions ($NO_3^{-\circ}$, $PO_4^{3-\circ}$, $SiO_4^{4-\circ}$, AOU°) or deep reconstruction (ΔC_{dis}^{π}). Pre-industrial surface sea-air CO_2 disequilibrium was estimated from Khatiwala et al. (2009) at surface by subtracting the product to the already computed C_T° and $C_T^{\pi SAT}$, and then deep-reconstructing it with the TMI as a conservative tracer. The effect of the surface salinity was removed from the surface total alkalinity by a factor of 66.4 proposed by Carter et al. (2014), and the detached value was propagated into the ocean interior. The resulting field was undone by the same factor obtaining the preformed total alkalinity (A_T°).

2.4. Results Validation

We used results from four independent C_{ant} methodologies (a back-calculation based method, two transient tracer data-based methods and a data-assimilated inversion model) to have a reference for our MCS-TMI estimates. In addition, we applied the TrOCA back-calculation method (Touratier et al., 2007) to evaluate the consistency of spatial patterns in our C_{ant} estimates. It is important to note that the TrOCA method has been shown to over-estimate global C_{ant} inventories by up to 50% (Yool et al., 2010). Therefore, we used TrOCA to validate our spatial distribution of C_{ant} rather than comparing absolute inventory values.

The first product used was Sabine et al. (2004), that provides a C_{ant} climatology centered in 1994, based on the back-calculation ΔC^* method (Gruber et al., 1996), and whose formulation served as a basis for our approach. The ΔC^* method assumes no sea-air oxygen disequilibrium but does include the ΔC_{dis}^{π} with two ways to obtain the term, both assuming bulk advection and a single ventilation age. The second product used came from Lauvset et al. (2016), which follows a transit time distributions (TTD) approach. The methodology considers that the C_{ant} is a conservative tracer that can be reconstructed in the entire ocean through the ocean circulation transport represented by a - *boundary propagator* (Hall et al., 2002)—Green's function. Instead of using MCS data, the

TTD approach relies on transient tracers as CFCs to derive the statistical description of the age distribution. Lauvset et al. (2016) product provides a C_{ant} climatology centered in 2002 that we brought to 1995 for comparison to our results, according to

$$C_{ant\ 1995} = C_{ant\ 2002} \cdot [(1 + 0.0191)^{\,1995-2002}]$$

where $C_{ant\ 1995}$ is the corrected C_{ant} for 1995 year; $C_{ant\ 2002}$ is the original product; and 0.0191 is the annual increase rate determined by Gruber et al. (2019) between 1994 and 2007 for the global ocean.

In line with the TTD approach but refined, we also used the Khatiwala et al. (2009) product, which presents an evolution of the Green's function (GF) method. It considered twenty-six C_{ant} source regions and allowed the ΔC_{dis}^{π} to undergo temporal and spatial changes for the first time. We used a 5-years C_{ant} average, centered at 1995. The product was regridded to the WOA13 $1^{\circ} \times 1^{\circ} \times 33$ levels grid by profile interpolation, and a constant density of 1024.5 kg m^{-3} was used for volumetric to mass conversion.

The last product we included was a data-assimilated inversion model that estimates C_{ant} distribution by considering it as a passive tracer within an abiotic carbon cycle model forced with atmospheric CO_2 (DeVries, 2022), that would represent, in a way, an advance in the resolution of transient tracer data methods, both at the level of mixture scale and source regions.

Once all the products were homogenized (i.e., same resolution gridding and same reference year), the C_{ant} concentrations were vertically integrated to get the column inventories. Additionally, C_{ant} column inventories were horizontally integrated in five oceanic regions (North Atlantic, South Atlantic, North Pacific, South Pacific and Indian oceans), as well as in the sum of these, to quantitatively evaluate the differences of our results with respect to four other reference methodologies, following the regions evaluated in Müller et al. (2023) (Figure S1 in Supporting Information S1). Given the difference in spatial coverage and product grids, total C_{ant} (integrated at vertical and horizontal level, up to depth of 3.5 km) was normalized per product area and scaled to a reference area (see Table S1 in Supporting Information S2) to better compare among products. The TrOCA method was excluded in the total C_{ant} inventories comparison. Note that for ΔC^* total C_{ant} inventories, negative values were set to zero according to literature (Müller et al., 2023; Sabine et al., 2004).

2.5. Sensitivity Analysis and Uncertainties

The MCS-TMI approach to estimate C_{ant} is subject to uncertainties that arise from two main sources: data-related errors and methodological errors. To evaluate the impact of each and quantify the overall uncertainty of our method, we conducted three sensitivity tests (*Case I, II* and *III*, described below) based on a Monte-Carlo analysis, with 300 simulations for each case.

In **Case I** *(data-related errors)* we quantified the uncertainty arising from errors in input data (WOA13 climatologies for T, S, O_2) and their propagation to derived variables (NN-nutrients and A_T and C_T). Since WOA13 climatologies do not provide error fields for the objectively analyzed T, S, O_2 climatologies, we used the standard error of the mean (SE). We used surface SE values (with no spatial correlation for any of the variable pairs), and we computed the SE's standard deviation (STD) for each variable. To ensure a conservative final error estimate, we adopted a two-sigma criterion ($p < 0.05$), resulting in introduced errors of 0.32°C, 0.12 PSU and 4% for T, S and O_2, respectively. We then generated 300 randomly perturbed fields for T, S, and O_2, which served as inputs for the CANYON-B NN to estimate nutrients (resulting in 300 new 3D fields of NO_3^-, PO_4^{3-}, SiO_4^4). Ultimately, this ensemble data set (300 newly generated fields of T, S, O_2, NO_3^-, PO_4^{3-} and SiO_4^{4-}) was used as input to NNGv2 (for A_T) and NNGv2LDEO (for C_T), generating 300 3D fields each of A_T and C_T. This procedure allowed errors in the derived variables (i.e., nutrients, A_T and C_T) to more accurately reflect the data processing flowchart and any potential correlations or interactions among them. To isolate data-related errors, we kept the $r_{o:c}^T$ term and TMI surface boundary conditions constant in *Case I*, by only altering from the second vertical layer to the bottom and, therefore obtaining the same 3D-TMI reconstructed variables (preformed properties and ΔC_{dis}^{π}) for each simulation.

In **Case II** *(methodological errors)* we evaluated the uncertainty that results from variations in the $r_{o:c}^T$ term and the TMI surface boundary conditions. This analysis was divided into two sub-cases: *Case II - subtype 1*, in which we assessed the sensitivity of the method to the $r_{o:c}^T$ term by setting a 10% of error in this parameter while keeping

the rest of variables unaltered; and *Case II - subtype 2*, in which we evaluated the uncertainty directly related to the TMI by introducing random errors only into the surface boundary conditions. For *Case II - subtype 2*, we used the 300 perturbed T, S and O_2 fields as in *Case I*, but only for the surface layer (while keeping the original data from the second vertical and below), and followed the subsequent processing workflow for nutrients and A_T and C_T as indicated for *Case I*. In addition, we considered a 5 µmol kg^{-1} error for the surface $\Delta C_{dis}{}^{\pi}$ TMI input layer (Khatiwala et al., 2009 product).

Finally, **Case III** *(combined uncertainty)* represents the combined effect of both data-related and methodological errors (i.e., *Case I* and *Case II*), thereby serving as the reference case for estimating the total uncertainty in the MCS-TMI method. The total method uncertainty (µmol kg^{-1}) was calculated as the mean of the STD 3D-matrix that resulted from the 300 Monte Carlo simulations in *Case III*. Additionally, the uncertainty of the total C_{ant} inventory (Pg C) was computed as the STD of the 300 total C_{ant} global inventories from *Case III*.

3. Results and Discussion

### 3.1. Biochemical Processes Representation

The $C_T{}^{\circ}$ in 1995 (Figure 2, panel H) results from the subtraction of the biological effect (Figure 2, panel B and C) to the C_T. Biogeochemical processes representation is one of the most important steps in a back-calculation approach. We represented them through changes in C_T due to the organic matter (OM) remineralization and the carbonate pump. Both the OM remineralization (Figure 2, panel B), and the excess of alkalinity due to $CaCO_3$ dissolution (i.e., carbonate pump; Figure 2, panel C), presented a similar distribution, increasing their values from the North Atlantic as moving toward the North Pacific, after passing through the SO. Biogeochemical processes low-values in the North Atlantic coincide with the newly formed, and recently ventilated, North Atlantic Deep Water (NADW) water mass. The NADW is the most abundant water mass in the deep Atlantic (Liu & Tanhua, 2021), and spreads southward mixing with the older Antarctic Bottom Water (AABW), that moves northwards in depth, along with the ventilated Antarctic Intermediate Water (AAIW), positioned above the NADW. Likewise, the AABW spreads toward the North Pacific and the Indian Ocean at depth, representing the dominant water mass at depth, with the AAIW also spreading northwards above the AABW. Consequently, both biogeochemical processes reach their maximum accumulation in the North Pacific, coinciding with the oldest water masses ages (Figure S2 in Supporting Information S1), and consistent with the well-described ocean circulation (Broecker & Peng, 1982; Talley, 2013). This evidences that, in terms of circulation patterns given by the TMI, biological processes are overall well reproduced in our approach, since they present an overall aging trend characterized by the extended time that water masses spend without contact with the atmosphere (Craig, 1971; Figure S2 in Supporting Information S1). Additionally, that the $C_T{}^{\circ}$ has a consistent pattern when compared to its analog under pre-industrial conditions ($C_T{}^{\circ\pi}$; Figure 2, panel I) also suggests a good integration and representation of the biological activity.

3.1.1. Organic Matter Remineralization and O$_2$ Disequilibrium

The OM respiration (Figure 2, panel E), represented as the difference between the AOU and its preformed condition, controls most of the OM remineralization pattern and contributes up to 98.8% of its variability. Opposite, the denitrification pattern (Figure 2, panel K) has a low impact on OM remineralization when compared to respiration. The denitrification process contributes, in average, to the OM remineralization around 0.8 µmol kg^{-1}, which is ~80 times lower than the average contribution of respiration (64 µmol kg^{-1}).

In general, respiration process is correlated with the water mass age. The more the time since the water mass left contact with the atmosphere the more biological aging (Craig, 1971; Figure S2 in Supporting Information S1), as the oxygen consumption due to respiration and then C_T release. This inverse pattern between the C_T and the respiration and their correlation with the water masses age is reflected in the age-based oxygen to carbon stoichiometric ratio proposed (Figure 2, panel D), that represents a function of the water masses ideal age according to respiration. Using the fixed $r_{o:c}$ ratios from Anderson and Sarmiento (1994) and Anderson (1995) results in an average difference of ~5 µmol kg^{-1} of C_{ant} among them from ideal ages over 500 years (Figure S3 in Supporting Information S1), but particularly both generated an upward trend in the mean C_{ant} values as the water masses ideal age increases that the $r_{o:c}{}^{T}$ proposed attenuates (Figure S3 in Supporting Information S1). Even so, in terms of OM respiration, shallow—recently formed—layers (up to ~500 m) also present high oxygen utilization coinciding with high biological activity, wherein AOU may not be that elevated but increases rapidly. In particular, the
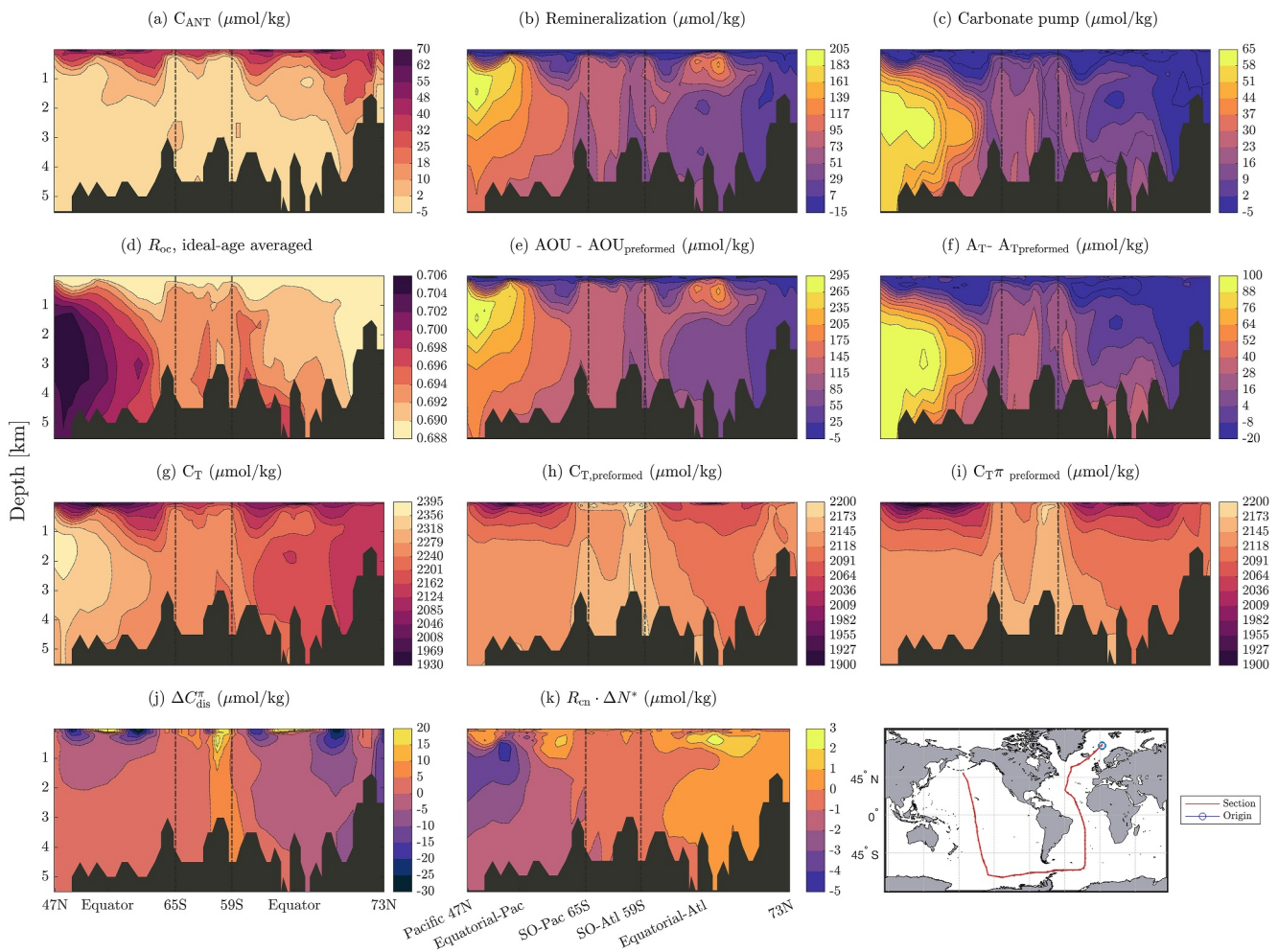
Figure 2. Transoceanic section, showing vertical C_{ant} distribution and biogeochemical and physicochemical processes (centered in 1995), from 73°N Atlantic up to 47°N Pacific, connecting the start-end section through the Southern Ocean (SO). The two vertical lines define the end of the Atlantic basin through the SO (SO-Atl 59°S), and the beginning of the Pacific basin (SO-Pac 65°S). Panels: (a) Anthropogenic carbon (C_{ant}), (b) remineralization term (see Section 2.1), (c) carbonate pump term (see Section 2.1), converted to carbon concentrations, (d) age-based oxygen to carbon stoichiometric ratio, (e) difference between AOU and preformed AOU, (f) difference between Total Alkalinity and preformed Total Alkalinity, (g) total inorganic carbon from Broullón et al. (2020), (h) preformed total inorganic carbon, from subtracting biological panels B and C to panel G, (i) pre-industrial preformed total inorganic carbon, (j) sea-air CO_2 disequilibrium and, (k) denitrification process, expressed in carbon concentrations.

Atlantic Ocean presents a shallow low-oxygen pool that coincides with the well-known Atlantic oxygen minimum zone, possibly generated because of a mixing limitation due to vertical and horizontal constraints, as boundaries formed by interactions with subtropical gyres, or warm temperatures (Carter et al., 2021).

As an improvement in a back-calculation approach, we considered a global sea-air O_2 disequilibrium independent of the sea-air CO_2 disequilibrium. Our approach uses the AOU, that reflects oxygen depletion relative to saturation, and the subtraction of its preformed condition (AOU°) corrects for the oxygen disequilibrium (Figure S4 in Supporting Information S1) that is often observed in deep water formation regions (Ito et al., 2004). Therefore, we inferred respiration from True Oxygen Utilization (TOU) instead of AOU (e.g., Ito et al., 2004; Koeve & Kähler, 2016). Until now, the only gaseous disequilibrium considered was the pre-industrial CO_2 disequilibrium (Gruber et al., 2019; Sabine et al., 2004), which, when considered on its own, could erroneously include the O_2 imbalance on it (Equation S1 in Supporting Information S1), and may underestimate the relevance of disequilibrium in carbon storage (Khatiwala et al., 2019). The correction increased the total C_{ant} inventory by 7.2 Pg C, indicating that not accounting for the O_2 disequilibrium underestimates the total global C_{ant} inventory by 6%. When examining the respiration process, a bigger impact is observed, as it corrects the overestimation of oxygen consumption by up to 8.5%, when integrated globally. Thus, our results confirm the evidence that AOU-based

estimations overestimate respiration (Carter et al., 2021; Duteil et al., 2013), in particular in the South Atlantic and deep horizons, which agrees with Carter et al. (2021) that found the deep ocean and the Southern Ocean are the most impacted regions.

Furthermore, including the sea-air O_2 imbalance (i.e., using AOU-AOUº, or TOU, instead of AOU) in oxygen consumption reduces the unexplained variability of nitrate and phosphate depletion by 17% and 28% (Figure S5 in Supporting Information S1). Indeed, $r_{o:n}$ stoichiometric ratio (inferred from the inverse of the linear regressions slope), resulting from the adjustment after including sea-air O_2 imbalance in the AOU term (TOU), gets more centered between those of Anderson and Sarmiento (1994) for NO_3^- and Anderson (1995) than the ones from assuming that O_2 is fully equilibrated in winter surface layer. Our results agree with a strong correlation between nutrients and oxygen consumption, presenting a similar correlation pattern with the ideal water masses age (Figure S2 and S5 in Supporting Information S1). This is also consistent with the most ΔN^* negative values, that is, higher denitrification, found in the Pacific Ocean (Figure 2) and Indian Ocean (Figure S6 in Supporting Information S1), as nitrate consumption increases when oxygen becomes limiting (Middelburg, 2019). However, the overall denitrification pattern does not exhibit a strong relationship with the ideal water masses age ($R^2 = 0.41$), or with TOU ($R^2 = 0.55$). The lack of correlation could be attributed to the presence of N_2 fixation zones or high TOU values in ventilated waters with high biological activity.

3.1.2. The Carbonate Pump

The carbonate pump (Figure 2, panel C) represents changes in A_T due to formation and dissolution of calcium carbonate ($CaCO_3$), along with the A_T reduced by respiration-derived acids. The term is mostly mediated by the pattern of the difference between the A_T and its preformed condition (Figure 2, panel F). However, the impact of the acid-derived biological effect (OM respiration) also affects, coinciding with previous studies that note its contribution throughout the water column (Liang et al., 2023). This is especially evident in the North Pacific, where respiration contributes to locate the accumulation carbonate pump maximum shallower than that of the total and preformed alkalinity difference by itself. This suggests that, when inferring the excess of alkalinity due to $CaCO_3$ dissolution, respiration representation is relevant, especially in old water masses. In turn, the deeper location of the carbonate pump maximum versus the remineralization maximum would be consistent since organic matter remineralization is potentially a faster, and shallower, occurring process (Carter et al., 2014, 2021; Francois et al., 2002; Klaas & Archer, 2002).

On the other hand, the carbonate pump presents a strong correlation with ideal water masses age (Figure S2 in Supporting Information S1), as well as the one that silicate opal dissolution (silicate increase) shows (Figure S5 in Supporting Information S1). In addition, there is a relationship between the carbonate pump and silicate consumption of 0.98 (Figure S5 in Supporting Information S1) close to the relationship of 0.96 shown by Rubin and Key (2002), which enforces the consistency of the TMI model when obtaining preformed nutrients.

3.2. Validation of the C_{ant} Distribution at Global and Regional Scale

The C_{ant} invasion in depth since the pre-industrial era is shown at Figure 2 at panel A, and shows an overall decrease in the C_{ant} signal as depth increases. The largest C_{ant} concentrations are found at the surface, where shallow and warm ocean layers are located, consistent with the fact that warmer waters present lower Revelle factor values (Broecker et al., 1979; Hauck & Völker, 2015; Zeebe & Wolf-Gladrow, 2001), meaning that are more efficient in the anthropogenic CO_2 uptake (Hauck & Völker, 2015; Sabine et al., 2004; Völker et al., 2002) than colder waters (Figure S7 in Supporting Information S1). In particular, the highest C_{ant} concentrations are observed within subtropical regions, coinciding with Central Waters formation (Cianca et al., 2007; Talley, 2013; Álvarez et al., 2004). In these warm regions, the C_{ant} signal penetrates in depth consistent with the described circulation of subtropical gyres (Reid, 1997), in contrast to equatorial upwelling regions where C_{ant} vertical signal raises (Figure 2, panel A). Additionally, ocean circulation plays a key role in transporting C_{ant}-rich waters from other regions to the subtropical gyres (DeVries et al., 2023), thereby enhancing the accumulation of C_{ant} in these areas.

The depth-integrated spatial distribution of C_{ant} (Figure 3, panel A) reveals the North Atlantic basin as the greatest C_{ant} reservoir, with the Labrador Sea exhibiting the highest concentrations within the region. Thus, the deepest and strongest C_{ant} vertical invasion is found in the North Atlantic (NA) basin (Figure 2, panel A), which coincides with previous studies (e.g., Gruber et al., 1996; Kötzinger et al., 1999; Wanninkhof et al., 1999), even extending
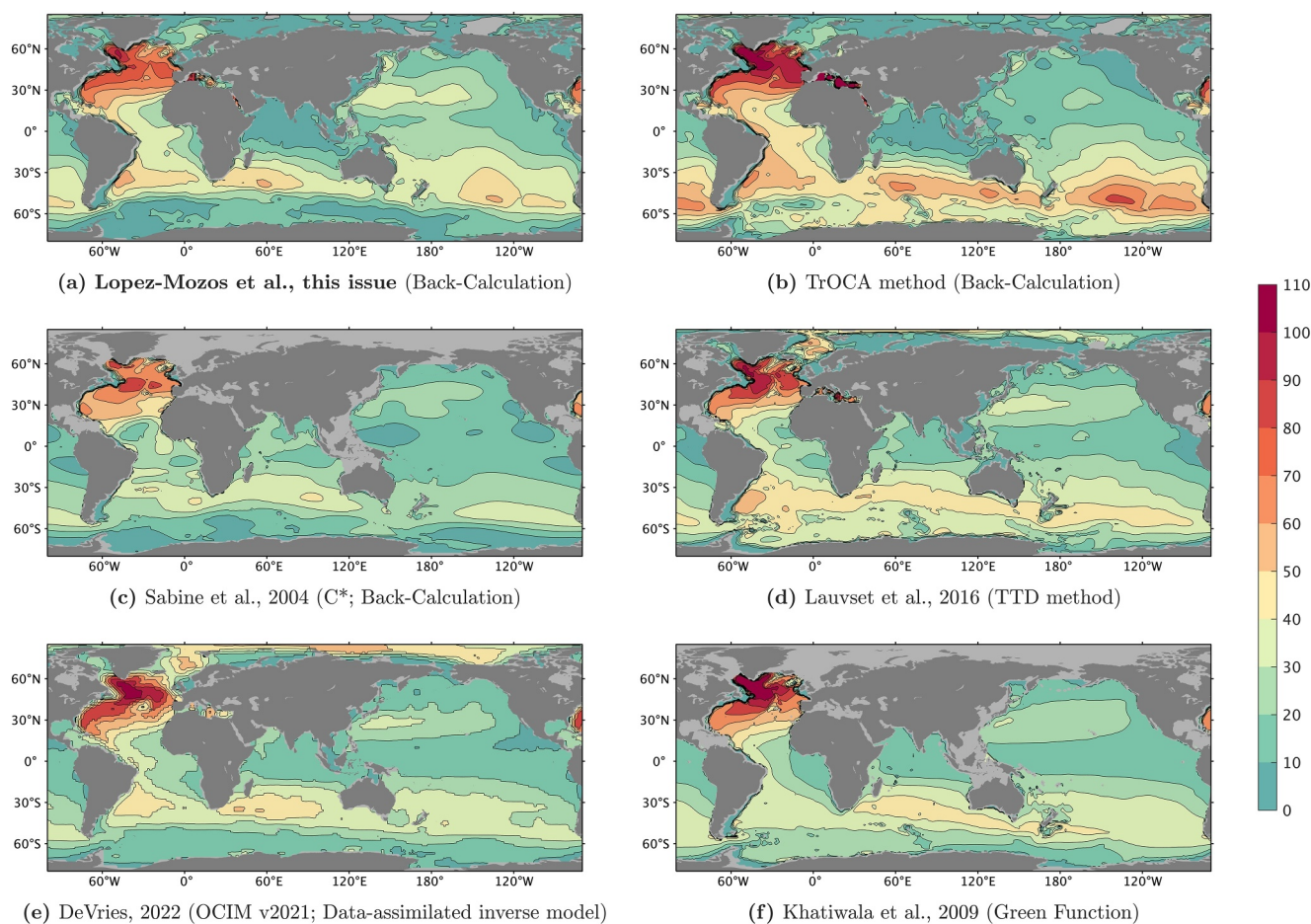
Figure 3. C_{ant} column inventories (molC m^{-2}), centered in 1995, integrated from surface up to 3,500 m from six independent C_{ant} methodologies. Gray Arctic marine zones in panels (a) and (b) are negative out-of-scale values. For Sabine et al. (2004) product negative C_{ant} values have been maintained.

the C_{ant} signal below 3,000 m. Moreover, such invasion is consistent with the own basin circulation, where strong C_{ant} invasion is linked to the strong deep-ventilation (Fröb et al., 2018; Pérez et al., 2010). The C_{ant} pattern in the region shows a very similar distribution when compared to other methodologies (Figure 3), validating these results. Furthermore, when comparing total inventories quantitatively (Figure 4; see Section 2.4), our results (26.4 Pg C) are also consistent since they are inside the interquartile range for the NA, and in good agreement with the other four methods. In addition, the NA stands out as the largest C_{ant} reservoir per area globally (Table S1 in Supporting Information S2). However, our Nordic Seas C_{ant} column-inventory seems to be underestimated when compared to the TTD (Lauvset et al., 2016) and OCIMv21 (DeVries, 2022) approaches (Figure 3), which could also be supported by the fact that the region has been shown to be a present absorption area (Jeansson et al., 2023). This underestimation does not affect the NA total C_{ant} inventory, as the Nordic Seas is not included in the calculation of the NA total C_{ant} inventory. Not all products provide data for the Nordic Seas and Arctic region. Even so, a noticeable distinction is observed between our results and the TrOCA method (employed solely as an evaluative exercise of MCS data consistency) when compared to the GF and OCIMv2021. Both back-calculation approaches exhibit an almost identical lower pattern, suggesting a potential issue in the MCS data for the area. The fact that with the TrOCA exercise we utilize the same data aids in identifying possible flaws, indicating that divergences reflect genuine differences in approaches rather than arising from the use of different data sets. Conversely, convergences suggest consistency between the approaches.

There is a gradual decline in C_{ant} storage as we move southward into the South Atlantic (SA), culminating in a more significant accumulation within the SA subtropical gyre. Additionally, a zonal gradient is observed with elevated C_{ant} values along the western margin of the Atlantic. The described pattern coincides with the rest of methodologies (Figure 3), with which we also agree on the presence of a C_{ant} accumulation belt that connects the
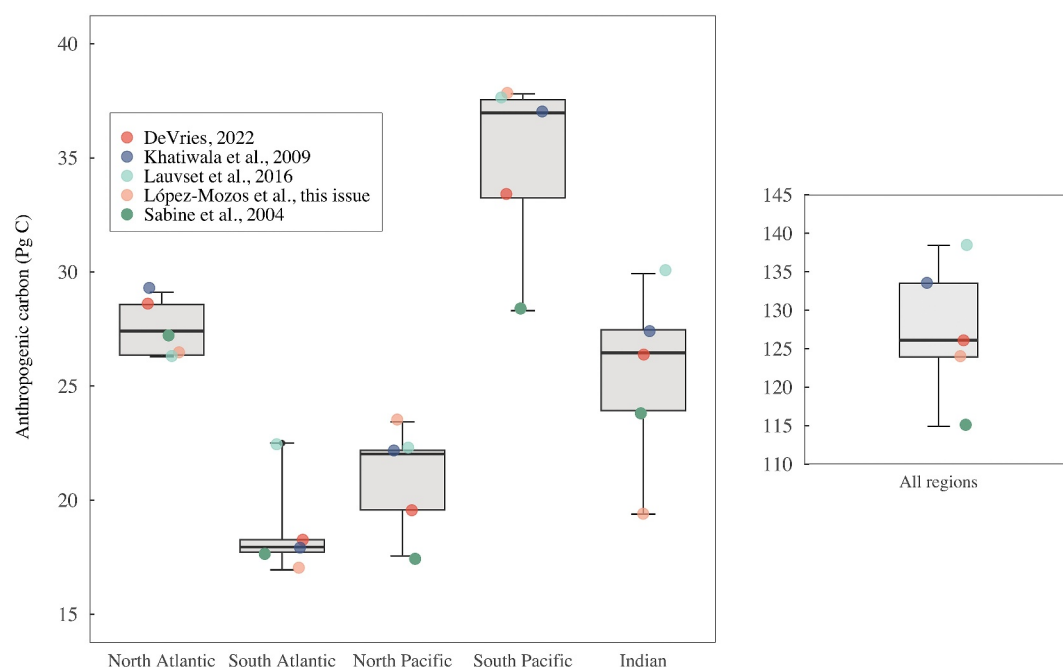
Figure 4. Boxplots of C_{ant} total inventories (Pg C), resulted from integration of C_{ant} column inventories over each ocean basin, normalized by each basin's product area and multiplied by a reference area (see Table S1 in Supporting Information S2). Individual data points represent results obtained from five independent methodologies of C_{ant}, as specified in the figure legend: DeVries (2022; OCIMv2021, data-assimilation model), Khatiwala et al. (2009; Green function), Lauvset et al. (2016; TTD method), López-Mozos et al. (this issue; Back-Calculation) and Sabine et al. (2004; Back-Calculation). Each box plot corresponds to a specific ocean basin, with the last one (*All regions*) representing the sum of the first five. Negative values were removed for Sabine et al. (2004).

subtropical gyres of the Southern hemisphere. However, with respect to the other methodologies, and even among them, there are differences in the magnitude and location of that accumulation (Figure 3). In particular, our results agree with the TTD method and the OCIMv2021 model in the Argentine Basin, with a decreasing C_{ant} content toward the east. Interestingly, when looking to the total C_{ant} inventories, our results in the SA (16.9 Pg C) are slightly lower than other methodologies (Figure 4; Table S1 in Supporting Information S2), and are closer to Khatiwala et al. (2009) method (GF method hereafter) and the ΔC^* method (Sabine et al., 2004). This suggests that, although our C_{ant} spatial pattern is consistent with other methodologies (Figure 3), our SA total C_{ant} inventory may be slightly underestimated (Figure 4). This potential underestimation is reasonable given that the SA region shows low dispersion among methods, and our results are quite close to the mean (Table S1 in Supporting Information S2). The lower value could be attributed to our relatively low C_{ant} values south of 60ºS (Figure 3) which are included in the total SA inventory computation. South of 60ºS, our C_{ant} depth-integrated values exhibit a significant reduction, making the Antarctic region one of the areas with our lowest C_{ant} column inventories (Figure 3). In the Antarctic region, our approach yields slightly higher values compared to the ΔC^* method, with both methods reporting the lowest values. Further discussion will be addressed at Section 3.4.

In the Pacific basin, a contrast in C_{ant} column inventories becomes noticeable when comparing the southern and northern regions. The South Pacific (SP) region presents higher C_{ant} concentrations in comparison to its northern counterpart (Figure 3, panel A). Moreover, the SP has a higher total C_{ant} inventory (37.8 Pg C vs. 23.4 Pg C in the North Pacific), even when taking into account their respective areas (Table S1 in Supporting Information S2). This north-south difference is consistent with the rest of methodologies (Figure 3). Notably, this spatial distribution is characterized by a zonal gradient wherein C_{ant} concentrations gradually diminish from east to west in the southern region. In contrast, the northern region exhibits higher C_{ant} values closer to its western margin and the Sea of Okhotsk. The North Pacific (NP) C_{ant} column inventory (Figure 3, panel A) presents a similar pattern to the TTD method and OCIMv2021 model ones (Figure 3), but with a higher inventory (Figure 4). Interestingly, TrOCA method has been shown to overestimate C_{ant} globally and regionally (Table S1 in Supporting Information S2), but for the NP there is almost no detectable C_{ant} signal. The difference between our results and that of

TrOCA, despite using a common MCS data, reveals a feasible methodological divergence. We showed that the denitrification process has a low impact on the remineralization term compared to respiration (see Section 3.1.1). However, when integrated over depth can have a bigger impact on remineralization, especially in regions with high denitrification as the NP (Figure 2, panel K), supporting the relevance of accounting for denitrification in back-calculation approaches (e.g., Gruber & Sarmiento, 1997).

In the SP, we agree with the rest of methodologies by presenting a more horizontal-extensive C_{ant} column inventory (Figure 3). We present a maximum of C_{ant} in the subtropical region, coinciding with that of the TTD method, in a cyclonic structure, as already evidenced (e.g., Sabine et al., 2002). This maximum is more intense than that of the other methodologies, showing a wider structure than, for example, the TTD method, which is narrower. The similarity between our wider structure and the one presented by TrOCA and even the ΔC*, which presents a less intense accumulation, could be attributed to the MCS data of the region. On the other hand, the Indian Ocean has the same cyclonic structure of C_{ant} over the 30ºS, which also appears in the methods that do not use MCS data, pointing such accumulation as quite realistic. In the Southern Indian, there is a similar pattern between our approach and OCIMv2021 model, and we also present similarities with the TTD and GF methods. In contrast, for the northern Indian, all methodologies present low values with a two-by-two agreement between OCIMv2021 and the GF method, the ΔC* and TTD methods, and TrOCA and our results. In the Indian Ocean, we show the regional total C_{ant} inventory farthest from the average of the methodologies used, almost 5 Pg C below it.

The total ocean C_{ant} inventory given by our approach is 124 ± 7 Pg C, close to the median value among the other methods (Figure 4 and Table S1 in Supporting Information S2). Despite this, we present disparities at regional level compensated on a global scale (Figure 4 and Table S1 in Supporting Information S2). As already mentioned, our approach provides consistent values for the Atlantic Ocean (Figure 4), both at Northern and Southern basins, with slightly below-mean values for both regions. In contrast, in the Pacific Ocean we present slightly higher values when compared to the rest of methodologies, with the highest data dispersion among methods found in the South Pacific. Finally, in the Indian Ocean we provide the lowest values when compared to the rest. The next sections (Sections 3.3 and 3.4) will combine the outcomes of the sensitivity analysis and the deep-C_{ant} column inventories. The results integration will contribute to discern if the differences can be attributed to the MCS data used and/or the proposed approach.

3.3. Sensitivity Analysis

Three sensitivity cases were considered (Section 2.5) to discern between the uncertainty generated by data-related errors (*Case I*) and methodological errors (*Case II*), as well as to quantify the final uncertainty of our method and the global C_{ant} inventory uncertainty (*Case III*). Data-related errors (Figure S8 in Supporting Information S1) contribute to the total method uncertainty by ± 4.5 µmol kg^{-1}, which, when integrated over depth, actually generates a low uncertainty in the total inventory of C_{ant} (STD = 0.3 Pg C; $N = 300$). This is consistent with the fact that random errors in measurements do not have a strong influence on total inventories, as long as they are not spatially biased (Müller et al., 2023) and compensate each other. In contrast, methodological errors (Figure S9 in Supporting Information S1) have a smaller impact on the total method uncertainty, of about ±0.1 and 2.2 µmol kg^{-1} for *subtype 1* and *subtype 2* respectively but, when integrated over depth, their contribution to the total inventory of C_{ant} uncertainty is larger than that of data-related errors (STD = 2.0 Pg C for *subtype 1*; STD = 6.7 Pg C for *subtype 2*; both $N = 300$). The combination of the last two cases, that is, *Case III* (Figure S10 in Supporting Information S1), results in a total method uncertainty of ±5.6 µmol kg^{-1}, which is mainly governed by data-related errors along the water column (*Case I*); and a total C_{ant} inventory uncertainty of ±7.1 Pg C, primarily governed by methodological errors (*Case II*)—more specifically, by the effect of errors on the TMI surface boundary conditions.

3.4. C_{ant} Distribution at Depth

The total ocean C_{ant} inventory at depth (from 3,500 to 5,500 m) estimated by our approach is 4.4 ± 3.4 Pg C. This amount, when multiplied by the mean annual C_{ant} growth rate from Gruber et al. (2019) of 1.9%, yields to an annual rate of 0.08 PgC yr^{-1}. Over the 13 years of Gruber et al. (2019) study, this rate accounts for 1.2 Pg C at depth, which is consistent with Gruber et al. (2019) estimate of 1 Pg C at depth. The averaged C_{ant} below 3,500 m (Figure 5) also assesses and validates C_{ant} estimations by discerning whether the C_{ant} presence could be attributed to methodological uncertainty or a feasible presence of C_{ant} (Figure S11 in Supporting Information S1). Globally,
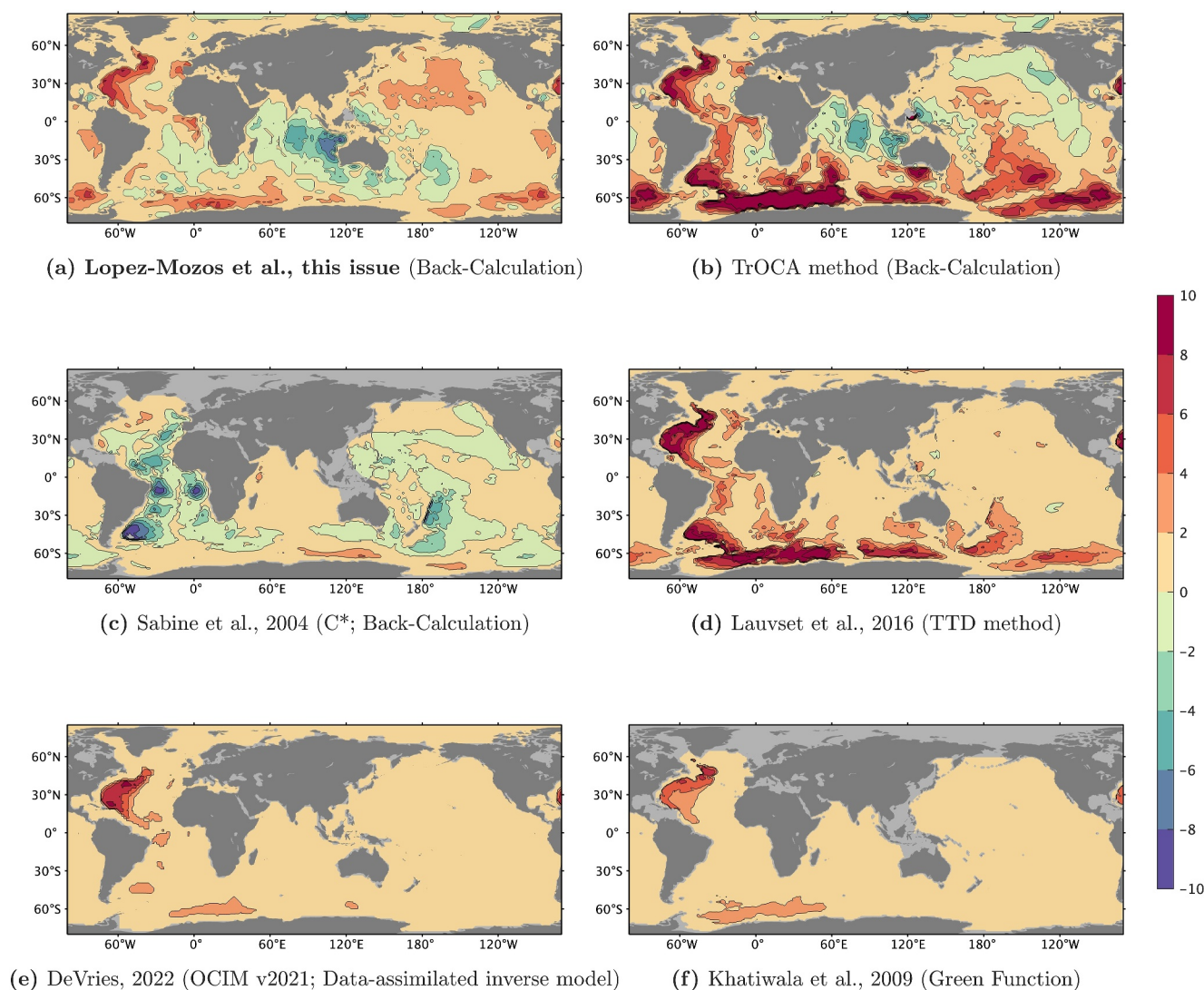
Figure 5. Averaged C_{ant} column concentration (μmolC kg^{-1}) integrated below 3 500 m up to 5,500 m (5,580 m for OCIM v2021), centered in 1995, from six independent C_{ant} methodologies. For Sabine et al. (2004) negative C_{ant} values have been maintained.

the spatial pattern of our deep-C_{ant} results falls between the TTD method versus OCIMv2021 model GF method. In contrast, we mainly differ at depth with the ΔC^*, with which, although we also show negative values in the global integral, the biases are not as negative and neither coincide spatially.

The elevated C_{ant} presence in the deep western NA coincides with the results of other methodologies and is also consistent with previous evidences of deep-C_{ant} invasion in the NA (Gruber et al., 2019; Pérez et al., 2008; Raimondi et al., 2021; Rhein et al., 2017; Vázquez-Rodríguez et al., 2009). This suggests that a deep-C_{ant} signal in the western NA is realistic, supported by the sensitivity analysis results (Figure S11 in Supporting Information S1). Moreover, we observe local C_{ant} signals along the Atlantic, such as in the deep Eastern NA basin or the Argentine Basin, which coincide with the TTD method and OCIMv2021, and are also consistent with previous studies (Ríos et al., 2010, 2012). The deep-C_{ant} pattern in the SO, which matches the TTD method, suggests a realistic accumulation, as supported by the GF method and OCIMv2021 model which also show such invasion, especially between 10ºW–60ºE longitudes that comprises the Lazarev to Cooperation seas (Figure S11 in Supporting Information S1). This agrees with recent C_{ant} findings in the dominant water mass at depth (i.e., the AABW) in the SO for one decade later (Ohashi et al., 2023). In addition, it seems reasonable that our approach shows less accumulation of C_{ant} in the SO than the TTD method because of its full CFCs equilibrium assumption (Matear et al., 2003; Waugh et al., 2006). The SO is a region where the uncertainties of climate change are high

(Hauck et al., 2023), but there is increasing evidence, such as deep-warming (Kouketsu et al., 2011), suggesting that there could be more anthropogenic signal than expected from an ice-sheet isolated ocean. Additionally, in the Pacific-SO region we also present a deep-C_{ant} signal, coinciding with both the TTD method and TrOCA patterns.

Similar to the C_{ant} integration above 3,500 m, the Indian and North Pacific regions exhibit distinct deep C_{ant}-accumulation patterns compared to the rest (Figure 5). In both regions, our method cannot demonstrate that C_{ant} presence is distinguishable from zero (Figure S11 in Supporting Information S1), indicating that the C_{ant} presence is not statistically significant. The North Pacific shows a slight mean positive C_{ant} concentration (1.7 µmol kg^{-1} ± 1.0; Figure 5) when compared to the methodologies that are not based on MCS data. In contrast, we observe a negative pattern in the Indian Ocean which aligns with the negative TrOCA pattern, a method used as an input-data consistency exercise. The match in negative bias suggests there may be an issue with the MCS data used. Furthermore, sensitivity test *Case II* revealed that the Indian Ocean has greater uncertainty at depth than other regions when altering imposed TMI surface boundary conditions. Additionally, bottom points around Australia and from Mawson to Ross Sea are subject to increased uncertainty (Gebbie & Huybers, 2010). Therefore, our biased results in the Indian Ocean could result from a combination of input-data quality and the methodological approach.

Interestingly, a recent study (Müller et al., 2023) showed that some cruises used for the GLODAPv2 database in the Indian Ocean provided their CO_2 data slightly biased during the period used in this study, generating underestimations of C_{ant} in the Indian Ocean. This means that such bias could also affect the neural network (NN)-derived C_T and A_T climatological data we used here, which, once integrated over depth, could generate an impact because of the large volume of deep layers (Müller et al., 2023). Particularly, the study proposed corrections for the next update GLODAPv3 for the Indian Ocean that would explain - as they fit with - our negative-biased C_{ant} results in the region. Since our MCS data comes from a NN-derived climatology, we consider that such correction must be included in a new NN-MCS derived climatology with the next GLODAPv3 data, supporting the need for the program's continuity and its data quality control.

4. Summary and Conclusions

We presented a back-calculation method to estimate the steady-state component of oceanic anthropogenic CO_2 (C_{ant}), that relies on marine carbonate-system (MCS) data-based climatologies and the steady-state ocean circulation model TMI (Gebbie & Huybers, 2010). This novel approach provides a coherent total C_{ant} inventory that compares well with other (four) independent methodologies, proving it to be a valid tool for back-calculation approaches, and supporting the versatility of data-assimilated inverse models for biogeochemistry studies (as in e.g., Carter et al., 2021; Davila et al., 2022; Lauvset et al., 2020; Liang et al., 2023; Sulpis et al., 2023).

As a novelty to former back-calculation methods, our method refined the oxygen saturation assumption by accounting for the sea-air oxygen disequilibrium, which enhances the global C_{ant} inventory estimate by 6%. However, and as inherent to all back-calculation approaches, the method is not exempt from limitations. The sensitivity analysis performed led us to conclude that the deep (below 3,500 m) inventories in the Indian and Pacific Oceans were the least confident estimates at the regional scale. Tracking-back potential sources of error, we related such regional discrepancies to limitations inherent to the input data and the TMI performance. Small surface areas in the TMI surface boundary conditions can have a large impact on the deep-ocean (Gebbie & Huybers, 2011). As such, if the quality of the data in these boundary-condition regions is compromised due to, for example, scarce sampling coverage, then the propagation of its less accurately determined surface properties to depth might influence the deep regional C_{ant} inventories. Besides, since most of the total C_{ant} inventory uncertainty also comes from the errors at the surface TMI boundary conditions, it would also influence the magnitude of the final uncertainty. In this study, the MCS data climatology used was centered in 1995, and based on in-situ data spanning 1972–2012. Thus, our result is subject to the propagation of surface boundary conditions in certain under sampled regions, as in the Southern Ocean, which might have impacted the regional deep C_{ant} inventory estimates of the Indian and Pacific Oceans. The advancement in new climatologies based on the most recent observations (e.g., WOA23, Keppler et al., 2023; Kolodziejczyk et al., 2024) will open up the possibility of extending MCS based-C_{ant} inventories beyond the 2000s, and thus likely reducing the input-data limitation of the present method.

Another important point to consider is the surface boundary condition for the $\Delta C_{dis}{}^{\pi}$ term. Getting this term is not trivial, and future work should be addressed to explore alternative ways to compute it, for instance, by means of

numerical simulations (Matsumoto & Gruber, 2005) and/or a compendium of the most recent Coupled Model Intercomparison Project (CMIP6) models. Finally, recent advances are also opening the door to include the seasonal variability of the ocean circulation transport operators in inverse modeling (Huang et al., 2021), so the approach presented here could be applied to other mixing schemes.

Assessing the distribution and storage of C_{ant} in the ocean is crucial in the context of climate change (Intergovernmental Panel on Climate Change IPCC, 2019). Nevertheless, it implies distinguishing a signal of less than 4% from the dissolved inorganic carbon ocean reservoir, for which no single optimal method exists. Hence, we need to continue advancing with a broad range of approaches. In situ MCS data are the most accurate ocean carbon data sets to date. Sustained international research programs like GO-SHIP, along with the Global Ocean Data Analysis Project (GLODAP) quality control efforts, are essential for providing the research community with full-depth global ocean highly accurate MCS data, which serve as a key reference data set for, for example, model validation, artificial intelligence (AI) learning and verification, or novel autonomous sensor calibration. This study emphasizes the value of MCS data-based approaches to compute C_{ant} inventories by providing a useful proof-of-concept method that will serve as a base for further progress.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The Total Matrix Intercomparison software (TMI) can be accessed at Gebbie et al. (2023). The climatologies of A_T, C_T, oxygen and nutrients are available at the data repository of the Spanish National Research Council (CSIC; https://digital.csic.es/handle/10261/194411 Broullón et al., 2019; http://hdl.handle.net/10261/200537; Broullón et al., 2020). Khatiwala et al. (2009)'s product used can be accessed at Müller (2023).

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