Assessing the Conserved Behavior of Dissolved Organic Carbon in the Deep Ocean

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ASSESSING THE CONSERVED BEHAVIOR OF DISSOLVED ORGANIC CARBON IN THE DEEP OCEAN

By
Sarah Kathryn Jirikowic Bercovici

A DISSERTATION

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ORGANIC CARBON IN THE DEEP OCEAN

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The global ocean contains a massive reservoir (662±32 Pg C) of dissolved organic carbon (DOC), and its dynamics, particularly in the deepest zones, are only slowly being understood. DOC in the deep ocean is ubiquitously low in concentration (~35 to 48 µmol kg\(^{-1}\)) and aged (4000 to 6000 years), persisting for multiple meridional overturning circulation cycles. Deep waters relatively enriched in DOC form in the North Atlantic. They migrate to the Southern Ocean (SO) to mix with waters from Antarctic shelves and the deep Pacific and Indian Oceans, in turn forming the voluminous circumpolar waters. The latter ultimately feed back into the Atlantic, Pacific, and Indian basins as bottom and intermediate waters. The goal of this dissertation is to assess evidence for local versus remote processes in influencing the distribution of DOC in the deep ocean. We use both large-scale datasets and isotopic and molecular composition data to understand the dynamics of the DOC pool on a global scale, though with an emphasis on the southern hemisphere. Chapter 2 focuses on DOC in Antarctic shelf systems and Antarctic Bottom Water (AABW) formation; Chapter 3 looks at the mostly conservative behavior of DOC in the deep SO; Chapter 4 considers the radiocarbon content of DOC in the South Indian Ocean (SIO) to assess the age of DOC; and Chapter 5 looks at the radiocarbon and molecular composition of DOC in the far North Pacific. In Chapter 6, findings are summarized.
One potential local source of DOC to the deep SO is export from Antarctic shelf systems. Antarctica’s continental shelves generate the densest waters in the world ocean and are responsible for the formation of AABW. AABW has the potential to sequester carbon in the deep ocean for millennia. DOC enrichment in dense shelf waters (DSW) in the Ross Sea was quantified and the potential for DOC to be sequestered into AABW was assessed. Ross Sea DSW was enriched in DOC by ~7 µmol kg\(^{-1}\) relative to the incoming source waters (initial conditions), primarily due to deep vertical mixing of DOC-enriched surface waters. The total DOC excess in DSW suggests that 4.0±0.6 Tg DOC y\(^{-1}\) is exported off the shelf. However, this exported fraction does not appear to persist in newly formed AABW and is likely remineralized, sequestering this carbon as TCO\(_2\) in the deep ocean.

A test of the conservative behavior of DOC in the Southern Ocean was assessed by considering its transport within deep water masses (North Atlantic Deep Water (NADW), Indian Deep Water (IDW), and Pacific Deep Water (PDW)). Multiple approaches (multiple linear regression, mass transport, and mass balance calculations) were used with data from CLIVAR Repeat Hydrography sections to evaluate the system. DOC concentrations in the deep SO and CDW largely reflect the linear mixing of those several deep waters entering the system from the north. Mass balance suggests too that the relatively depleted DOC radiocarbon content in the deep SO is a conserved property, but limited radiocarbon profiles in the SIO prevent a full analysis of the conserved behavior of \(^{14}\)C age of DOC.

Consequently, to further test for the conservative behavior of the \(^{14}\)C age of DOC in the SO, the \(^{14}\)C age of DOC in the SIO was assessed; these data complete a survey of
ages in the major deep water masses entrained into the SO. Four profiles of the $^{14}$C content of DOC spanning the SIO were collected, ranging from the Polar Front (56°S) to the subtropics (29°S). Surface waters had bulk radiocarbon ages of ~4400 years at the Polar Front and ~2000 $^{14}$C years in the subtropics. At depth, mean radiocarbon age of DOC in CDW was 5302±160 $^{14}$C years, while that in IDW was significantly older at 5557±81 $^{14}$C years. A high-salinity remnant of NADW intruding into the deep SIO had a distinctly younger radiocarbon age for DOC (~5100 $^{14}$C years). Multiple linear regression of $^{14}$C ages was used to assess the transport of DOC in the SIO. These results additionally confirm the conservative behavior of DOC in the deep Southern Ocean.

To assess how the conserved behavior of DOC can be related to the molecular composition of dissolved organic matter (DOM), the $^{14}$C age of DOC was coupled with DOM composition in PDW in the far deep North Pacific (FNP), where the ocean’s oldest water masses are located. DOM in this region has an old radiocarbon age (~6400 years old) and an overall molecular composition comprised of intrinsically stable compounds with low reactivities. By correlating radiocarbon age with each molecular formulae in solid-phase extracted DOM, the majority of DOM in PDW was found to have low reactivity and slow removal rates, especially in comparison with the DOM composition from the deep North Atlantic.

Overall, this dissertation uses large-scale biogeochemical distributions as well as isotopic and molecular composition techniques to show that DOC cycling in the deep SO and SIO are due to mixing. As Antarctic shelf systems do not export DOC to the deep SO, instead DOC distributions and $^{14}$C age of DOC in the SO are largely controlled by mixing of NADW, IDW, and PDW. In addition, the SIO exhibits $^{14}$C ages of DOC
consistent with water mass transports into that basin. Finally, the degraded molecular characteristic and old age of PDW in the FNP suggests that DOM in that region is low in reactivity and has not been renewed for long timescales.
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LIST OF ACRONYMS

Although each of these acronyms are defined upon first use in the text below, here is a list of the definitions of all acronyms used in this dissertation.

Physical and chemical entities:
CFC: chlorofluorocarbon
DOC/DOM: dissolved organic carbon / matter
HMW: high molecular weight
LMW: low molecular weight
TCO$_2$/ΣCO$_2$/DIC: total carbon dioxide / dissolved inorganic carbon
$\gamma^n$: neutral density anomaly
$\theta$: potential temperature

Water masses:
AABW: Antarctic Bottom Water
AAIW: Antarctic Intermediate Water
AASW: Antarctic Surface Water
CDW: Circumpolar Deep Water
LCDW: Lower CDW
MCDW: Modified CDW
UCDW: Upper CDW
DSW: Dense Shelf Water
IDW: Indian Deep Water
NADW: North Atlantic Deep Water
NPIW: North Pacific Intermediate Water
PDW: Pacific Deep Water
SAMW: Sub-Antarctic Mode Water
SSW: Subtropical Surface Water

Regions and large-scale physical processes:
ACC: Antarctic Circumpolar Current
AMOC: Atlantic Meridional Overturning Circulation
CNP/FNP: Central / Far North Pacific
MOC: Meridional Overturning Circulation
NIO/SIO: North / South Indian Ocean
SAF: Sub-Antarctic Front
SO: Southern Ocean

Methodology, materials, and field and laboratory techniques:
AMS: Accelerator Mass Spectrometer
CTD: Conductivity Temperature Depth sensor
FT-ICR-MS: Fourier Transform Ion Cyclotron Resonance Mass Spectrometer
GF/F: Glass Fiber Filter
MLR: Multiple Linear Regression
SPE: Solid Phase Extraction
Chapter 1: Introduction

1.1. Perspective

Meridional overturning circulation (MOC) of the ocean plays a fundamental role on the biogeochemical reservoirs of oxygen, inorganic carbon (TCO$_2$), nutrients, and dissolved organic matter (DOM). In MOC, waters relatively enriched in oxygen and DOM, and depleted in nutrients and TCO$_2$, sink in the North Atlantic due to a loss in heat and buoyancy, and form North Atlantic Deep Water (NADW). NADW migrates to the Southern Ocean and upwells, mixing with waters from Antarctic shelves and the deep Pacific and Indian Oceans, forming the voluminous deep circumpolar pool. Circumpolar Deep Water and Antarctic Bottom Water (CDW and AABW, respectively) then migrate northward, filling the basins of the Atlantic, Pacific, and Indian Oceans, and contribute to the continued production of NADW, Indian Deep Water (IDW), and Pacific Deep Water (PDW).

While the oxygen, TCO$_2$, and nutrient distributions in the deep oceans are well described, the behavior of the DOM pool as it undergoes deep MOC is largely unknown. In this work, I assess deep DOM cycling through studying dissolved organic carbon (DOC), the carbon component of DOM. Whether or not DOC in the deep ocean is truly recalcitrant, following the linear mixing of deep water masses as it transits the ocean’s conveyer (Druffel et al., 1992; Hansell and Carlson, 1998; Hansell et al., 2009), or whether it has lifetimes on the scales of decades (Follett et al., 2014), remains a topic of debate. This dissertation work describes basin-wide distributions of DOC, biogeochemical datasets from Antarctic shelves, and molecular and isotopic variations of DOM to assess its conserved behavior in the ocean’s deep layers.
1.2. **Background**

The global ocean contains the world’s largest reservoir (662±32 Pg C) of reduced carbon in the form of DOC, rivaling the atmospheric content of CO$_2$. DOC is predominantly formed at the ocean surface through primary production (Carlson and Hansell, 2015). A portion of this newly produced DOC undergoes transformations that render it recalcitrant and resistant to microbial breakdown (Jiao et al., 2010; Hansell, 2012). The accumulation of this recalcitrant DOC constitutes >95% of DOC in the ocean, being found throughout the water column. It is introduced to the ocean’s interior by overturning circulation (Hansell et al., 2009). With an average age of up to 6000-6500 $^{14}$C years (Bauer et al., 1992; Druffel et al., 1992; Zigah et al., 2017), DOC survives multiple meridional overturning cycles.

DOC gradients across the deep ocean are relatively variable; DOC concentrations are highest at depth (48 µmol kg$^{-1}$) in the North Atlantic near the formation of NADW, due to the surface subtropical characteristic of those waters (Hansell et al., 1998; 2009). Deep waters reach around 40 µmol kg$^{-1}$ in the Southern Ocean (SO) and Indian Ocean (Ogawa et al., 1999; Bercovici and Hansell, 2016), and ~37 µmol kg$^{-1}$ in the deep Pacific (Hansell et al., 2009, 2013). Some studies have suggested that these concentrations are a result of slow removal over time (Hansell et al., 1998), whereas others have suggested linear mixing of conserved parameters and localized sinks (Hansell et al., 2009, 2013; Bercovici and Hansell, 2016).

Other studies have suggested that this offset shows that the DOM pool is dynamic and consists of multiple components (Loh et al., 2004; Repeta and Aluwihare, 2006; Walker et al., 2011; Follett et al., 2014; Zigah et al., 2017). These studies show that
different components of DOM that are separated by size and polarity have different isotopic signatures, ranging from high molecular weight material with modern radiocarbon ages, to ancient hydrophobic low molecular weight material. Additionally, while DOC in the deepest ocean layers is typified as having great age, there have been suggestions of quantitatively significant inputs of recalcitrant (i.e., resistant to microbial consumption) yet relatively modern DOC by processes other than overturning circulation. Proposed mechanisms include solubilization of organic particles exported from the euphotic zone (Follett et al., 2014), the microbial transformation of that solubilized material to a recalcitrant form (i.e., the microbial carbon pump) (Jiao et al., 2010), and chemoautotrophic production of DOM (Hansman et al., 2009; Reinthaler et al., 2010).

While NADW is enriched with DOC upon its formation, whether the AABW deep-water cell in the SO contributes DOC to the deep ocean is largely unknown. A source of DOC specific to the SO is local overturning, with export of organic matter from Antarctic shelves during the formation of AABW. Antarctic shelf waters not only play an important role in deep water formation, but they enrich their waters with carbon and oxygen through massive seasonal phytoplankton blooms and brine rejection. Although these shelves have been found to accumulate DOC in their surface waters and export sinking particles (Arrigo et al., 1999, Arrigo et al., 2008, Carlson et al., 2000), whether that DOC is exported from the shelves remains unknown.

Other than Antarctic shelves, local sources of DOC to the SO include the solubilization of sinking particles (Follett et al., 2014). As CDW in the SO itself is comprised primarily of NADW, IDW, and PDW, these sources must be taken into consideration. In addition to concentration, the $^{14}$C age of DOC gives insights to the
nature of the CDW pool. However, there have been few $^{14}$C profiles of DOC ($^{14}$C-DOC) collected in the world’s ocean. Prior studies using $^{14}$C-DOC profiles from the Atlantic, Pacific, and SO came to the conclusion that the $^{14}$C-DOC age of DOC in the deep Southern Ocean is too old to be due to simple water mass migration (Druffel et al., 1992; Druffel and Bauer, 2000; Follett et al., 2014). However, these studies did not consider that IDW makes up ~35% of the CDW pool (Talley, 2013). Measurements of $^{14}$C-DOC from the South Indian Ocean (SIO) would therefore allow for a better understanding on the controls of DOC cycling in the deep ocean on a global scale.

Molecular composition techniques are useful in understanding controls of DOM cycling in the deep ocean, especially when coupled with other techniques (such as $^{14}$C-DOC measurements). Assessing the change in the molecular and isotopic compositions of deep DOM from different regions in the deep ocean therefore gives insights as to the reactivity of that pool of DOM. If the DOM pool is highly dynamic and renewed on decadal timescales, fingerprints of that process should be indicated in a correlation of the molecular composition of the DOM with its $^{14}$C age. If, on the other hand, the DOM pool were largely a conserved property, it would have molecular composition that is universal in different oceanic realms.

1.3. Objective

The primary objective of this research is to understand the controls on DOC cycling in the deep ocean. This research addresses all of the major ocean basins, but focuses on Antarctic shelf systems, the SO, the SIO, and the far North Pacific (FNP). The key questions of this research are listed below:
1. Do Antarctic shelves (such as the Ross Sea) contribute DOC to the deep and bottom waters of the Southern Ocean?

2. How is the DOC pool in CDW influenced by the allochthonous input of NADW, IDW, and PDW?

3. Does the radiocarbon content of the Southern Ocean and the South Indian Ocean reflect local or remote contributions to the DOC in deep water?

4. Does radiocarbon content and molecular composition in the North Pacific reflect local or remote contributions to the DOC in deep water?

In this dissertation, I address each of these questions through analyzing i.) the DOC distributions and export mechanisms of the Ross Sea, ii.) the DOC distributions in the Atlantic, Pacific, Indian, and Southern Oceans, iii.) the $^{14}$C ages of DOC in the SIO, and iv.) the molecular composition and $^{14}$C age of solid phase extracted DOM in the FNP. My goal with all of these analyses is to assess the remote (vs. local) nature of DOC in the deep ocean; I seek to understand if DOC cycling is highly dynamic and independent of meridional overturning, or whether it behaves conservatively and is controlled with meridional overturning.
CHAPTER 2: Dissolved Organic Carbon in the Ross Sea: Deep Enrichment and Export

2.1. Background

Antarctica’s continental shelves play important roles in the modification of major water masses, primarily through the formation of AABW. The Ross Sea continental shelf is a biologically productive system (Smith et al., 2012) where DSW are formed (Jacobs et al., 1985). In addition, waters in the Ross Sea are said to account for ~25% of bottom waters formed globally (Orsi et al., 2002). Understanding the physical and biogeochemical transformations of DSW are especially important, as these waters play a substantial role in the global deep ocean’s carbon and oxygen cycles.

Westward currents along the continental slope largely influence circulation in the Ross Sea. These currents originate from the Ross Gyre and are seasonally variable, as the gyre shrinks from summer to winter. Instabilities in these currents generate intrusions of CDW at the eastern, central, and western shelf breaks (Fig. 2.1) (Jacobs, 1991; Dinniman et al., 2011; Kohut et al., 2013). This CDW mixes with Antarctic Surface Waters (AASW) and winter waters to form modified circumpolar deep water (MCDW) (Jacobs et al., 1985; Sweeney, 2003) (Fig. 2.2). MCDW supplies heat, salt, and nutrients to the Ross Sea shelf (Smith et al., 2012). On the shelf, DSW is formed through brine rejection from the surface layer into deeper waters as sea ice forms during the late summer and autumn (Fig. 2.2). These processes are especially prevalent in the western Ross Sea, which hosts two large polynyas (Ross Sea Polynya and Terra Nova Bay Polynya). Due to the late season’s cold atmospheric temperatures and strong katabatic and regional winds, these local polynyas rapidly reject brine and export sea ice, generating the most saline
DSW in the Ross Sea (Jacobs and Comiso, 1989; Budillon et al., 2003; Orsi and Wiederwohl, 2009; Fig. 2.2). DSW flows off the shelf in western topographic troughs (especially the Drygalski trough) near Cape Adare where it mixes with CDW to form AABW (Orsi et al., 2002; Gordon et al., 2004; 2015; Whitworth and Orsi, 2006) (Fig. 2.1; Fig. 2.2).

**Figure 2.1.** Station map of data employed in this analysis. Orange stations were occupied in the Ross Sea during the TRACERS (NBP1302) expedition (February through March, 2013). Purple stations are those occupied in the Pacific sector of the Southern Ocean in Feb., 2011. The dashed line outlines the 3D section in Fig. 2.3, starting in the eastern Ross Sea near Cape Colbeck and ending near the shelf slope at Cape Adare.

In addition to its unique hydrography, the Ross Sea hosts the largest seasonal phytoplankton bloom on Antarctic continental shelves (Arrigo et al., 2015). Modeling studies suggest that these blooms result in atmospheric CO$_2$ sinks equivalent to 13 Tg C yr$^{-1}$, or 27% of the Southern Ocean’s carbon sink (Arrigo et al., 2008). However,
biogeochemical data suggests that the Ross Sea is not a large atmospheric CO$_2$ sink. Sweeney (2003) found no evidence for TCO$_2$ enrichment in DSW relative to source waters. In addition, Carlson et al. (2000) found no evidence for DOC or POC enrichment in DSW relative to source waters. This discrepancy between the models and biogeochemical data needs to be addressed. Here, we use data from the 2013 TRACERS expedition (TRacing Algal Carbon Export in the Ross Sea) to assess DOC cycling in the first late-summer carbon process study in the Ross Sea (DeJong et al., 2017). We report the first evidence for DOC enrichment in Ross Sea DSW and assess the export potential of DOC into newly formed AABW.

Figure 2.2. Scheme of the Ross Sea. The yellow arrow represents incoming waters (MCDW). This scheme shows biogeochemical processes that have the potential to introduce carbon into DSW (orange layer). At the onset of winter, cooler temperatures and katabatic winds cause brine rejection (see arrows with katabatic winds pushing ice and generating brine). Processes that can introduce DOC into the DSW include the rejection of brine (accounted for by salinity normalization), the rejection of sinking particles (dashed white arrows), and vertical mixing (pink arrows). The red arrow shows outflowing DSW at the shelf slope, which mixes with CDW to form AABW.
2.2. Methods

Data employed in this study (Fig. 2.1) are from the TRACERS cruise (http://www.bco-dmo.org/deployment/547873) and the CLIVAR Repeat Hydrography ocean section S04P (Sabine et al., 2012). Both cruises were conducted aboard the RVIB Nathaniel B. Palmer and details on sampling and methods are given in the data reports. Briefly, salinity, temperature, and oxygen measurements were obtained using a SeaBird 911+ CTD. Salinity was calibrated using discrete samples at 24° C on a Guildline 8400 Autosal four-electrode salinometer. For the TRACERS cruise, TCO₂ samples were collected following the protocols of Dickson et al. (2007). Analytical and calibration methodology for this cruise is described in DeJong et al. (2015). DOC samples were collected from the Niskin bottles by in-line filtration through pre-combusted 0.7 μM GF/F filters. Measurements were made by high temperature combustion (Dickson et al., 2007) and quality controlled using carbon reference material (Hansell Lab, U. Miami). We normalized all data here to a salinity of 34.5, the mean salinity of the Ross Sea, to account for salinity effects such as dilution via ice melt/precipitation and concentration via brine rejection (Sweeney, 2003).

2.3. Results and Discussion

In the following sections, we assess the enrichment of DOC in DSW and identify the responsible processes. Then, we estimate the fluxes and enrichment of DOC in newly formed AABW using multiple linear regression (MLR).
2.3.1. Evidence for DOC enrichment in DSW

Following Orsi and Wiederwohl (2009), we define MCDW as waters in the Ross Sea between the neutral density ($\gamma^n$) surfaces of 28 and 28.27 kg m$^{-3}$ (Table 2.1; Fig. 2.3A). MCDW is the main source water onto the Ross Shelf and is formed by the mixing of CDW and AASW at the shelf slope (Fig. 2.3A; Jacobs, 1991; Assmann et al., 2005; Dinniman et al., 2003, 2011). In this study, we use CLIVAR S04P data from the eastern shelf break near Cape Colbeck to represent our CDW and AASW at the shelf slope (AASW$_{\text{slope}}$) unmodified end-members (latitude <70°S, longitude ~150°W; Table 2.1; Fig. 2.1). We defined CDW as waters with $\gamma^n$ between 28.0 and 28.27 kg m$^{-3}$, and with $\theta$ greater than 0.5 °C (Orsi et al., 1999; Orsi and Wiederwohl, 2009)(Table 2.1). We define AASW as waters with neutral densities <28.0 kg m$^{-3}$ (Table 2.1; Orsi and Wiederwohl, 2009).

We use on-shelf data from the TRACERS cruise (Fig. 2.3A) to identify the mean salinity of MCDW (28.27 > $\gamma^n$ > 28.0 kg m$^{-3}$; Orsi and Wiederwohl, 2009). Given that the mean salinity of CDW is 34.72±0.01 and the mean salinity of AASW$_{\text{slope}}$ is 33.7±0.2, we calculated the ratio of CDW and AASW$_{\text{slope}}$ to form MCDW (salinity=34.47±0.05, Table 2.1) by assuming that salinity on the shelf is conservative (i.e., not yet impacted by processes such as brine rejection). The salinities of different water masses are shown in Table 2.1. CDW and AASW$_{\text{slope}}$ fractions required to generate MCDW are calculated as:

\[ f_{CDW} = (S_{AASW} - S_{MCDW})/(S_{AASW} - S_{CDW}) \]  \hspace{1cm} (2.1)

\[ f_{AASW} = 1 - f_{CDW} \]  \hspace{1cm} (2.2)
where \( S \) is the mean salinity for each water mass and \( f \) represents the fraction of each water mass. With this approach, the fractions of CDW and AASW_slope \( (f_{\text{CDW}} \text{ and } f_{\text{AASW}}) \) that form MCDW are 0.75±0.24 and 0.25±0.02, respectively.

Figure 2.3. A. Salinity with neutral density anomaly \( (\gamma_n) \) overlays, B. Oxygen, and C. DOC of the U-shaped section illustrated in Fig 2. Fig. 2.3A shows a schematic of water mass mixing in the Ross Sea, where CDW and AASW mix to form MCDW on the shelf. It also illustrates DSW in the western Ross Sea and the overflow of these waters at the Adare shelf slope to form AABW. The white boxes in B and C show oxygen and DOC distributions, respectively, of newly formed AABW.
With these fractions, the expected concentration of a variable on the Ross Shelf during the initial condition, based on conservative behavior, is calculated:

\[ s_{MCDW} = f_{CDW} s_{CDW} + f_{AASW} s_{AASW} \]  

(2.3)

where \( s_{CDW} \) and \( s_{AASW} \) are the observed mean concentrations of the biogeochemical parameter of interest, and \( s_{MCDW} \) is the calculated concentration during initial condition, based on water mass mixing.

Table 2.1. Physical and biogeochemical parameters of Ross Sea and Ross shelf slope water masses. Constraints are based on literature definitions of water masses (AASW, MCDW, and DSW constraints based on Orsi and Wiederwohl, 2009, Jacobs and Fairbanks, 1985; AABW (taken from the western shelf slope near Cape Adare) and CDW (taken from the eastern shelf slope, near Cape Colbeck) from Orsi et al., 1999, Orsi et al., 2002, Orsi and Wiederwohl, 2009, Talley 2013). AASW\textsubscript{slope} is AASW taken at the Ross Shelf slope, and is unaltered by the biology occurring on the shelf. AASW\textsubscript{shelf} represents the AASW in the Ross Sea and the result of the primary productivity occurring at the surface in the Ross Sea; both of these water masses are separated with a \(\gamma^n\) value less than 28 kg m\(^{-3}\) (Orsi and Wiederwohl., 2009). Water masses were isolated using salinity, potential temperature, neutral density (\(\gamma^n\)), and oxygen gradients. Unaltered parameters for MCDW are calculated based on salinity gradients between CDW and AASW at the eastern shelf slope (equations 1 through 3), given the \(\gamma^n\) values laying between 28 and 28.3 kg m\(^{-3}\) (Orsi and Wiederwohl, 2009). We define DSW as those shelf waters with a \(\gamma^n\) value > 28.3 kg m\(^{-3}\) (Orsi and Wiederwohl., 2009). The error for each parameter represents the standard deviation within the given water mass.

<table>
<thead>
<tr>
<th>Water mass</th>
<th>Cruise</th>
<th>Salinity</th>
<th>(\theta) (°C)</th>
<th>(\gamma^n) (kg m(^{-3}))</th>
<th>(O_2) (µmol kg(^{-1}))</th>
<th>TCO(_2) (µmol kg(^{-1}))</th>
<th>DOC (µmol kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDW</td>
<td>S04P</td>
<td>34.72±0.01</td>
<td>0.8±0.2</td>
<td>28.16±0.03</td>
<td>197±5</td>
<td>2259±5</td>
<td>40.0±0.7</td>
</tr>
<tr>
<td>AASW\textsubscript{slope}</td>
<td>S04P</td>
<td>33.7±0.2</td>
<td>-0.7±0.5</td>
<td>27.3±0.2</td>
<td>343±20</td>
<td>2158±22</td>
<td>45.1±1.6</td>
</tr>
<tr>
<td>AASW\textsubscript{shelf}</td>
<td>TRACERS</td>
<td>33.8±0.2</td>
<td>-1.6±0.3</td>
<td>27.4±0.2</td>
<td>355±12</td>
<td>2114±24</td>
<td>55.9±1.6</td>
</tr>
<tr>
<td>MCDW</td>
<td>TRACERS</td>
<td>34.47±0.05</td>
<td>0.4±0.9</td>
<td>28.02±0.01</td>
<td>237±0.3</td>
<td>2234±0.3</td>
<td>41.0±0.3</td>
</tr>
<tr>
<td>DSW</td>
<td>TRACERS</td>
<td>34.69±0.06</td>
<td>-1.88±0.07</td>
<td>28.62±0.09</td>
<td>283±6</td>
<td>2232±6</td>
<td>48.4±1.7</td>
</tr>
<tr>
<td>AABW</td>
<td>S04P</td>
<td>34.70±0.01</td>
<td>-0.008±0.1</td>
<td>28.30±0.01</td>
<td>226±9</td>
<td>2258±3</td>
<td>40.2±0.3</td>
</tr>
</tbody>
</table>
When applying equation 3 to our data, we find that when CDW (DOC=40.0±0.7 \( \mu \text{mol kg}^{-1} \)) upwells into the Ross Sea and mixes with AASW\(_{\text{slope}}\) (DOC=45.1±1.6 \( \mu \text{mol kg}^{-1} \)) in a 0.75±0.24:0.25±0.02 ratio, the resultant DOC concentration is 41.0±0.3 \( \mu \text{mol kg}^{-1} \) (Table 2.1 and 2; Fig. 2.4A and C, solid red vertical line).

**Figure 2.4.** A. Salinity (black open circles), and DOC (red filled circles) vs. depth in the western Ross Sea (longitudes west of 180°) from the TRACERS expedition. B. Salinity vs. DOC between 100 and 600 m in the western Ross Sea (data outlined in rectangle in 4A). C. Salinity (black open circles), and DOC (red closed circles) vs. depth in the eastern Ross Sea (longitudes east of 180°) from the TRACERS expedition. D. Salinity vs. DOC between 100 and 600 m in the eastern Ross Sea. In plots 4A and 4C, the red line represents the concentration of DOC at initial state in MCDW (41.0±0.3 \( \mu \text{mol kg}^{-1} \); Table 2.1).
We compare our approach to that of Sweeney (2003) to estimate the contribution of source waters (CDW and AASW_{slope}) to form MCDW. Based on Jacobs et al. (1985), Sweeney (2003) assumed that inflowing waters were composed of 50%CDW + 50%AASW, where AASW_{slope} in this case comprises both AASW and the winter water (surface waters resulting from fresh mixing of winter ice). These results suggest that inflowing DOC concentrations would be 42.6±1.7 µmol kg\(^{-1}\), only ~1-2 µmol kg\(^{-1}\) higher than that value estimated from mixing (41.0±0.3 µmol kg\(^{-1}\); equations 1-3). These results are much lower than any DOC concentration in the Ross Sea due to the low DOC concentrations throughout the entire water column in the open Southern Ocean (Ogawa et al., 1999; Hansell et al., 2009).

The concentration of DOC in DSW is elevated compared to the background concentration (Table 2.1). Overall, DOC was enriched by a mean of 7.4±1.7 µmol kg\(^{-1}\) (from that initial state of 41.0±0.3 µmol kg\(^{-1}\) in MCDW to 48.4±1.7 µmol kg\(^{-1}\) in DSW; Table 2.1; Fig. 2.3C; Fig. 2.4B). These findings suggest that DOC in the Ross Sea DSW is enriched relative to its source waters (Fig. 2.4A). In the following section, we discuss the possible mechanisms involved in bringing DOC to the DSW layer.

### 2.3.2. Mechanisms for DOC enrichment in the deeper layer of the Ross Sea

Due to the phytoplankton bloom that was occurring during the TRACERS occupation, the highest DOC concentrations (~61 µmol kg\(^{-1}\)) were found in the western Ross Sea near Terra Nova Bay, with an overall mean of 55.9±1.6 µmol kg\(^{-1}\) in the surface waters (Table 2.1). DOC concentrations decreased with depth, reaching ~50 µmol kg\(^{-1}\) at about 100 m and as low as ~43 µmol kg\(^{-1}\) at 1200 m (Fig. 2.4A). The decrease in DOC
between ~100 and 600 m is gradual and mirrors the salinity gradient (Fig. 2.4A, outlined in box), showing entrainment of DOC into the DSW by vertical mixing.

To determine if these salinity and DOC gradients between 100 and 600 m track one another directly, DOC and salinity values in the western Ross Sea (latitude <65° S and longitudes west of 180°) lying between 100 m to 600 m were regressed (Fig. 2.4B; \(R^2=0.74\), \(p<0.001\)). We also isolated two end members for this mixing process, which were defined by the mean values of DOC and salinity at ~100 m (\(N=35\)) and at ~600 m (\(N=22\)). We found that at 100 m, mean salinity was 34.61±0.02 and mean DOC was 50.7±0.5 \(\mu\)mol kg\(^{-1}\). At 600 m, mean salinity was 34.76±0.02, and mean DOC was 46.3±0.5 \(\mu\)mol kg\(^{-1}\). A linear relationship between these two end members generates the following equation:

\[
s_{DOC} = -28.67 \times S + 1042.8
\]  

(2.4)

where \(s_{DOC}\) is the salinity-predicted DOC concentration (\(\mu\)mol kg\(^{-1}\)) and \(S\) is the salinity. Between 100 and 600 m, salinity-estimated DOC \((s_{DOC})\) concentration (using equation 4), and observed DOC concentrations track each other closely (Fig. 2.4B). These results imply that vertical mixing is a primary mechanism that causes the DSW to become enriched in DOC. As vertical mixing increases in extent, depth, and rate in the austral autumn, it effectively homogenizes the water column, providing a mechanism for DOC to mix to depth.

The hydrography in the eastern Ross Sea differs from the west. Brine rejection and associated convection during sea ice formation in polynyas of the western Ross Sea results in a locally thick layer of high salinity shelf water. The deep convection results in western shelf water that is more saline (and thus denser) than eastern shelf waters, where
such deep convection does not occur. The consequent shoaling of density surfaces from east to west results in a thinning of the lighter AASW layer from east to west; AASW reaches to 400 m in the east, while the AASW layer in the west is only 50 m thick (Fig 3A, 4A C; Orsi and Wiederwohl, 2009).

Similar to the west, however, DOC and salinity in the eastern Ross Sea exhibit a gradient with depth (Fig. 2.4C), suggestive again that vertical mixing controls both the salinity and DOC gradients with depth. However, these gradients are not related linearly (Fig. 2.4D). Regardless, DOC concentrations in the east below 100 m range from 50 to 45 \( \mu \text{mol kg}^{-1} \), with a mean of 47.1±0.8 \( \mu \text{mol kg}^{-1} \), comparable to those concentrations below 100 m observed in the west.

While DOC behaves conservatively across most of the Ross Sea, there are some localized anomalies where non-conservative attributes are indicated. The most striking anomaly is in the >1200 m deep Drygalski trough in the western Ross Sea (Fig 2.2; Fig. 2.6). The trough contains some of the densest shelf waters in the Ross Sea due to the Terra Nova Bay polynya, which generates brine. If equation 2.4 is extended to those data in the trough, the mean observed DOC concentration (45.3±1.1 \( \mu \text{mol kg}^{-1} \)) is similar to the average sDOC concentration (45.9±0.4 \( \mu \text{mol kg}^{-1} \); note that all biogeochemical data has been salinity-normalized to 34.5 to remove the effect of brine rejection). However, there is a significant difference in observed versus salinity-predicted DOC concentrations in that region (t-test p=0.005; Fig. 2.5, Fig. 2.6). This difference is likely because in the deepest regions of the trough, DOC concentrations reach a minimum of ~42 \( \mu \text{mol kg}^{-1} \), while sDOC values are around ~45 to 46 \( \mu \text{mol kg}^{-1} \) (Fig. 2.5, Fig. 2.6).
These localized low concentrations of DOC in the deepest layers of the Drygalski trough (Fig. 2.6) imply that there is some net consumption of DOC. A potential reason for this localized consumption of DOC is the residence time of those deepest waters at the bottom of the trough. While waters in the western Ross Sea have mean residence times reported from 4 (Trumbore et al., 1991) to ~6 to 7 years (Rivaro et al., 2015), those dense, brine-enhanced waters at the bottom of the Drygalski trough may have even longer residence times. These results preclude a quantitatively important impact of solubilized sinking particles on DOC distributions in DSW in the western Ross Sea. If sinking particles were primarily responsible for the DOC elevation at depth, the DOC concentrations at depth would exceed those estimated by the salinity-mixing curve. However, we find that DOC concentrations either follow the salinity-mixing curve (so DOC is conservative there), or are less than what mixing would predict in the deeper layers (net removal). Nonetheless, the vast majority of DSW has enhanced DOC concentrations. As DSW in the western Ross Sea is exported at the Antarctic Shelf slope near Cape Adare (Gordon et al., 2004; Gordon et al., 2015), this DOC-enriched DSW has the potential to bring organic carbon into AABW.

2.3.3. Export of DOC into newly formed AABW

Given that DOC appears to persist in the Ross Sea, it has the potential to be exported at the shelf slope into newly formed AABW. Different literature has reported varying residence times for waters in the Ross Sea, ranging from ~3 to 8 years. Trumbore et al (1991) used CFC concentrations to estimate that the residence time of western shelf waters was ~4 years. Sweeney (2003) calculated a mean residence time of shelf waters to be ~6 years, and Rivaro et al (2015) similarly calculated residence times in the western
Ross Sea to be ~6 to 7 years. Jacobs et al (1985) reports a shelf water export of 1.4 Sv based on a ~6 year residence time. Given this export value, and the mean DOC enrichments in DSW (~7 µmol kg\(^{-1}\), Section 3.1), the total export of DOC off the western shelf is ~4 Tg C y\(^{-1}\). A modeling study by Arrigo et al. (2008) found that the Ross Sea is a large atmospheric CO\(_2\) sink (13 Tg C y\(^{-1}\)). However, until now there had been no evidence for carbon enrichment in Ross Sea DSW (Sweeney, 2003; Carlson et al., 2000).

The ~4 Tg C y\(^{-1}\) of DOC that is exported off the Ross Sea shelf accounts for ~30% of the 13 Tg C y\(^{-1}\) sink and thus helps balance the Ross Sea carbon budget.

![Figure 2.5](image.png)

**Figure 2.5.** Measured DOC (red), and salinity-predicted DOC (black) over the whole water column in the western Ross Sea.

Similar to Sweeney (2003), we observe that the mean TCO\(_2\) concentrations of incoming MCDW and outflowing DSW are essentially the same (2234±8 µmol kg\(^{-1}\) and 2232±6 µmol kg\(^{-1}\), respectively; Table 2.1), indicating that TCO\(_2\) is not the primary form of carbon that is exported off the Ross Shelf. Even with our new DOC data, the Ross Sea
carbon budget is not balanced if we assume that the Ross Sea is a large atmospheric CO\textsubscript{2} sink. Regardless, here we report that a substantial amount of DOC is exported along with the export of DSW.

**Figure 2.6.** Section plots (outlined in map) of the neutral density anomaly ($\gamma^\prime$, top) and DOC (bottom) in the Drygalski trough, showing the deepest, densest DSW have the lowest DOC concentrations.

Since shelf water is enriched with DOC relative to the deep off-shelf system, we may expect to see its signature in newly formed AABW, as observed in the oxygen signatures (Fig. 2.3B, white box). In contrast to oxygen, DOC is not enriched in the overflow waters, indicating non-conservative behavior upon export from the shelf (Fig. 2.3C, white box, Fig. 2.7C). To test for the non-conservative behavior of DOC mixing in deep water masses off the shelf, MLR was employed (Fig. 2.7), using potential
temperature ($\theta$) and salinity ($S$) from DSW and CDW as conservative tracers in the formation of AABW. Here, MLR treats the observed biogeochemical data of interest:

$$d_{\text{meas}} = \theta \ast a + S \ast b + c$$

where $d_{\text{meas}}$ is measured biogeochemical data, assumed to be a function of $\theta$ and $S$ and $a$ and $b$ are weights of each conservative variable, with $c$ as a constant offset.

The data employed in this MLR (N=510) are shelf water data from the TRACERS cruise (longitudes west of 180°, $\gamma^{n}>28.27$ kg m$^{-3}$, depth>100 m) and circumpolar and bottom water from the CLIVAR S04P cruise from near Cape Adare, (latitude>67°S, longitudes west of 169°E, $\gamma^{n}>28$ kg m$^{-3}$, depth>100 m). AABW was separated from CDW in the CLIVAR S04P data by using a cutoff of $\gamma^{n} \geq 28.27$ kg m$^{-3}$ (Orsi et al., 1999; Orsi and Wiederwohl, 2009). A similar analysis was applied to the deep circumpolar waters of the Southern Ocean by Bercovici and Hansell (2016).

The MLR-predicted mean DOC concentration in newly formed AABW at Cape Adare is 43.5±0.8 µmol kg$^{-1}$ (Fig. 2.7A, black symbols at neutral density 28.3-28.4 kg m$^{-3}$), while that observed at Cape Adare was 40.2±0.3 µmol kg$^{-1}$ (Fig. 2.7A, green data symbols), leaving a 3.3±0.8 µmol/kg deficit (t-test p<0.001; Fig. 2.7A). In fact, the highest-MLR predicted DOC (~45 µmol kg$^{-1}$) in newly formed AABW also has the highest neutral density, thus the strongest DSW characteristic. This signature is absent in the observed data.
Table 2.2. $R^2$ values of the MLR regression, and observed, MLR-estimated, and anomalies for oxygen, TCO$_2$, and DOC concentrations of AABW near Cape Adare.

<table>
<thead>
<tr>
<th></th>
<th>Oxygen (µmol kg$^{-1}$)</th>
<th>TCO$_2$ (µmol kg$^{-1}$)</th>
<th>DOC (µmol kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^2$ (observed vs. MLR)</td>
<td>0.95</td>
<td>0.77</td>
<td>0.83</td>
</tr>
<tr>
<td>AABW (observed at Adare, N=27)</td>
<td>226±9</td>
<td>2258±3</td>
<td>40.2±0.3</td>
</tr>
<tr>
<td>AABW (MLR predicted at Adare, N=27)</td>
<td>230±6</td>
<td>2249±2</td>
<td>43.5±0.8</td>
</tr>
<tr>
<td>AABW anomaly (observed-MLR)</td>
<td>-4±11</td>
<td>9±4</td>
<td>-3.3±0.8</td>
</tr>
</tbody>
</table>

To determine whether the DOC sink in AABW is consistent with removal by respiration, the same MLR was employed on the oxygen and TCO$_2$ data (Fig. 2.7). The mean MLR-predicted oxygen concentration in AABW is 230±6 µmol kg$^{-1}$ (Fig. 2.7B, black symbols between neutral density 28.3 to 28.4 kg m$^{-3}$) while the observed mean oxygen concentration is 226±9 µmol kg$^{-1}$ (Fig. 2.7B, green data symbols). The MLR-predicted oxygen and observed oxygen at Cape Adare are not significantly different (t-test p=0.1), and the 4 µmol kg$^{-1}$ difference between the two parameters is smaller than its standard deviation (4±11 µmol kg$^{-1}$). The mean MLR-predicted TCO$_2$ concentration in AABW is 2249±2 µmol kg$^{-1}$ (Fig. 2.7C, black symbols at $\gamma^\alpha$ ranging from 28.3-28.4 kg m$^{-3}$), while the measured concentration is 2258±3 µmol kg$^{-1}$ (Fig. 2.7C, green data symbols), suggesting a 9±4 µmol kg$^{-1}$ surplus (t-test p<0.001). More detailed data ($R^2$ values, and mean observed and predicted values in AABW) from the MLR are in Table 2.2. While oxygen anomalies are not observable beyond the standard deviation of the measurement, the DIC surplus in AABW compared to expected values from the MLR is consistent with ~ 3 µmol kg$^{-1}$ of DOC being remineralized (Fig. 2.7).
Figure 2.7. Neutral density anomaly ($\gamma^n$) vs. DOC (A), Oxygen (B), and TCO$_2$ (C) concentrations. Colored data are measured data, while black data are those predicted through MLR. Red data is DSW data taken from the TRACERS cruise in the western Ross Sea. Blue data represent CDW and green data represent AABW; both are taken from CLIVAR S04P (see details of the regressions in Table 2.2).

DOC distributions in the open Southern Ocean are conservative (Bercovici and Hansell, 2016), thus the organic material produced locally in the Southern Ocean or on Antarctic shelves does not leave a lasting signature in the deep Southern Ocean’s DOC pool. Consistent with that observation, DOC produced in the Ross Sea appears to be
consumed before export into AABW. Therefore, while this result implies that the Ross Sea does not contribute to the deep DOC pool of the Southern Ocean, it shows that this carbon is sequestered into AABW as CO$_2$.

The turnover of a given DOC fraction is highly variable (hours to millennia), depending on the concentration, composition, availability of macronutrients, and microbial community structure (Arrieta et al., 2015; Carlson et al., 2004; Hansell et al., 2009; Hansell et al., 2012). Additionally, DOC that escapes immediate mineralization in one ocean realm can be consumed in another, with separation in space and time (Carlson et al., 2011). For example, Carlson et al (1994) found in the Sargasso Sea that microbial communities below the mixed layer consumed DOC that was recalcitrant to those communities in the surface layer. Similarly, microbial communities in the mesopelagic South Pacific gyre consumed DOC that was recalcitrant to microbial communities in the upper mixed layer (Letscher et al., 2015). In this study, we observe a comparable process occurring in Antarctic shelf systems and the Southern Ocean; DOC that persists in Ross DSW is remineralized upon export into newly formed AABW.

2.4. Conclusion

In this analysis, we show that DOC produced in the Ross Sea is conservatively mixed down into DSW via vertical mixing. Although there are low DOC values in the deep Drygalski trough that imply further removal given time, DOC distributions in the majority of the subsurface western Ross Sea can be largely explained by this mixing. The total enrichment of DOC yields an export of $\sim$4 Tg C y$^{-1}$ of DOC from the Ross Sea, implying sequestration of this material into new AABW. However, upon DSW export
and formation of AABW, the DOC that accumulates on the Ross shelf disappears, likely supporting the microbial loop in the deep Southern Ocean. Our results suggest that DOC is an important form of carbon that is exported off the Ross Sea into the abyssal ocean, sustaining microbial communities in the Southern Ocean and thus sequestering carbon into the deep.
Chapter 3. Dissolved Organic Carbon in the Deep Southern Ocean: Local versus Distant Controls

3.1. Background

Marine DOC is predominantly formed at the ocean surface through primary production (Carlson and Hansell, 2015). A portion of newly produced DOC undergoes transformations that render it recalcitrant and resistant to microbial breakdown (Jiao et al., 2010; Hansell, 2012). The refractory fraction of the accumulated DOC, constituting >95% of DOC in the ocean, is found throughout the water column, introduced to the interior by overturning circulation (Hansell et al., 2009). With average ages of up to 6000 years (Bauer et al., 1992; Druffel et al., 1992), this fraction survives multiple meridional overturning cycles. Prior analyses on DOC in the deep ocean have conflicted, describing both conservative and nonconservative traits: the deep DOC field has been reported as uniform in distribution yet local inputs have been suggested as quantitatively important.

An additional source of DOC specific to the Southern Ocean could be local overturning, with export of organic matter from Antarctic shelves upon the formation of AABW (as discussed in Chapter 2). Primary production in the Southern Ocean generates 1949±70.1 Tg C per year; the Ross and Weddell Antarctic shelves are responsible for ~50% of this production due to their massive seasonal phytoplankton blooms (Arrigo et al., 2008). While these blooms result in particle export and surface DOC accumulation (Arrigo et al., 1999, Arrigo et al., 2008, Carlson et al., 2000), the DOC does not make it off the shelves and thus does not contribute to the deep pool of DOC (Chapter 2; Bercovici et al., 2017).
Here, we test whether the DOC concentrations in the deep Southern Ocean demonstrate a dynamic system or whether they are governed by allochthonous mixing. Evidence for the quantitative importance of such processes would exist if DOC concentrations and radiocarbon ages in the deep layer diverge from those expected from linear mixing of the source water masses. A question we pose is whether localized processes leave an observable signal in the DOC concentrations of the deep circumpolar waters beyond that expected through this mixing. As the Southern Ocean receives waters of distinctive character from the Atlantic, Pacific, and Indian basins, as well as local shelf inputs (i.e., bottom water formation), we focus on the mixing of those deep waters in the Antarctic Circumpolar Current (ACC).

3.2. Hydrographic context

Here we consider the formation of CDW and AABW, using analyses by previous authors that established contributions of NADW, IDW, and PDW (Broecker, 1991; Gordon, 1986; Schmitz, 1995; Lumpkin and Speer, 2007; Talley, 2013). CDW is formed through the upwelling of deep water masses (Schmitz, 1995; Lumpkin and Speer, 2007) sourced from the Atlantic, Indian, and Pacific Oceans and is distinguished by upper (UCDW) and lower (LCDW) components, as the core of each has distinct sources (Orsi et al., 2002).

We additionally consider the input of Antarctic shelf waters in the formation of AABW (Jacobs et al., 1985; Orsi et al., 1999). The definitions employed here for water masses are given in Table 3.1, while their physical properties, as relevant to this analysis, are in Table 3.2.
Table 3.1. Cruises and hydrographic parameters employed to characterize water masses of interest. Water mass constraints were based on salinity, potential temperature, isopycnal, and oxygen restrictions as defined by Talley (2007; 2013a,b), Patterson and Whitworth (1990), Kolterman et al. (2011), Gordon (1986), Lumpkin and Speer (2007), and Orsi and Whitworth (2004) for NADW, IDW, and PDW, and Orsi et al (1999; 2002) for AABW, and UCDW and LCDW.

<table>
<thead>
<tr>
<th>Water masses</th>
<th>Cruises employed</th>
<th>Latitude</th>
<th>Depth (m)</th>
<th>Salinity</th>
<th>$\theta$ (°C)</th>
<th>$\gamma_n$ (kg/m$^3$)</th>
<th>Other (µmol kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NADW</td>
<td>A16N/S</td>
<td>20°S-40°S</td>
<td>&gt;1000</td>
<td>S&gt;34.6</td>
<td>2≤$\theta$≤4</td>
<td>≥28.05</td>
<td>SiO$_4$&lt;110</td>
</tr>
<tr>
<td></td>
<td>I08S I09N SR03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O$_2$≥190</td>
</tr>
<tr>
<td>IDW</td>
<td></td>
<td>20°S-40°S</td>
<td>&gt;1000</td>
<td>S&gt;34.5</td>
<td>2≤$\theta$≤4</td>
<td></td>
<td>O$_2$&lt;190</td>
</tr>
<tr>
<td>PDW</td>
<td>P16N/S P18</td>
<td>20°S-40°S</td>
<td>&gt;1000</td>
<td>S&gt;34.5</td>
<td>0≤$\theta$≤4</td>
<td></td>
<td>O$_2$&lt;190</td>
</tr>
<tr>
<td>UCDW</td>
<td>S04P A16S P16S P18 I08S</td>
<td>&gt;50°S</td>
<td>150-1500</td>
<td>S&gt;34.6</td>
<td>0≤$\theta$≤2</td>
<td>27.84-28.05</td>
<td>O$_2$&lt;190</td>
</tr>
<tr>
<td>LCDW</td>
<td>Same as UCDW</td>
<td>&gt;50°S</td>
<td>1500-3000</td>
<td>S&gt;34.6</td>
<td>1≤$\theta$≤1.5</td>
<td>28.05-28.27</td>
<td>220&gt;O$_2$&gt;190</td>
</tr>
<tr>
<td>AABW</td>
<td>Same as UCDW</td>
<td>&gt;50°S</td>
<td>&gt;3000</td>
<td>S&gt;34.6</td>
<td>0≤$\theta$≤0.5</td>
<td>&gt;28.27</td>
<td>CFC-11&gt;O D O$_2$&gt;200</td>
</tr>
</tbody>
</table>

Overturning circulation of deep waters on the global scale is depicted in Fig. 3.1. NADW originates from warm, saline subtropical surface waters, carried northward by the Gulf Stream (Broecker, 1991). Once these waters reach high latitudes, they become cool and dense, forming waters that invade the deep Atlantic to travel south. Unlike NADW with its surface water origins, IDW and PDW ultimately originate from near-bottom circumpolar waters formed in the Southern Ocean (De Vries and Primeau, 2011). IDW forms from AABW/LCDW mixing with a small portion of NADW; it is subsequently freshened and warmed by Subantarctic Mode Water (SAMW) as it upwells and flows towards the Southern Ocean (Talley, 2013). PDW is formed in the North Pacific by mixing of northward flowing LCDW with low salinity subpolar intermediate waters.
(IW), whereupon it flows southward to rejoin the Southern Ocean. In CDW itself, the NADW contribution is primarily found in LCDW, giving it a saltier, denser, oxygen-enriched and nutrient-deprived character in comparison to the oxygen-depleted and nutrient-enriched UCDW, which in turn is strongly derived from PDW and IDW (Orsi et al., 2002).

**Table 3.2.** Water masses, number of samples per water mass (N), physical characterizations (mean salinity, mean potential temperature ($\theta$), mean neutral density ($\gamma_n$)), mean oxygen, and mean DOC concentrations ($\pm$standard deviation) for each water mass.

<table>
<thead>
<tr>
<th>Water mass</th>
<th>N</th>
<th>Salinity</th>
<th>$\theta$ (°C)</th>
<th>$\gamma_n$ (kg/m³)</th>
<th>$O_2$ (µmol/kg)</th>
<th>DOC (µmol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NADW</td>
<td>96</td>
<td>34.84±0.08</td>
<td>2.63±0.3</td>
<td>28.0±0.08</td>
<td>228±20</td>
<td>41.2±0.6</td>
</tr>
<tr>
<td>IDW</td>
<td>144</td>
<td>34.65±0.07</td>
<td>2.5±0.7</td>
<td>27.9±0.1</td>
<td>162±15</td>
<td>40.8±0.4</td>
</tr>
<tr>
<td>PDW</td>
<td>127</td>
<td>34.64±0.06</td>
<td>1.9±0.6</td>
<td>27.9±0.1</td>
<td>158±13</td>
<td>37.0±1.0</td>
</tr>
<tr>
<td>UCDW</td>
<td>372</td>
<td>34.71±0.03</td>
<td>1.6±0.2</td>
<td>28.0±0.05</td>
<td>183±4</td>
<td>40.8±1.0</td>
</tr>
<tr>
<td>LCDW</td>
<td>451</td>
<td>34.71±0.02</td>
<td>0.6±0.4</td>
<td>28.2±0.06</td>
<td>207±7</td>
<td>40.1±0.8</td>
</tr>
<tr>
<td>AABW</td>
<td>416</td>
<td>34.69±0.01</td>
<td>-0.02±0.2</td>
<td>28.3±0.02</td>
<td>219±6</td>
<td>40.2±0.7</td>
</tr>
</tbody>
</table>

AABW, the Southern Ocean’s abyssal water mass, results from the cooling and mixing of LCDW with dense shelf overflow waters produced in Antarctic shelf systems (Carmack, 1977; Jacobs et al., 1985). AABW is separated from the other major water masses through a neutral density ($\gamma_n$) cutoff of 28.27 kg / m³ (Orsi et al., 1999) (Table 1). Although AABW is formed at the continental shelf slope all along the Antarctic continent, the main Antarctic shelves responsible for formation are those of the Weddell and Ross Seas (Jacobs et al., 1985) (Fig. 3.1), with lesser contributions from the
Amundsen Sea and Antarctic Peninsula. Considering the transports from the Atlantic, Indian, and Pacific Oceans, CDW/AABW is renewed at 29 Sv (Fig. 3.1; Talley, 2013a).

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**Figure 3.1.** Schematic of deep water mass exchanges between the Southern Ocean and the deep Atlantic, Indian, and Pacific Oceans of relevance to this analysis. Southward flows of NADW (17.6 Sv), IDW (15.7 Sv), and PDW (8.8 Sv) are at 30°S. Once NADW reaches the Polar Front, 12.7 Sv of NADW merges with the CDW, and the remaining 4.9 Sv contributes to form SAMW/AAIW. Due to their similar character, southward flowing PDW and IDW are indistinguishable as they merge within the ACC; 16.3 Sv of this mixture (IDW and PDW) contributes to CDW/AABW, while the remaining 8.2 Sv contributes to SAMW/AAIW. The net flow of SAMW/AAIW is northward in the Atlantic and Pacific basins, but southward in the Indian basin, as the southward flow of Indian Intermediate Water is greater than the northward flow of SAMW/AAIW, thus generating a net flow southward of intermediate waters (Schmitz, 1995). Figure based on Schmitz (1995), Lumpkin and Speer (2007), and Talley (2013a).

---

### 3.3. Analytical approach

To answer the question on whether local DOC inputs leave an observable signature in the deep CDW, we assessed the CDW DOC concentrations using three approaches. To determine if DOC is conserved with simple mixing of NADW, IDW, and PDW, we compared the mean measured DOC concentration (DOC<sub>meas</sub>) in CDW to i) that
expected by net volume transports (\( \text{DOC}_{\text{transports}} \)) of NADW, IDW, and PDW (Fig. 3.1),
ii) that estimated by a binary mixing model of NADW, IDW, and PDW (\( \text{DOC}_{\text{binary}} \)), and
iii) that estimated from MLR (\( \text{DOC}_{\text{MLR}} \)) of data from CLIVAR Repeat Hydrography
sections (Fig. 3.2).

**Figure 3.2.** CLIVAR transects used in this analysis

Data were taken from sections in the Atlantic (A16N and A16S; Baringer et al., 2014; Wanninkhof et al., 2015), the Indian (I08S, I09N, and SR03; Feely et al., 2007a, b; Rintoul and Rosenberg, 2014), the Pacific (P16S, P16N, P18; Feely et al., 2008a, b), and the Southern (S04P) Oceans (Sabine et al., 2012). \( \Delta^{14}\text{C-DIC} \) data, used to assess the
validity of our mixing analysis (Section 5.2), were obtained from previous occupations of
A16N (Peltola et al., 2005) and A16S (Wanninkhof et al., 2006), and the above cited
sources for P16N and P16S, and I08S and I09N.
3.4. DOC in the Deep Waters

Near its formation region, NADW has DOC concentrations of ~48 µmol kg⁻¹ (Fig. 3.3). Through mixing and removal during advection into the southern hemisphere (here values are reported for the zone 20-40°S), DOC declines to ~41 µmol kg⁻¹ (Table 1, Fig. 3.3) (Hansell and Carlson, 1998; Carlson et al., 2010). IDW has a fairly constant DOC concentration, like that of the NADW in the southern hemisphere (~41 µmol kg⁻¹, Fig. 3.3, Table 3.1). The PDW DOC concentration is ~37 µmol kg⁻¹ (Fig. 3.3), ~4 µmol kg⁻¹ lower than that of NADW and IDW.

Across the three deep water masses of the Southern Ocean (UCDW, LCDW and AABW at >50°S; Section 2), DOC concentrations were relatively uniform, ranging from ~39 to ~42 µmol kg⁻¹ (Fig. 3.3). The mean concentrations were 40.8±1.0 µmol kg⁻¹, 40.1±0.8 µmol kg⁻¹, and 40.2±0.7 µmol kg⁻¹, respectively (Table 3.2, 3.3); the overall mean of these waters was 40.4±0.8 (Table 3.3). In sum, mean DOC in the deep ACC is similar (within 1 µmol kg⁻¹) to that in NADW and IDW, but ~3 to 4 µmol kg⁻¹ higher than in PDW (Table 3.2).

Table 3.3. Measured DOC (DOC_{meas}; µmol kg⁻¹), DOC predicted by MLR analysis (DOC_{MLR}; µmol kg⁻¹), mean DOC (DOC_{binary}; µmol kg⁻¹) calculated with the binary mixing model, and mean DOC calculated with deep water transports (DOC_{transports}).

<table>
<thead>
<tr>
<th></th>
<th>DOC_{meas}</th>
<th>DOC_{MLR}</th>
<th>DOC_{binary}</th>
<th>DOC_{transports}</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCDW</td>
<td>40.8±1.0</td>
<td>40.1±0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LCDW</td>
<td>40.1±0.8</td>
<td>39.6±0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AABW</td>
<td>40.2±0.7</td>
<td>39.2±0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean DOC in S. Ocean</td>
<td>40.4±0.8</td>
<td>39.6±0.5</td>
<td>40.1±0.6</td>
<td>40±2</td>
</tr>
</tbody>
</table>

There were some relatively elevated values (>42 µmol kg⁻¹) in the deep circumpolar layers; 48 of 372 (13%), 15 of 451 (3.3%), and 7 of 416 (1.7%) observations in UCDW, LCDW, and AABW, respectively. Some of these elevated values could be
due to simple analytical imprecision or other errors while some could be regional anomalies, as discussed in Section 5.1.

Figure 3.3. DOC concentrations within NADW, IDW, PDW, UCDW, LCDW, and AABW versus latitude. Water mass constraints are defined in Table 1 caption.

3.4.1. Water mass transport analysis

At 30°S, ~ 17.6 Sv of NADW, 15.7 Sv of IDW, and 8.8 Sv of PDW flow southward to the Southern Ocean (Talley, 2013a). Once there, 4.9 Sv of NADW are upwelled to ultimately form SAMW and AAIW, while the remaining 12.7 Sv contributes to the CDW/AABW pool (Talley, 2013a; Fig. 3.1).

As IDW and PDW flow into the ACC, they mix into the UCDW layer and hence their sources become indistinguishable. Thus, to estimate the resultant concentration of DOC after mixing of these water masses in the Southern Ocean, the volume transports of IDW (15.7 Sv) and PDW (8.8 Sv) at 30°S (Talley, 2013a) were applied to the respective mean DOC concentrations (Table 3.2).

\[ [DOC_{I+P}] = \frac{15.7 \text{ Sv} \cdot [DOC_{IDW}] + 8.8 \text{ Sv} \cdot [DOC_{PDW}]}{15.7 \text{ Sv} + 8.8 \text{ Sv}} \]  

(3.1)
where \([DOC_{IDW}]\) and \([DOC_{PDW}]\) are the mean DOC concentrations in IDW and PDW at 20-40°S and \([DOC_{I+P}]\) is the concentration of DOC from the merged transports of these two water masses. Using this equation, and the mean concentrations of DOC between 20 and 40°S of IDW and PDW (Table 3.2), \([DOC_{I+P}] = 39.4\pm0.6 \mu\text{mol kg}^{-1}\).

DOC in the deep ACC is in turn a result of mixing between NADW and the IDW/PDW mixture, with their observed and estimated (immediately above) DOC concentrations, respectively. DOC in the deep ACC, subsequent to this mixing, is calculated here, where 12.7 Sv of NADW mixes with 16.3 Sv of the IDW/PDW mixture (Talley, 2013a). Given these transports, the concentration of DOC (\([DOC_{transports}]\)) in the deep ACC is estimated:

\[
[DOC_{transports}] = \frac{16.3 \text{Sv} \times [DOC_{I+P}] + 12.7 \text{Sv} \times [DOC_{NADW}]}{16.3 \text{Sv} + 12.7 \text{Sv}}
\]

(3.2)

where \([DOC_{NADW}]\) is the mean concentration of DOC in NADW between 20 and 40°S and \([DOC_{transports}]\) is the mean DOC concentration in the deep ACC estimated through these water mass transports (Table 3). Predicted DOC (\(DOC_{transports} = 40\pm2 \mu\text{mol kg}^{-1}\)), including propagation of an assumed 5% uncertainty in mass transports, is indistinguishable from the mean observed DOC (\(DOC_{meas} = 40.4\pm0.8 \mu\text{mol kg}^{-1}\)).

3.4.2. Simple Binary Mixing Model

A second test of the conservative behavior of DOC in the deep ACC is a two component mixing analysis for the water masses of interest. As there are in fact three end-members involved (NADW, IDW, PDW), the binary mixing model requires simplification of the system. Here we consider two distinct end-members: one originating from the Atlantic sector and one from the merged Indian-Pacific sector (all data from 20-
40°S). Salinity and $\gamma_0$ are essentially identical in southward flowing IDW and PDW (Table 2), so the DOC from the Indian-Pacific sector is estimated as one end-member (as in Orsi et al. 2002 in their considering AABW formation) using equation 1.

The fractions of the Atlantic ($F_A$) and the Indian-Pacific ($F_{I+P}$) end members are determined using salinity as the conservative tracer:

$$F_A = \frac{(S_{NADW}-S_{CDW})}{(S_{NADW}-S_{IDW+PDW})} \quad (3.3)$$

and

$$F_{I+P} = 1 - F_A \quad (3.4)$$

where $S_{NADW}$, $S_{CDW}$, and $S_{IDW+PDW}$ are the salinities of NADW (34.84±0.08), CDW (34.71±0.03), and IDW+PDW (34.65±0.07), respectively (Table 2). Using this method, $F_A = 36\%$ and $F_{I+P} = 64\%$.

The DOC concentration of CDW expected from this binary mixing was found as follows:

$$[DOC]_{binary} = F_A \times [DOC]_{NADW} + F_{I+P} \times [DOC]_{I+P} \quad (3.5)$$

where $[DOC]_{binary}$ is the concentration of DOC in CDW. In this case, the calculated and error propagated $[DOC]_{binary}$ is 40.1±0.6 µmol kg$^{-1}$, qualitatively the same as the mean measured DOC concentration (40.4±0.8 µmol kg$^{-1}$).

3.4.3. Multiple Linear Regression

Here a multiple linear regression (MLR) model (Bostock et al., 2013; Sabine et al., 2008; Wallace, 1995) establishes the relationship between measured DOC and observed hydrographic variables in the 3 primary end-members (NADW, PDW, and IDW). In this model, DOC observed on the CLIVAR sections (Fig. 3.2) is considered a result of linear mixing between these water masses, using conservative tracers $\theta$, salinity...
with a constant of 35 removed), $\gamma_n$, apparent oxygen utilization (AOU), and a constant offset ($\beta$). AOU was used in this case because it distinguishes IDW and PDW; both of these water masses have similar salinities and $\theta$, but the AOU in PDW is substantially higher than that in IDW.

\[
[DOC]_{MLR} = \alpha_1 \theta + \alpha_2 (S-35) + \alpha_3 (\gamma_n) + \alpha_4 (AOU) + \beta
\]  

where $[DOC]_{MLR}$ is the concentration of DOC predicted by the regression, $\alpha_1$, $\alpha_2$, $\alpha_3$, and $\alpha_4$ are the regression coefficients determined by a singular value decomposition, weighting the relative contributions of each parameter to the DOC concentration (coefficients given in Table 3.4).

Table 3.4. Coefficients and constant derived from the MLR, residual standard error (RSE; $\mu$mol kg$^{-1}$), and $R^2$ of the regression.

<table>
<thead>
<tr>
<th>$\alpha_1$ ($\theta$)</th>
<th>$\alpha_2$ ($S-35$)</th>
<th>$\alpha_3$ ($\gamma_n$)</th>
<th>$\alpha_4$ (AOU)</th>
<th>Constant</th>
<th>RSE</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.217</td>
<td>3.9841</td>
<td>-6.0161</td>
<td>-0.0210</td>
<td>213.4378</td>
<td>2.5</td>
<td>0.90</td>
</tr>
</tbody>
</table>

The predicted DOC concentrations ($[DOC]_{MLR}$) were 40.1±0.2 $\mu$mol kg$^{-1}$, 39.6±0.3 $\mu$mol kg$^{-1}$, and 39.2±0.1 $\mu$mol kg$^{-1}$ for UCDW, LCDW, and AABW, respectively, with a mean of 39.6±0.5 $\mu$mol kg$^{-1}$ (Table 3). This optimization includes all data reported from the CLIVAR Repeat Hydrography cruises shown in Fig. 3.2. MLR relies on variability in its predictors (i.e. salinity, $\theta$, $\gamma_n$, and AOU), which in the case of NADW, IDW, and PDW, is lacking because the ranges amongst these variables are narrow in the deep waters (Table 2). Thus, to generate a complete mixing curve, we used all data from the CLIVAR lines (Fig. 3.4A,B). The regression consisted of 10832 data with an $R^2$ of 0.90 (Fig. 3.4A, Table 3.4, p<0.001). The standard error for $[DOC]_{MLR}$ over the entire regression is 2.6 $\mu$mol kg$^{-1}$, while that for the deep Southern Ocean data alone
is 1.1 \(\mu\text{mol kg}^{-1}\) (Table 3.4). The greatest deviation of the residuals in the model occurs in the upper 1000 m (Fig. 3.4C).

![Figure 3.4](image)

**Figure 3.4.** A) Measured DOC vs. DOC predicted from the MLR of the whole water column. B) Measured DOC vs. DOC predicted from the MLR zoomed in to the deep DOC values. C) DOC residuals from the MLR (DOC\(_{\text{meas}}\)-DOC\(_{\text{MLR}}\)) versus depth in the water column. UCDW, LCDW, and AABW are highlighted in orange, green, and cyan, respectively.

3.5. Discussion

3.5.1. Conservative vs. nonconservative behavior of DOC in the Southern Ocean

The mass transport, binary mixing, and MLR calculations showed that DOC concentrations found in the deep Southern Ocean are equivalent to those expected given mixing and transport of NADW, IDW, and PDW. As evidence is absent for localized inputs having a large-scale, observable effect on the Southern Ocean DOC, DOC concentration there is apparently a conserved variable.
There was some evidence of relatively elevated DOC concentrations (>42 µmol kg\(^{-1}\)) in the circumpolar waters (described above): 13% of UCDW, 3.3% of LCDW, and 1.7% of the AABW were above 42 µmol kg\(^{-1}\). This elevation is evident in the MLR residuals versus depth, in particular in the upper layer (Fig. 3.4C orange symbols). As the UCDW layer was present as shallow as ~150 m, both vertical mixing and solubilization of sinking particles could be an explanation for these enhanced values. When the data from UCDW are constrained to depths >500 m, these elevated values essentially disappear, bringing the mean DOC from ~40.8±0.8 µmol/kg (N=372) to 40.1±0.8 µmol/kg (N=97).

The majority of the elevated values were on 2 of the 6 CLIVAR lines crossing the Southern Ocean (I08S and P16S); there were no elevated DOC values apparent in the deep circumpolar layers on S04P, SR03, A16S, or P18. The reason behind the elevated values on I08S and P16S could be either regional (local) anomalies or analytical errors. On I08S (Fig. 3.2), the elevated DOC observations appear in one region, from 58°S to 66°S, near the Amery shelf, suggestive of a localized input at the shelf break. Northward of 58°S, there are essentially no elevated DOC values, implying that if there is an enrichment of organic matter at the Amery shelf slope, it is diluted to the point beyond detection, or consumed, as observed in the Ross Sea (Chapter 2). We do not observe any local DOC enrichment in the Pacific or Atlantic sectors of the Southern Ocean near the Ross or Weddell Seas, which is consistent with previous studies that suggest that DOC produced on Antarctic Shelves during bloom events is consumed within its season of production (Kähler et al., 1997; Carlson et al., 1998, 2000).

On P16S (Fig. 3.2), the anomalous DOC values are more randomly scattered, and
perhaps more likely due to analytical imprecision. These few elevated DOC values are addressed by Follett et al (2014), and are used to illustrate the importance of sinking particle solubilization in modifying the Southern Ocean’s DOC concentration and isotopic composition. They proposed that 20 to 50% of sinking particles are solubilized to a semi-labile form of DOC that persists for decades, thus present to concentrations of 7-12 µmol kg$^{-1}$ on top of a refractory pool. They further suggest that in the Southern Ocean, this semi-labile pool is observable beyond background levels. In contrast, we find that the distribution of DOC in the Southern Ocean reflects linear mixing; the elevated DOC values noted by Follett et al. (2014) are not ubiquitous, and instead appear to be isolated (I08S and P16S; Fig. 3.2). Though there may be some localized elevation in the Southern Ocean, it is apparently regional and does not persist. We found no evidence for widely distributed inputs of DOC, with lifetimes of years or decades, by processes such as solubilization of sinking particles. Indeed, given the homogeneity of DOC in the deep Southern Ocean, it appears that bottom waters are not enriched, precluding a quantitatively important contribution by that process.

Sinking particles nevertheless are important sources of DOC to heterotrophic microbes at great ocean depths (Andersson et al., 2004; Nagata et al., 2010), including the deep Southern Ocean (Aristegui et al., 2002). As we are unable to analytically resolve an accumulation of bulk DOC due to this solubilization, we infer that most DOC released by sinking particles is consumed on a relatively short time scale. While there is evidence for DOC accumulation associated with sinking particles at great depths (e.g. traceable as fluorescent dissolved organic matter and as RuBisCO: Yamashita et al., 2010, and
Orellana and Hansell, 2012, respectively), it is apparently present at submicromolar concentrations, lying below the analytical resolution of bulk DOC measurements.

3.5.2. Addressing the radiocarbon age of Southern Ocean DOC

Early reports of whole water column $\Delta^{14}$C DOC profiles were from the western North Atlantic and the central North Pacific Oceans (CNP; Druffel et al., 1992), and the Southern Ocean (Druffel and Bauer, 2000). The radiocarbon age of DOC in the deep North Pacific is ~2000 $^{14}$C years older than in the North Atlantic. In the Southern Ocean, the radiocarbon content is similar to that of the North Pacific, thus perhaps being more depleted than expected given aging anticipated as the carbon moves with the deep limb of the meridional overturning circulation (Druffel and Bauer, 2000).

Studies that addressed this apparent discrepancy in the Southern Ocean’s radiocarbon suggested local inputs of radiocarbon depleted DOC as a cause. For example, Druffel and Bauer (2000) hypothesized that $^{14}$C-depleted DOC is introduced from the continental margin sediments, consistent with their interpretation of $^{14}$C gradients in the North Pacific (Bauer and Druffel, 1998). Through molecular composition analysis of DOM in the Weddell Sea and the Atlantic sector of the Southern Ocean, Lechtenfeld et al. (2014) suggested that advection and upwelling in high southern latitudes could cause enhanced sequestration of refractory DOC, explaining its nonconservative age. Follett et al. (2014) suggested that relatively $^{14}$C depleted DOC is added to the deep Southern Ocean by solubilization of sinking biogenic particles, themselves holding a depleted $^{14}$C signature due to formation with aged (upwelled) inorganic carbon, thus giving an aged radiocarbon signal. These studies all demonstrate
that the bulk DOC pool is comprised of multiple components, each with distinct molecular composition and isotopic character. They explain these findings through suggesting that a fraction of the bulk DOC pool is locally sourced.

But are local processes such as those proposed actually required to explain the radiocarbon content of DOC in the deep Southern Ocean? Could the conservative input of DOC carried by NADW, IDW, PDW, as described above, simply create the radiocarbon profile of the Southern Ocean? To assess this scenario, we first conduct a mass balance assessment on $\Delta^{14}C$-DIC, testing for the role of simple mixing in determining its value in the deep Southern Ocean, and then extend this assessment to $\Delta^{14}C$-DOC using the same calculations for volume transports as described above (Section 4.1).

We use $\Delta^{14}C$-DIC data of NADW and PDW reported in the Southern Hemisphere (south of 0°) from the CLIVAR lines A16, P16, and P18. In the mid southern latitudes of the Indian Ocean, an influx of 5 Sv of NADW, as well as mixing with overlying SAMW, enriches IDW with younger $^{14}C$ (Table 3.5; Fig. 3.5 top; Talley, 2013a). To account for these modifications, the $^{14}C$-DIC age for IDW prior to mixing with SAMW was taken between 0 and 20°S from CLIVAR I08S. The $\Delta^{14}C$-DIC data for the Southern Ocean deep waters were taken from CLIVAR lines A16S, P16S, P18, I08S, and S04P (at >50°S; Fig. 3.2).

The $\Delta^{14}C$ of DIC in the NADW is relatively younger than that found in IDW or PDW, and the values in the circumpolar layers reflect a mixture of these three water masses (Fig. 3.5 top). We find that NADW in the Southern Hemisphere has a $^{14}C$ age of
~800 $^{14}$C years (-106±16‰; Table 3.5), PDW has a $^{14}$C age of ~1800 $^{14}$C years (-202±17‰; Table 3.5) and IDW has a $^{14}$C age of ~1600 $^{14}$C years (-188±7‰; Table 3.5), agreeing with Stuiver et al. (1983).

Table 3.5. Water masses, number of samples per water mass (N), and mean $\Delta^{14}$C-DIC value (±standard deviation) for each water mass. Each water mass has been constrained using the same parameters as defined in Table 1, except their latitudinal constraints which are 0 to 50°S for NADW and PDW, 0 to 20°S for IDW, and >50°S for UCDW, LCDW, and AABW.

<table>
<thead>
<tr>
<th>Water mass</th>
<th>N</th>
<th>$\Delta^{14}$C-DIC (%)</th>
<th>$\Delta^{14}$C-DIC$_{transports}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NADW</td>
<td>47</td>
<td>-106±16</td>
<td></td>
</tr>
<tr>
<td>IDW</td>
<td>40</td>
<td>-188±7</td>
<td></td>
</tr>
<tr>
<td>PDW</td>
<td>85</td>
<td>-202±17</td>
<td></td>
</tr>
<tr>
<td>UCDW</td>
<td>79</td>
<td>-152±8</td>
<td></td>
</tr>
<tr>
<td>LCDW</td>
<td>89</td>
<td>-159±6</td>
<td></td>
</tr>
<tr>
<td>AABW</td>
<td>59</td>
<td>-158±9</td>
<td></td>
</tr>
<tr>
<td>Mean $\Delta^{14}$C in SO</td>
<td></td>
<td>-156±8</td>
<td>-155±13</td>
</tr>
</tbody>
</table>

In the deep Southern Ocean, the mean measured $^{14}$C-DIC age ranges narrowly around 1300 years old (-156±8‰ Table 3.3, Table 3.5). We find that the transport estimated (Equations 1 and 2) $^{14}$C age of the DIC in the Southern Ocean, given the uncertainty of the incoming NADW, IDW, and PDW, would likewise be ~1300 $^{14}$C years (or -155±13‰; Table 3.3, Table 3.5). These estimated and observed $\Delta^{14}$C-DIC values are the same; as such, the $^{14}$C-DIC ages in CDW reflect that of linear mixing of waters from the Atlantic, Indian, and Pacific.

As the $^{14}$C-DIC ages appear to follow the mass transport equations, we then extend our approach to $\Delta^{14}$C-DOC, for which there are far fewer data. $^{14}$C-DOC ages are available from the North Atlantic (Druffel et al., 1992), the South Atlantic (E. Druffel, pers. comm.), the SO (Druffel and Bauer, 2000), the South Pacific (Druffel et al., 2015), and the CNP (Druffel et al., 1992). $\Delta^{14}$C-DOC data do not exist in the Indian Ocean, so
our approach is to back-calculate the $\Delta^{14}$C-DOC range required in IDW to replicate the observed radiocarbon in the Southern Ocean, as balanced by inputs from the Pacific (PDW) and the Atlantic (NADW), described in Section 4.1. If the estimate for the IDW is as one might expect given its location in the global thermohaline circulation, then the Southern Ocean DOC can be taken to have a radiocarbon content as expected by linear mixing.

**Figure 3.5.** Top: $\Delta^{14}$C-DIC (‰) of NADW (blue), IDW (red), PDW (grey), UCDW (orange), LCDW (green), and AABW (cyan) versus latitude in the Southern Hemisphere. The latitudinal constraints employed in the $\Delta^{14}$C-DIC data are listed in Table 5; these data were obtained from the CLIVAR cruises listed in Section 5.2 (cruise tracks in Fig. 2.2). Bottom: Mean $\Delta^{14}$C-DOC (‰; ± standard deviation; bottom) of the deep Atlantic (blue; E. Druffel pers. comm.), Indian (red; estimated in Section 5.2), Pacific (grey; Druffel et al., 2015), and Southern (green; Druffel and Bauer, 2000) Oceans versus latitude in the Southern Hemisphere.
Given the radiocarbon age of DOC within PDW of the South Pacific, ranging from ~5500 to 6300 $^{14}$C years old (-524±13‰ (N=27); Druffel et al., 2015, Fig. 3.5 bottom), the age of NADW of the South Atlantic, ~5100 $^{14}$C years old (-471±9‰ (N=19); Druffel et al., 2016, Fig. 3.5 bottom), and Southern Ocean values ranging between 5200 to 5800 $^{14}$C years old (-501±12‰ (N=16); Druffel and Bauer, 2000, Fig. 3.5 bottom), mass balance requires that the deep IDW $^{14}$C age ranges between 5300 to 6300 $^{14}$C years old (-524±26‰; Fig 3.5. bottom). The result of this calculation is that DOC in the IDW should be older than that in the South Atlantic (i.e., NADW alone) and similar if not slightly younger than in the Pacific. As IDW has as its sources CDW and NADW, the estimate may be reasonable, as DOC in IDW has an estimated radiocarbon content lying between NADW and PDW. If this calculation of the IDW radiocarbon content in DOC in fact reflects the system, then we infer that the $\Delta^{14}$C DOC values in the deep Southern Ocean are simply a result of conservative inputs from NADW, PDW and IDW.

3.6. Conclusion

Here we tested for the conservative behavior of DOC in the circumpolar waters of the Southern Ocean. We do not observe locally added DOC to persist in the deep layers, nor do we observe local sinks. Instead, the DOC distributions result from linear mixing of the Atlantic, Indian, and Pacific deep waters. While the scarcity of radiocarbon data of DOC from all ocean basins is problematic and requires future investigation, the radiocarbon-depleted character of DOC found in the Southern Ocean is consistent with conserved inputs.
Chapter 4. Radiocarbon Content of Dissolved Organic Matter in the South Indian Ocean

4.1. Background

Radiocarbon signatures provide information on the lifetime of the DOC pool and are thus crucial for understanding the pool’s dynamics. Previously published $^{14}$C data indicate that the mean age of deep DOC ranges from ~4000 in the North Atlantic to ~6500 $^{14}$C years in the North Pacific (Druffel et al., 1992, 2015; Zigah et al., 2017), suggesting that DOC persists in the ocean’s deep layers for millennia. However, this age range is estimated from relatively few water column profiles in the global ocean. Radiocarbon profiles have not previously been reported for the Indian Ocean. It is an important system as its deep waters comprise ~35% of the source waters to the circumpolar waters in the SO, the abyssal waters of all major ocean basins (Schmitz, 1995; Talley, 2013). Here, we present four profiles of radiocarbon of DOC in the South Indian Ocean (SIO), finding that radiocarbon ages of DOC there are distinguishable by water mass and largely reflect those expected based on water mass transports. These $^{14}$C-DOC ages from the SIO help to understand the $^{14}$C-DOC ages in the deep Southern Ocean.

The SIO is surrounded by the African and Australian continents. The Agulhas Current (the western boundary current of the SIO) flows poleward, opposite to NADW, CDW, and AABW (Gordon, 1985; Schmitz, 1995; Beal et al., 2006). NADW (identified by its high salinity core) exits the Atlantic south of Africa and a portion of it flows into the southwest Indian Ocean, poleward of the Agulhas Current, where it joins the Indian’s CDW layer (Talley, 2013). As the Indian Ocean is surrounded by continents northward of tropical latitudes, this CDW layer flows into the North Indian Ocean (NIO), entraining local intermediate waters to form IDW. IDW flows back towards the SO,
ultimately contributing to both the Antarctic Intermediate Water (AAIW)/SAMW and the CDW water masses (Talley, 2013). AAIW and SAMW lay above the CDW isopycnal (Fig. 4.1B); while AAIW is primarily derived from SO waters, SAMW has inputs from subtropical surface water (SSW), indicated by its higher salinity. These warm and saline SSW are largely formed in the SIO basin (Beal et al., 2006), reflecting the excess evaporation over precipitation characteristic of subtropical gyre systems (Fig. 4.1B).

DOC concentrations in the deep Indian Ocean are homogenously low, reflecting a mixture of their NADW and CDW source waters and showing no lasting signature of the exported surface-derived organic material (Hansell and Carlson, 1998; Doval and Hansell, 2000, Hansell, 2009, Hansell et al., 2009). IDW plays a substantial role in CDW formation, accounting for ~35% of the total pool (Schmitz, 1995; Talley, 2013). Consequently, DOC concentrations in CDW reflect a mixture of IDW, NADW, and PDW. Our understanding of the DOC in the cycle of the Indian Ocean is incomplete, and radiocarbon measurements will improve our knowledge of the system.

4.2. Methods

4.2.1. Sampling for \(^{14}C\)-DOC

Samples were collected aboard the RV Revelle in the austral summer of 2016 during the occupation of line I08S by the Global Ocean Ship-Based Hydrographic Investigation (GO-SHIP) program (Fig. 4.1A; all data available in Tables S1-S4; MacDonald et al., 2017). Samples (~850 mL) were collected into 1-L pre-combusted amber glass bottles and immediately frozen at -20ºC. Upper layer samples (those samples from depths<450 m) were filtered with 0.7 µM combusted GF/F filters to remove
particulate organic material. To ensure that there was no $^{14}$C contamination aboard the RV Revelle, SWAB tests (University of Miami) were conducted prior to departure to test for broad, high levels of $^{14}$C contamination aboard the ship. Swipe tests (Woods Hole Oceanographic Institute, WHOI) were conducted on the Niskin bottle spigots and air-valves at two of the stations where $^{14}$C-DOC was sampled (stations 30 and 70) to test for any low level of $^{14}$C contamination on our sampling equipment. Both SWAB and swipe tests came back clean.

4.2.2. Radiocarbon analyses

All $^{14}$C-DOC samples (45) were processed at the National Ocean Science Accelerator Mass Spectrometer (NOSAMS) at WHOI. Thawed samples were acidified to pH 2 with phosphoric acid and purged with helium gas to remove inorganic carbon. Organic carbon was extracted from the water samples using UV-oxidation and cryogenic extraction (following the method of Beaupré et al, 2007). The resultant carbon (in the form of CO$_2$) was converted to graphite with H$_2$ on an iron catalyst and the $^{14}$C atoms were counted using the AMS (Longworth et al., 2015; McNichol et al., 2004; Roberts et al., 2010). Instrumental precision on radiocarbon samples based on standard errors and multiple analyses ranges from 2-5‰ (~20 to 50 $^{14}$C years). The mean extraction efficiency (CO$_2$ recovered via cryogenic extraction divided by DOC concentration $\times$ 100) of the radiocarbon data here is 99±5%.
Figure 4.1. A.) Map depicting the 2016 occupation of the GO-SHIP I08S line. Black stations represent all I08S stations, yellow stations represent those stations where samples for $^{14}$C-DOC analyses were collected. B.) Section plot of salinity along I08S. IDW is identified with AOU (~150 μmol kg$^{-1}$), and is isolated in the contour. Labeled deep water masses include the northward flowing CDW, the southward flowing IDW, and NADW originating from south of Africa (Talley, 2013). The labeled subsurface water masses are AAIW and SAMW and SSW. C.) Section plot of MLR-predicted radiocarbon age with observed radiocarbon age overlaid in colored circles. The black contours represent the practical salinity of the NADW core (34.75).
4.2.3. Hydrographic measurements and DOC

Salinity, temperature, and oxygen data were processed by the Scripps Oceanographic Data Facility and are publicly available at the GO-SHIP Carbon Hydrographic Data Office (CCHDO) website (https://cchdo.ucsd.edu/) (MacDonald et al., 2017). Apparent oxygen utilization (AOU) was calculated by subtracting measured oxygen from the saturation value computed at the potential temperature ($\theta$) of the sample and 1 atm total pressure (Murray and Riley, 1969). DOC samples were collected into glass vials and acidified with HCl onboard; surface samples (depth<250 m) were filtered with pre-combusted 0.7 µM GF/F filters. DOC measurements were made in the lab (Carlson Lab, UC Santa Barbara) by high temperature combustion (Dickson et al., 2007), and quality controlled using carbon reference material (Hansell Lab, U. Miami).

4.3. Results and Discussion

The radiocarbon results reported here are from distinct water masses and latitude-dependent attributes, spanning from the Polar Front (PF) at 56°S to the subtropics at 29°S (Fig. 4.1, Fig 2A). Data relevant to this analysis are provided in Tables S1 through S4. In this section, we report radiocarbon results in terms of Radiocarbon Ages (Stuiver and Pollach, 1977); however, per mil values are available for each age in Tables S1-S4.

4.3.1. Radiocarbon age of DOC in SIO surface waters

The surface distribution of radiocarbon reflects the difference in latitudes between the four stations occupied (Fig. 4.2A). At the PF, (Station 30; Fig. 4.1A; Table S1), mean salinity was 33.79±0.07, and $\theta$ ranged from 1.5 to 2.3°C (Table S1). DOC concentrations
were ~42 µmol kg\(^{-1}\) and the radiocarbon ages ranged from 4390 to 4420 (mean of 4405±21 \(^{14}\)C years; Table S1). Surface waters at the PF derive from aged, upwelled water; as such, DOC concentrations in surface waters in the SO are uniformly low (Ogawa et al., 1999; Hansell et al., 2009). This uniformity is observed in the radiocarbon data as well. The surface ages are slightly older than those reported at a similar latitude in the Pacific Sector of the SO (3986±156 \(^{14}\)C years; profile taken at 54ºS, Druffel and Bauer, 2000). These different ages are likely due to phytoplankton blooms in the SO, which are seasonally and interannually variable. The samples reported here were collected in late February, whereas those previous data were collected in late December. The Pacific samples were collected when the average DOC concentrations were 50±2 µmol kg\(^{-1}\) (N=6, d>250; Druffel and Bauer, 2000), whereas the average DOC concentrations reported here only reached ~42 µmol kg\(^{-1}\) (Table S1). The higher concentrations in the Pacific likely reflected increased primary production, a source of more modern carbon. Past studies used satellite chlorophyll data to show that blooms are generally strongest in December (the austral summer) (Sullivan et al., 1993; Borrione and Schlitzer, 2013). Late February is after the main phytoplankton bloom has occurred.

Near the Subantarctic Front (SAF; Station 52; 45ºS; Fig. 4.1A), there was more stratification in both the physical and biogeochemical variables (Fig. 4.1B). Waters in the upper 150 m had salinities of ~34, θ of ~10ºC, DOC concentrations of 46 to 49 µmol kg\(^{-1}\), and radiocarbon ages ranging from 3600 to 3700 \(^{14}\)C years (3650±14 \(^{14}\)C years, N=3; Table S2). In the subtropical SIO (Stations 70 and 82 at 35º and 29ºS, respectively) surface waters were warm and stratified. The surface layer salinities reached ~36 with DOC concentrations ranging from 60 to 70 µmol kg\(^{-1}\) (Fig. 4.1B; Tables S3 and S4).
Surface values of radiocarbon in the SIO subtropical gyre (upper 50 m) ranged from 2000 to 2340 $^{14}$C years and reflect those $^{14}$C ages in subtropical gyres of other ocean regions. In the subtropical North Atlantic, surface values were $\sim$1979±236 $^{14}$C years (Druffel et al., 1992). In the subtropical CNP, the radiocarbon ages measured in the late 1980’s were between 1506 and 2404 $^{14}$C years (Druffel et al., 1992). Recently, in the surface waters north of Hawaii, ages ranged from $\sim$1526 to 2210 $^{14}$C years old (Walker et al., 2011, 2016; Follett et al., 2014; Zigah et al., 2017); these results show that subtropical surface waters in all major ocean basins have similar $^{14}$C ages.

4.3.2. Radiocarbon ages of DOC in deep water masses of the SIO

While the surface radiocarbon ages changed with latitude along 108S, the hydrographic variables, DOC concentrations, and radiocarbon ages within the deep water masses showed greater homogeneity (Fig. 4.1C). Mean salinity in combined CDW/AABW at 56ºS was 34.69 (±0.03) while $\theta$ ranged from -0.3ºC in AABW to 2.2ºC in CDW (Table S1). DOC concentrations were uniformly $\sim$39 µmol kg$^{-1}$ and radiocarbon ages ranged from 4680 to 5670 $^{14}$C years (5290±289 $^{14}$C years; Table S1; Fig. 4.1C; Fig. 4.2A). One sample in CDW at 1047 m had an anomalously young age of $\sim$4680 $^{14}$C years, which is taken to be an artifact of sampling (see further consideration in Section 3.4). Excluding that value, the mean age of the CDW pool was 5359±178 $^{14}$C years. These data are similar to those from the Pacific sector of the SO, where radiocarbon ages ranged between 5200 and 5800 years (5526±39 $^{14}$C years, Druffel and Bauer, 2000). Reported radiocarbon ages of DOC in CDW are homogenous, reflecting the massive pool of CDW surrounding Antarctica.
At 45°S, CDW was largely absent because sampling was done above the relatively shallow (~3000 m) Southeast Indian Ridge. The deep waters present at <3000 m (NADW) had θ of 2-3°C, and DOC concentrations of ~39 µmol kg⁻¹ with a mean radiocarbon age of 5191±91 ¹⁴C years (N=5; Table S2). NADW enters the southwest Indian Ocean at 5 Sv (Talley, 2013), evident as a high salinity core (Fig. 4.1B) with relatively younger ¹⁴C-DOC ages (Fig. 4.1C). NADW in the South Atlantic, upstream of our sampling, had an age of 5056±30 ¹⁴C years (Druffel et al., 2016); the ages in the SIO are slightly older than those in the South Atlantic (Fig. 4.1B, C; Table S2, S3; Fig. 4.3), consistent with aging of the water mass downstream from its source. In the deep subtropics (Stations 70 and 82), DOC concentrations in CDW (with a NADW imprint) were ~39 µmol kg⁻¹ and the mean age was 5323±156 ¹⁴C years (N=4), a few hundred years older than at 45°S.

Figure 4.2. Depth profiles of radiocarbon age (¹⁴C years).
IDW was distinguishable in the SIO subtropical gyre stations between ~1500-2700 m, evidenced by its relatively high AOU (>150 µmol kg$^{-1}$; Fig. 4.1B, Table S3); DOC concentrations in IDW were ~39 µmol kg$^{-1}$ and radiocarbon ages were the oldest observed at 5695±310 $^{14}$C years (N=7; Tables S3 and S4). At 29ºS, sampling was over a ridge, so the water column reached only ~2700 m, and the deepest waters collected were IDW (Fig. 4.1B; Table S4). The radiocarbon age of the deepest sample at this station was ~6310 $^{14}$C years, anomalously older than the other ages of IDW (discussed further in the following section). The mean $^{14}$C-DOC age in IDW at that site is 5557±81 $^{14}$C years (N=7, Table S4) when excluding the anomalous value.

As IDW is the return flow of CDW upwelled along its route to the NIO, it characteristically is an older water mass (Talley, 2013), with a high AOU due to oxygen minima originating from the north (Fig. 4.1B). DOC of IDW has a younger age in comparison to PDW in the South Pacific (~5900±40 $^{14}$C years; N=27; Fig. 4.3; Druffel et al., 2015), likely due to shorter residence time (Stuiver et al., 1983; Matsumoto, 2007). We find that radiocarbon ages of IDW were significantly older than its source water CDW (t-test p=0.002; Fig. 4.1C).

4.3.3 Assessing $^{14}$C-DOC age of the SO

CDW in the SO has IDW, NADW, and PDW as its sources (Talley, 2013) and DOC concentrations there reflect these inputs (Bercovici and Hansell, 2016). However, a dearth of data have prevented a similar analysis for $^{14}$C-DOC ages in the SO. Bercovici and Hansell (2016) used mass balance of $^{14}$C-DOC ages of CDW (5520±40 $^{14}$C years; Druffel and Bauer, 2000), NADW (5056±30 $^{14}$C years; Druffel et al., 2016), and PDW
(5904±47 $^{14}$C years, Druffel et al., 2015), and the transports of those water masses (Schmitz, 1995; Talley, 2013), to predict $^{14}$C-DOC ages in IDW.

**Figure 4.3.** Scheme depicting SO water mass mixing of differently-aged waters in the Atlantic, Pacific, and Indian Oceans surrounding Antarctica. The black curves around Antarctic represent the movement of the CDW pool along the ACC. The red, purple, and green curves are PDW, NADW, and IDW entering the CDW pool. The age of CDW, ~5400 $^{14}$C years, reflects a mixture of these three incoming water masses, and flows out in each of these major basins (depicted by the orange arrows). The colored dashed lines in each ocean represent the mixing or upwelling of CDW into the return-flow water mass.

Our previous analyses estimated that if DOC in the SO system is largely conserved, IDW values needed to lie between ~5300 and 6300 $^{14}$C years. Values observed in IDW in this analysis had a mean of 5557±81 $^{14}$C years, falling within the
predicted age. Given that we now have observed ages of NADW, IDW, and PDW, we can use the same approach to re-estimate the radiocarbon age of the SO as the unknown. To estimate the radiocarbon content of the SO, the equation (adapted from Talley, 2013) is therefore:

\[
[D Omar^14 C_{CDW}] = \frac{16.3 \text{ Sv} [D Omar^14 C_{I+P}] + 12.7 \text{ Sv} [D Omar^14 C_{NADW}]}{16.3 \text{ Sv} + 12.7 \text{ Sv}}
\] (4.1)

where \(D Omar^14 C_{CDW}\) is the estimated radiocarbon content (in parts per thousand, \(^\circ\); Stuiver and Polach, 1977) of DOC in the Southern Ocean, \(D Omar^14 C_{NADW}\) is the observed radiocarbon content of NADW, and \(D Omar^14 C_{I+P}\) is the observed radiocarbon content of IDW and PDW, which is defined as:

\[
[D Omar^14 C_{I+P}] = \frac{15.7 \text{ Sv} [D Omar^14 C_{IDW}] + 8.8 \text{ Sv} [D Omar^14 C_{PDW}]}{15.7 \text{ Sv} + 8.8 \text{ Sv}}
\] (4.2)

where \(D Omar^14 C_{IDW}\) and \(D Omar^14 C_{PDW}\) are the estimated radiocarbon values of DOM in IDW and PDW, respectively. The estimated age of \(D Omar^14 C_{I+P}\) is 5682±94 years (-511±19\(^\circ\)) and the estimated age of \(D Omar^14 C_{CDW}\) is 5408±98 years (-494±20\(^\circ\)), consistent with our observed mean \(^{14}\)C-DOC age in CDW at 56\(^\circ\)S (5359±178 \(^{14}\)C years, -491±30\(^\circ\); Fig. 4.3). These results imply that \(^{14}\)C-DOC ages in the SO reflect a mixture of their source waters (NADW, PDW, IDW), rather than local processes, control the ages observed (Fig. 4.3).

4.3.4. MLR of radiocarbon data in the SIO

To assess whether \(^{14}\)C-DOC ages reflect local or remote controls, an MLR with salinity, \(\theta\), and AOU as our predictors was employed, following Bercovici and Hansell (2016). The reason AOU was used in this MLR is described in Chapter 2 and is used to differentiate between IDW and PDW. The MLR equation is:
\[ [\text{14C Age}]_{MLR} = a_1 \times \theta + a_2 \times sal + a_3 \times AOU + \beta \] (4.3)

where \( \theta \) is in degrees, \( sal \) is the practical salinity, \( a_1-a_3 \) are the weights of each component, and \( \beta \) is the y-intercept. With these data, \( a_1 \) is -69, \( a_2 \) is -419, \( a_3 \) is 9, and \( \beta \) is 18729. With these parameters, we modeled a \(^{14}\text{C}-\text{DOC} \) age controlled by mixing. The observed radiocarbon ages showed good agreement with the modeled radiocarbon ages (slope=1, \( R^2 = 0.95, p<0.001; \) Fig. 4.4).

This outcome indicates that \(^{14}\text{C}-\text{DOC} \) ages in the deep SIO largely follow conserved processes; the ages are not made demonstratively younger or older by processes beyond simple linear mixing and in situ aging. When looking at deep water masses, the observed age of CDW (5302±160 \(^{14}\text{C} \) years) is not significantly different than the MLR-predicted age (5336±63 \(^{14}\text{C} \) years; t-test \( p=0.26 \)). The mean observed age of IDW (5562±81 \(^{14}\text{C} \) years) is also not significantly different than the mean predicted age of IDW (5481±128 \(^{14}\text{C} \) years; t-test \( p=0.24 \)).

At the surface, the MLR-predicted ages are quite similar to observed ages (Fig. 4.1C). Near the PF, where the observed surface water has a \(^{14}\text{C}-\text{DOC} \) age of 4405±21 years, the predicted age is 4402±73 \(^{14}\text{C} \) years. The SAF \(^{14}\text{C} \) ages at 45°S are similar as well; the mean age is 3650±14 \(^{14}\text{C} \) years while the mean predicted age is 3747±6 \(^{14}\text{C} \) years. The range in ages in subtropical surface waters also reflects the MLR-predicted ages (Fig. 4.1C).

Due to the good agreement between the observed and MLR-predicted radiocarbon ages (Fig. 4.4), the predicted radiocarbon distribution across the SIO basin can be visualized (Fig. 4.1C). However, due to the first-order decay of radiocarbon, this type of linear analysis cannot be interpreted on a global scale. In this particular analysis, we use
MLR because of the relatively small scale. More specifically, a parcel of deep water formed near Antarctica will re-surface back at the Polar Front after 335 years in the Indian Ocean (Stuiver et al., 1983). Thus, given the meridional extent of the Indian Ocean (from Antarctica at ~60ºS to near ~10ºN near India), a parcel of water would take roughly ~2 years to cross one latitudinal degree. Further studies using CFC ages suggest that a parcel of AABW may move even faster into the SIO basin; these studies report a transit time into the Crozet basin (at ~32ºS) to be between 15 and 25 years (Fine, 1993; Haine et al., 1998).

![Graph](image_url)

**Figure 4.4.** Observed radiocarbon age vs. MLR-predicted radiocarbon age of all samples. With a slope of 1, $R^2=0.95$ (p<0.001).

Given that our analysis covers ~20º in latitude (50ºS to 30ºS), this aging effect would be ~40 years. That timeframe is not huge in comparison to the error of the $^{14}$C measurement (2 to 5‰, ~25 years) and to the age differences between water masses of interest (i.e. the ~300 year difference between the $^{14}$C age of DOC in CDW and IDW).
In this case, there's a high correlation (R²=0.95, p<0.001) between the observed and modeled ¹⁴C ages, so the aging effect is small, and the ~300 ¹⁴C year offset between IDW and CDW reflects the ~300 year lifetime of a parcel of water in the deep Indian Ocean.

In this analysis, the MLR approach can be used to identify deviations between predicted and observed values caused by processes such as inputs from hydrothermal vents (Druffel et al., 2015) or solubilization of sinking particles (Follett et al., 2014). There are two areas that may reflect these processes; the single relatively modern age (4860 years at depth=1047; Table S1) in CDW at 56°S and the one anomalously old carbon (6310 years at 2647 m; Table S4; Fig. 4.1C) in the IDW pool at 29°S. We cannot discount these anomalous values as being due to sampling or analytical errors. However, it is interesting to speculate that these anomalies could be due to local processes.

Particle export and solubilization was proposed as a mechanism for enhancing deep DOC concentrations in the SO (Follett et al., 2014). The relatively modern ¹⁴C age at ~1000 m could be due to such particle solubilization. Sinking particles would have a modern ¹⁴C age and could explain this anomaly. In the SO, this modern radiocarbon age would reflect the age of DI ¹⁴C in the surface waters, which is roughly -50 to -100‰, or ~300 to 800 ¹⁴C years old. The age of this anomalously young sample is 4680 ¹⁴C years with a DOC concentration of 39.5 µmol kg⁻¹ (Table S1). The mean age and DOC of CDW with this sample removed is 5331±168 ¹⁴C years and 39.1±0.5 µmol kg⁻¹, respectively. Given the difference in age (650 ¹⁴C years), the difference in DOC concentration (0.4±0.5 µmol kg⁻¹), and the estimated ¹⁴C age of modern DOC (-50 to 100‰), we use a simple mass balance to assess whether this shift in age would be observable in the DOC concentration as well. This simple mass balance would require a
~2 to 4 µmol kg\(^{-1}\) modern DOC addition to shift the age from 5331 to 4680 \(^{14}\)C years. However, there is no observable enrichment of the DOC concentration in the anomalous sample and the others.

The second deviation between predicted and measured values is the very old age in the deepest sample at 29ºS, collected at the Broken Ridge (Fig. 4.1). It is possible that at these ridges, DOC ages are older due to a hydrothermal influence or re-suspension of ancient sedimentary material (Druffel et al., 2015; Bauer and Druffel, 1998). For this one sample there are no characteristic biogeochemical features of a vent system (i.e. silicic acid, temperature, or salinity anomalies) that would indicate substantial hydrothermal influence at this site. Without further biogeochemical data, it is not possible to tell whether this datum is an artifact.

4.3.5. Addressing multiple age classes within bulk DOM

Even though the radiocarbon ages of DOC in the SIO appear to be largely controlled by water mass mixing, local inputs are likely occurring ephemerally. Our interpretation of these data is that as a whole, the bulk DOC age and concentrations reflect linear mixing, and thus behave conservatively. However, recent studies report that the deep DOM pool is highly dynamic (Follett et al. 2014; Druffel et al., 2015; 2016) and a complex mixture of compounds with various ages and reactivities (Walker et al., 2011; 2016; Loh et al., 2004; Zigah et al., 2017; Flerus et al., 2012; Lechtenfeld et al., 2014). With our dataset, we are unable to assess the complexity of the DOM pool in the SIO. Still, we find that in the SIO, the bulk \(^{14}\)C-DOC age reflects large-scale meridional overturning circulation. With these new \(^{14}\)C-DOC data from the SIO, we are able to
differentiate the ages of different water masses; IDW is significantly older than underlying CDW, and the high-salinity NADW core observed in the transect is has a younger $^{14}$C-DOC age (Fig. 4.1B, 4.1C). It has been challenging to reconcile the interpretation of bulk $^{14}$C-DOC age with the interpretation of separate DOM fractions. Furthermore, given our current state of knowledge, the same observations (such as $^{14}$C-DOC age in the SO) are being interpreted in vastly different ways. Future work should strive for a common ground to explain why the bulk DOC pool behaves conservatively, yet the separate components of DOM provide insights as to a more dynamic system.

4.5. Conclusions

We present the first $^{14}$C-DOC age distributions in the SIO. The age gradients between IDW and CDW are consistent with their respective downstream locations as regards the MOC. Furthermore, the high-salinity NADW core in the SIO has younger $^{14}$C-DOC ages, consistent with earlier observations in the South Atlantic.
4.6. Supplemental Tables

Table S4.1. Hydrographic and radiocarbon age data for station 30, at 55.6°S, 84.7°E (N=12).

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<th>[DOC] (µmol kg⁻¹)</th>
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(N=12)

Table S4.2. Hydrographic and radiocarbon age data for station 52, at 45.0°S, 95.0°E (N=10).

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**Table S4.3.** Hydrographic and radiocarbon age data for station 70, at 35.0°S, 95.0°E (N=12)

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**Table S4.4.** Hydrographic and radiocarbon age data for station 82, at 28.9 °S, 95.0°E (N=11)

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CHAPTER 5: Ageing and Molecular Changes of Dissolved Organic Matter Between Two Deep Oceanic End Members

5.1. Background

DOM is primarily derived at the surface ocean via primary production where it is either directly released into the water column or solubilized via heterotrophic consumption of particulate organic material (Carlson and Hansell, 2015). Although DOM is produced in the euphotic zone, >95% is contained in the dark ocean, where it survives multiple meridional overturning circulations (Druffel et al., 1992). However, the turnover time and overall fate of this large, deep pool are largely unknown. In this analysis, we look at the cycling of the deep pool of marine DOM using isotopic and compositional signatures.

The DOM pool is considered to be dynamic, consisting of multiple components (Loh et al., 2004; Repeta and Aluwihare, 2006; Walker et al., 2011; Follett et al., 2014; Zigah et al., 2017). Observations suggest small dissolved molecules are the most highly aged forms of organic matter and have much older radiocarbon ages than the larger components of the DOM pool (Loh et al., 2004; Walker et al., 2011; Benner and Amon, 2015). A recent study by Zigah et al. (2017) show that components of DOM separated by size and polarity have different isotopic signatures, ranging from neutral sugars with modern radiocarbon ages, to ancient (>10,000 years) hydrophobic, low molecular weight material.

Recently, the analytical capabilities of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) have allowed for advances in understanding the relationship between molecular composition of solid-phase extracted DOM (SPE-DOM)
and its $^{14}$C age ($^{14}$C-SPE-DOM). Two prior studies spanning the Atlantic Ocean provided a comprehensive ultra-high resolution dataset that coupled radiocarbon and molecular composition (Flerus et al., 2012; Lechtenfeld et al., 2014). These studies isolated the specific molecular formulae present in an FT-ICR-MS spectrum that correlated with radiocarbon age. Lechtenfeld et al. (2014) developed a first order degradation model between radiocarbon and individual molecular formulae. They suggested that there are some formulae within DOM that have a much longer residence time in the water column than the age of the bulk DOC pool would otherwise indicate. Using these greater residence times of the molecules in DOM, Lechtenfeld et al. identified ~361 molecular formula comprising the ‘island of stability’ (IOS), a group of compounds representing the most stable molecular composition in DOM in the Atlantic Ocean.

In this study, we extend the Lechtenfeld et al. model to SPE-DOM samples from the far North Pacific, where deep bulk DOM concentrations are at their lowest and radiocarbon ages at their oldest. We couple molecular composition of SPE-DOM with its radiocarbon age to determine the intrinsic stability of DOM in the far North Pacific.

5.2. Methods

Samples were collected on the Deep Ocean Refractory Carbon cruise (DORC; MV-1310) aboard the RV Melville in August 2013. Cruise station occupations are shown in Fig. 5.1; stations where SPE-DOM samples were collected are in pink. On this cruise, the only deep water mass present was Pacific Deep Water; as such, samples in this analysis will be distinguished by depth as opposed to by water mass. Below we describe the methods for each parameter discussed in this manuscript.
5.2.1. DOC measurements

DOC samples were collected from the Niskin bottles by in-line filtration through pre-combusted 0.7 µM GF/F filters. Measurements at depths >250 m were done on unfiltered water, but are representative of the DOC pool as POC typically makes a minor contribution at these depths (<1 µM). DOC was measured by high temperature combustion using a Shimadzu TOC-L with auto-injection (precision of +/- 1.5 µmol/kg) (Dickson et al., 2007). DOC measurements were quality controlled using Consensus Reference Material (CRM), distributed to the international oceanographic community by the Hansell laboratory. Low C and N reference water was employed to determine system blanks.

5.2.2. Sampling for Solid Phase Extraction (SPE)

Water samples were collected with a CTD at 5 m, 50 m, 1000 m, 2000 m, 3000 m water depth, and a few meters above the seafloor. 8 L of sample were filtered using 0.2 µm Supor filters, and acidified to pH 2 with high purity hydrochloric acid. SPE was performed on 1 g Mega Bond Elut PPL (Varian) cartridges (following the protocol of Dittmar et al., 2008). The SPE samples (SPE-DOM) were eluted in 8 mL of methanol and stored at -20°C until analysis.
Figure 5.1. Map of stations occupied by the RDOC cruise in the Gulf of Alaska. Pink dots show where samples were collected for this analysis.

5.2.3. Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS)

SPE-DOM samples were analyzed at the Helmholtz Facility in Munich, Germany, using a FT-ICR-MS (Apex Qe, Bruker Daltonics, Billerica, MA), equipped with a 12 T refrigerated actively shielded superconducting magnet (Bruker Biospin, Wissembourg, France). An Apollo II dual electrospray source source (ESI, Bruker), was used in negative ion mode (capillary voltage: -4200 V, infusion flow rate: 2 mL min\(^{-1}\)). Prior to measurement on the FT-ICR MS, extracts were diluted with methanol to obtain the same SPE-DOM concentration for all aliquots. The mass range of 147 to 2000 m/z was used with 512 scans per spectrum; the acquired spectra were externally calibrated with arginine clusters. These measurements were conducted to obtain high resolution mass spectra of the DOM samples collected in the NP.
Ions were singly charged and spectra were evaluated in the range of 200 to 600 mass to charge ratio (m/z) according to prior studies (Flerus et al., 2012, Lechtenfeld et al., 2014). This m/z represents the nominal mass depicted from the FT-ICR-MS divided by the charge of the ion. As ions were singly charged in this study, m/z in this case can be estimated as molecular weight. Molecular formulae were calculated from the m/z values with the same algorithm as described in Lechtenfeld et al. (2014). Relative peak magnitudes were normalized by calculating the mass peak magnitude divided by the summed magnitude of all mass peaks; only mass peaks having a normalized magnitude >0.005% were considered in this analysis. An initial quality control check was conducted to remove potential surfactants.

5.2.4. $^{14}$C measurements

Aliquots of the SPE methanol extracts (~0.15 mL) were transferred to pre-combusted Pyrex tubes (6 mm diameter). This tube then was transferred to a 1 cm diameter quartz tube, where solvent was removed of solvent under vacuum. Each sample was washed with milliQ ultrapure water and ultrapure methanol. The tube was flame sealed under vacuum and combusted to CO$_2$ at 750°C with a CuO/Ag catalyst (Sofer, 1980). The CO$_2$ was subsequently reduced with H$_2$ to graphite over a Co catalyst at the National Ocean Sciences Accelerator Mass Spectrometer (NOSAMS) facility at Woods Hole Oceanographic Institution (Woods Hole, MA). SPE DOC blanks did not yield any detectable amount of carbon (<1 nM C).
5.3. Results and Discussion

5.3.1. Bulk DOC concentrations and SPE-DOM radiocarbon ages

Bulk DOC concentrations of our samples collected for $^{14}$C content in the far North Pacific ranged from 36 to 71 $\mu$mol kg$^{-1}$ (Fig. 5.2A). In the surface layer (depths $\leq$ 50 m, N=8), DOC ranged from 51 to 71 $\mu$mol kg$^{-1}$ (59±7 $\mu$mol kg$^{-1}$), while at depths $\geq$ 1000 m (N=10), DOC ranged from 36 to 39 $\mu$mol kg$^{-1}$ (37 ±1 $\mu$mol kg$^{-1}$; Fig. 5.2A). These DOC concentrations are from whole water, the radiocarbon content and DOM composition (discussed in the following section) were from the solid-phase extracts of these samples. The extraction efficiency of the SPE-DOM was 41±10%; this efficiency was independent of depth and DOC concentration. $^{14}$C-SPE-DOM ages of the surface layer ranged from 2990 to 4320 years (3663±400 years), and 6070 to 6570 years at depth (6429±155 years) (Fig. 5.2B). The relationship between DOC concentration and radiocarbon age here is first order, similar to that described for the eastern North Atlantic in Lechtenfeld et al. (2014) (Fig. 5.3A, red curve; $R^2=0.89$). In combining the Atlantic and Pacific data, the relationship of DOC concentration and radiocarbon age is essentially the same to that of the Pacific alone (Fig. 5.3A, black dashed curve, $R^2=0.83$).

The deep SPE-DOM samples in the Pacific had $^{14}$C ages of 6429±155 years (N=10) while those in the deep Atlantic had ages of 4733±73 years (N=2) (Fig. 5.2B). This offset between the Atlantic and Pacific of ~1700 years shows that SPE-DOM is affected by ageing along with the ocean’s MOC deep limb; the difference is similar to the ~2000 year difference depicted in the first $^{14}$C profiles of DOM in the Atlantic and Pacific Oceans (Druffel et al., 1992).
The $^{14}$C-SPE-DOM reported here are similar to the measured bulk $^{14}$C-DOC taken in the deep Pacific Ocean of ~6000 to 6500 years (Druffel et al., 1992; Zigah et al., 2017; Druffel et al., 2016). While the radiocarbon ages between whole water and SPE-DOM are similar here, it is known that a fraction of the most polar (and presumably labile) proportion of the DOM is not recovered with extraction (e.g. compounds such as acetate). For example, Bauer et al. (1992) compared bulk versus solid-phase-extracted DOM; DOM extracted on the XAD resin was older than the $^{14}$C age of the bulk DOM.

**Figure 5.2.** A.) DOC concentration and B.) radiocarbon age vs. depth in the Pacific (red, data from this cruise; *MV 13-10*) and the Atlantic (black, data from Flerus et al., 2012).
Figure 5.3. A.) DOC concentration vs. its SPE-DOM-$^{14}$C. Black dots are Atlantic data and red dots are Pacific data. The red curve and equation represents the relationship of DOC vs. SPE-DOM-$^{14}$C with only Pacific data; the black curve and equation also include the Atlantic data. B.) Normalized degradation rate coefficient ($k_i/k_{DOC}$, calculated with equation 2) vs. calculated residence time ($t_R$, equation 2) for each molecular formula. The dashed horizontal line represents where $k_i/k_{DOC}=1$; compounds with $k_i/k_{DOC}<1$ degrade slower than the bulk DOC, whereas those with $k_i/k_{DOC}>1$ degrade more quickly. The dashed vertical line represents the mean residence time (~24,000 years) of all of the compounds.
5.3.2. *FT-ICR-MS Analysis*

From the FT-ICR-MS spectra (Fig. 5A), a total of 2726 molecular formulae were identified, with 2154 of these formulae present in all samples. The assigned formulae does not give insight as to its structural diversity. All peaks in these spectra represent singly charged ions, as indicated by the spacing between the $^{12}$C and $^{13}$C peaks. Because each peak represents a singly charged ion, the corresponding mass to charge ratio ($m/z$) is referred to as molecular mass.

The average molecular mass was 421±88 Da, and the average O/C and H/C ratios were 0.4±0.1 and 1.1±0.2, respectively. The relative reactivity of SPE-DOM can be approximated using the degradation index ($I_{\text{DEG}}$, Flerus et al., 2012). This index is comprised of five compounds that correlate positively with radiocarbon age ($C_{13}H_{18}O_{7}$, $C_{14}H_{20}O_{7}$, $C_{15}H_{22}O_{7}$, $C_{15}H_{22}O_{8}$, $C_{16}H_{24}O_{8}$) and five compounds that correlate negatively with age ($C_{17}H_{20}O_{9}$, $C_{19}H_{22}O_{10}$, $C_{20}H_{22}O_{10}$, $C_{20}H_{24}O_{11}$, $C_{21}H_{26}O_{11}$). We found that the mean $I_{\text{DEG}}$ in the deep Pacific was 0.947±0.007 and more degraded than in deep North Atlantic where the mean $I_{\text{DEG}}$ was 0.803±0.006.

The IOS is a subset of compounds found in all samples in the Atlantic and deemed intrinsically stable due to their correlation ($r>$0.65) with radiocarbon age. Here, we refer to all IOS molecular formulae from the Pacific as IOS$_p$. The mean molecular weight of the IOS$_p$ was 439±79 Daltons, similar to the average molecular weight of the total spectrum (including all compounds; Fig. 5.4), the O/C ratio was 0.5±0.1, and the H/C ratio was 1.2±0.1, occupying a narrower O/C and H/C range than the total distribution of peaks (Fig. 5.5). The IOS$_p$ formulae have a distribution within the carboxylic-rich alicyclic molecules (CRAM, Fig. 5.5, black outline) in Van Krevelen...
space; CRAM are formulae-identified refractory compounds present in ultrafiltered marine DOM (Hertkorn et al., 2006) exhibiting H/C ranges from 0.8 to 1.4 and O/C ranges from 0.25 to 0.75.

We can indirectly compare the spectra from the Pacific and the Atlantic through normalization; the sum of all MF magnitudes is normalized to equal 1, and the relative magnitude of each compound is described as a percentage of the total magnitude. The IOS$_p$ in the deep Pacific comprises a larger portion (~60%) of the SPE-DOM than in the Atlantic (~50%) (Fig. 5.5). Apparently, some formulae disappear between the Atlantic and the Pacific. In addition, DOC concentrations in the deep Pacific are $9\pm2$ µmol kg$^{-1}$ lower and SPE-DOM was 1,700±140 years older compared to the deep North Atlantic (Fig. 5.2). The gradient in I$_{DEG}$ between the Pacific (~0.95) and the Atlantic (~0.83) further indicates that SPE-DOM degrades with aging. Finally, the narrowing of formulae distribution around the IOS$_p$, indicates that as DOM is transported through the deep ocean, compounds that are not intrinsically stable are removed relative to the IOS$_p$ formulae. DOM in the deep Atlantic carries with it a surface signature representative of the Atlantic Meridional Overturning, in which surface-derived DOM is sequestered into newly formed NADW (Hansell et al., 2009). This is indicated by the higher DOC concentrations, younger radiocarbon ages, and lower I$_{DEG}$. In the far North Pacific, deep waters have been out of contact with the atmosphere for thousands of years. As such, less stable compounds in the DOM pool have been removed, and what remains is an intrinsically recalcitrant core of compounds (i.e. those similar in elemental ratios as the IOS$_p$), thus explaining why they are in larger proportion to the whole pool. It should be noted, however, that a direct comparison between the two datasets might be affected by
instrument conditions, as can be observed by a slight shift in the mass distribution of the spectra (Fig. 5.4).

**Figure 5.4.** FT-ICR-MS mass spectra of A.) a deep Pacific and B.) a deep Atlantic sample. The red and blue highlighted peaks represent those in the IOS.
Figure 5.5. Van Krevelen plots of A.) the deep Pacific and B.) the deep Atlantic, where the x-axis is the oxygen to carbon ratio (O/C) and the y-axis is the hydrogen to carbon ratio (H/C). The colored dots represent the IOS, the grey circle represents a general outline of the CRAM regions in Van Krevelen space, and the dashed black line is a reference around the majority of the molecular formulae present in the deep Atlantic Van Krevelen plot to show the decrease in molecular formulae from the deep Atlantic to the deep Pacific.
5.3.3. *Age and removal model*

To understand the removal of individual molecular formulae in the FT-ICR-MS in terms of how DOM ages, we used an ageing model, following the previously published method (Lechtenfeld et al, 2014). This age model relates the change in bulk DOC concentrations and the change in relative abundance of the hundreds of peaks found in the FT-ICR-MS spectra with $^{14}$C-SPE-DOM ages. To develop the age model, first the concentration of bulk DOC is exponentially related to its residence time:

\[
[DOC]_s = a_{DOC}^0 \times e^{(-k_{DOC} \times t_s)} \quad (5.1)
\]

where $[DOC]_s$ is the concentration of bulk DOC, $t_s$ is the measured residence time of the DOC (in radiocarbon years), $k_{DOC}$ is the degradation coefficient (in y$^{-1}$), $a_{DOC}^0$ is the y-intercept of the first order equation (i.e. the concentration of DOC in µmol kg$^{-1}$ if $t_s=0$). Given the first-order relationship between our bulk DOC concentrations and radiocarbon age, we found in our data that $a_{DOC}^0$ is 109.9 µmol kg$^{-1}$ and $k_{DOC}$ is 1.695x10$^{-4}$ y$^{-1}$ (Fig. 5.3A, red line).

This approach can be applied to the relative change in each peak in the FT-ICR-MS mass spectra with radiocarbon age. The age of each sample of bulk DOC is made up of a multitude of ages from each separate molecular formula, represented by the peaks in the FT-ICR-MS spectra. Based on this concept, and the correlation of the molecular formulae with age, we can calculate the removal rates of individual normalized peaks, based on their relative abundance in each sample. As such, for a given sample, $s$, each molecular formulae would have a removal rate defined as:

\[
M_{i,s} \times [DOC]_s = a_i^0 \times e^{(-k_i \times t_i)} \quad (5.2)
\]
where $M_{i,s}$ is the normalized peak magnitude of a compound ‘$i$’ in sample ‘$s$’ (used as a percentage), $[DOC]_s$ is the bulk DOC concentration of the sample, $t_i$ is the residence time of the given compound ‘$i$’ before it is removed, $a_i^0$ is the magnitude of compound $i$ that is present when $t_i=0$, and $k_i$ is the removal rate coefficient of compound $i$. The factor $M_{i,s} \times [DOC]_s$ is semi-quantitative as it is derived from the relative changes in peak magnitude in comparison to other samples.

In the degradation model for individual molecular formulae, we only considered peaks present in all samples where there is significant correlation between the molecular formulae and $^{14}$C age ($n=1,508, p<0.001$). Since DOC degrades at an apparent rate ($k_{DOC}$), and the degradation of each peak is normalized to the changes in bulk DOC concentration, the rate of degradation of each individual molecular formula can be related in terms of the rate of degradation of the bulk pool (i.e. $k_i/k_{DOC}$; Fig. 5.3B). Therefore, we can calculate the theoretical time, $t_i$, in which a single molecular formula would be fully degraded (i.e. when $M_{i,s} \times [DOC]_s < 0.01$ (% $\mu M$)). We find that $t_i$ values for our dataset ranged from 7,225 to 62,314 years (23,982±11,432 years), though those data with ages >40,000 years have the largest error bars, indicating the model’s limitations (Fig. 5.3B). In addition, ages >40,000 $^{14}$C years actually exceed the limits of aging measurable with (due $^{14}$C half life of ~6000 years). Therefore, in this interpretation, we are exceeding the limits of what $^{14}$C dating can tell us.

The results reported here are similar to the age model used the Atlantic, where the mean residence time for all formulae was 24,400±1,100 years. The mean residence time of compounds in the IOS is older (30,335±11,656 years) than the mean residence time of all compounds the dataset (23,982±11,432 years). When comparing $t_i$ with the OC/HC
ratio, we find that the longer the residence time (and thus the lower the removal rate; Fig. 6), the OC/HC ratio becomes more centralized into a group of molecular formulae with narrower ranges (O/C ranges from 0.35 to 0.59, H/C ranges from 0.95 to 1.47; Fig. 5.6). These compounds are within the CRAM subset of formulae and have H/C ranges from 0.8 to 1.4 and O/C ranges from 0.25 to 0.75.

If the Van Krevelen plots from the deep Pacific samples are viewed in terms of residence time, compounds with residence times > 30,000 years have H/C values of 1.2±0.1 and O/C values of 0.47±0.08. These ranges are virtually the same of those of the IOS: the O/C ratio was 0.5±0.1, and the H/C ratio was 1.2±0.1. CRAM compounds have H/C ranges from 0.8 to 1.4 and O/C ranges from 0.25 to 0.75.

**Figure 5.6.** Van Krevelen plot of the deep Pacific with calculated residence time, $t_i$, in colors.
5.3.4. Comparing molecular degradation of DOM to its bulk degradation

The prior studies of the Atlantic (Flerus, 2012; Lechtenfeld et al., 2014), using the removal rate of bulk DOM to predict a $^{14}$C-SPE-DOM age for the far North Pacific of 6,410±290 years. Our measured age of 6,429±155 years confirms their estimates and suggests that the molecular degradation modeling techniques can accurately predict the $^{14}$C ageing of DOM in whole water; the relationship between the molecular formulae of DOM with SPE-DOM $^{14}$C age gives insights as to the processes occurring in the bulk pool.

Beaupré and Aluwihare (2010) suggested a first order DOC degradation with radiocarbon age. This relationship is described as:

$$DOC_t \times \Delta^{14}C_t = DOC_b \times \Delta^{14}C_b + DOC_e \times \Delta^{14}C_e$$  (5.3)

where $t$ is the total, observed value, $b$ represents a ‘background’ fraction, and ‘e’ represents an ‘excess’ fraction. This equation is essentially describing DOM in two-components, where there is a background fraction ($DOC_b$), resistant to removal over large timescales, and a removable fraction ($DOC_e$), which is more susceptible to removal.

Existing bulk $^{14}$C-DOC data and their corresponding DOC concentrations from previous studies from all major ocean basins (Druffel et al., 1992, 2000, 2015, 2016; Zigah et al., 2017; Chapter 4) display a first order relationship of $^{14}$C-DOC vs. DOC concentration (Fig. 5.7; cyan circles). This relationship is observable in SPE-DO$^{14}$C ages from the Atlantic and Pacific data (Flerus et al., 2012, Lechtenfeld et al., 2014, this study; Fig. 5.7; green circles). This relationship is present regardless of depth or ocean basin (Fig. 5.7).
To determine whether this relationship between DOC concentration and radiocarbon age is expected given the relationship described in equation 3, we isolated ‘deep, refractory’ $^{14}$C ages from both bulk DOC and SPE-DOM; i.e. observed data from the deep ocean where DOC concentrations range from 37 to 40 $\mu$mol kg$^{-1}$ and radiocarbon ages ranged from ~4500 to 6500 years. If these values are used as the background fraction ($DOC_b$ and $\Delta^{14}C_b$ in equation 3), and the excess term ($DOC_e$ and $\Delta^{14}C_e$ in equation 3) is varied by 1 $\mu$M increments, each with an age of 350 years (-50‰), we reproduce DO$^{14}$C values through the upper water column (DOC >45 $\mu$M; Fig. 8, black).

**Figure 5.7.** DOC concentration versus radiocarbon age. Green data represent bulk $^{14}$C-DOC ages, blue data represent $^{14}$C-SPE-DOM ages, and black data represent those data modeled with equation 3.
However, what if the DOC in the deep is not truly the background fraction? To assess this hypothesis, individual compounds are removed from the bulk pool surrounding a core of intrinsically stable compounds; the compounds present in this core of intrinsically stable compounds have the longest residence times (Fig. 5.6). Rearranging equation 3 to solve for the background term, and subtracting excess DOC, the concentration of the background fraction stabilizes at $24\pm2\,\mu\text{mol kg}^{-1}$ (Fig. 5.7). We propose that this fraction ages continuously; if DOC were cycled throughout the ocean for tens of millennia without renewal, the formulae would slowly be narrowed to values around a core concentration of $\sim24\,\mu\text{mol kg}^{-1}$. Although there is no way to test this, comparing the $^{14}\text{C}$ age and FT-ICR-MS gradients from the Atlantic to the Pacific gives a glimpse into the process. The Pacific DOM pool has not been exposed to the atmosphere for $\sim2$ millennia. Compounds in the CRAM and IOS regions in the Pacific region also make up a larger relative proportion of the total abundance than they do in the Atlantic. As such, we propose that this core of formulae observed in the bulk DOM removal model (Fig. 5.7) are those present in the IOS and CRAM that we observe having large $t_R$ values.

While we suggest that there is a core of intrinsically stable molecular formulae that have the potential to persist in the ocean for millennia, recent work suggests that dilution is primarily what controls DOM dynamics in the deep ocean. In the dilution hypothesis, no portion of DOM is truly recalcitrant; its molecular diversity and low concentration in the deep is what prevents microbial uptake. While dilution must have an effect on degradability to a certain extent, our results demonstrate that stability is also related to the elemental composition of DOM, suggesting that if dilution is a control, both aspects are important for DOM cycling. It is possible that dilution acts on a certain
component of DOM, while another component of DOM is intrinsically stable and resistant to removal.

In theory, if the DOM pool was left to cycle in the deep ocean without being ventilated, formulae with higher removal rates would be eliminated from the pool, leaving a core of DOM that ages without further removal (on these time scales). The ideas surrounding both the dilution hypothesis and the intrinsically stable compounds described in this chapter both allow for this removal process. As such, the upwelling and renewal of deep waters in the North Atlantic renewing the pool, primarily through addition of labile, surface-derived DOM via primary production. AMOC is especially important as deep water formation in the Southern Ocean does not play a large role in adding DOM to the deep pool (Bercovici and Hansell, 2016; Bercovici et al., 2017; Chapter 2, Chapter 3). In the deep Pacific, DOC concentrations are at their lowest and ages are their oldest, more closely resembling the \(~24 \, \text{µmol kg}^{-1}\) recalcitrant core than in any other ocean basin.

5.4. Conclusions

We find that the $^{14}$C ages of SPE-DOM in the deep Pacific are \(~1700\) years older than in the deep Atlantic. We find that the DOM in the deep Pacific is more degraded and consequently that intrinsically stable compounds make up a higher relative proportion of deep waters there. We propose that the degradation of SPE-DOM gives insights to how the bulk pool degrades, as those compounds with the longest modeled residence times in the Pacific represent a core of intrinsically recalcitrant DOM. Without transport in the MOC, this core of intrinsically stable DOM could persist for millennia without degradation.
Chapter 6. Conclusions

My goal in this dissertation was to assess the conservative behavior of DOC in the deep ocean, mainly focusing on the southern hemisphere. To achieve this goal, I first tested whether Antarctic shelf systems provide a source of locally produced DOC to newly formed AABW and found that they do not. I then used water mass transports and mixing models to determine whether the concentration and $^{14}$C age of DOC in the deep SO is due to mixing. I found that, both, DOC concentration and $^{14}$C age reflected gradients expected with water mass mixing. I additionally show that the $^{14}$C ages of DOC in the SIO are characteristic of the distinct water masses in that region. I finally coupled molecular composition and $^{14}$C age of samples from the FNP to determine if molecular ageing was consistent with the bulk ageing of DOM in PDW. I found that, as a whole, the molecular composition of deep DOM has low reactivity and intrinsic stability. In the following I will discuss the conclusions of each chapter separately and then bring everything together to analyze the overall finding of this dissertation work.

6.1. DOC Export in Antarctic shelf systems

To address an important potential source of DOC to the deep ocean, I determine whether Antarctic shelves (i.e., the Ross Sea) act to bring new DOC into AABW. I show that the Ross Sea produces high amounts of DOC in the AASW layer, reaching up to 61 $\mu$mol kg$^{-1}$ at the surface. These high concentrations are consistent with Antarctica’s large seasonal phytoplankton blooms that produce massive amounts of organic matter (Arrigo et al., 2008). This surface-derived DOC is brought down into DSW via vertical mixing.
late in the season. This convection and downslope advection causes elevated DOC concentrations to be found in that deep water mass (≈47 to 49 µmol kg\(^{-1}\)), as compared to the incoming MCDW DOC concentration (41 µmol kg\(^{-1}\)). Although there are regionally low DOC values in the deep Drygalski trough that imply further removal given enough time, DOC distributions in DSW in the subsurface western Ross Sea are largely explained by vertical mixing from the surface.

Since DOC is surviving export in DSW, it has the potential to be sequestered into the deep SO. The total enrichment of DOC in DSW yields an export of ≈4 Tg C y\(^{-1}\) of DOC from the Ross Sea, implying sequestration of this material into new AABW and accounting for 1/3 of the total carbon sink reported in the Ross Sea. However, upon DSW export and formation of AABW, the DOC that accumulates on the Ross shelf disappears, supporting the microbial loop in the deep Southern Ocean and sequestering carbon into the deep as CO\(_2\). As the biogeochemistry around all Antarctic shelves is likely quite similar, I suggest that shelf-derived organic matter is consumed upon export to the deep ocean on all shelves, acting as a small source of TCO\(_2\) to the deep SO. In this first chapter, I ruled out a primary source of surfaced shelf derived DOC to the deep SO.

### 6.2. Controls on DOC and radiocarbon in the Southern Ocean and South Indian Ocean

In Chapter 3, I tested for the conservative behavior of DOC in the circumpolar waters of the Southern Ocean. I used three different simple mixing methods on data from the CLIVAR Repeat Hydrography sections (Fig. 3.2). I found using all three methods that DOC in the deep Southern Ocean is largely conserved. Although there were some localized anomalies with elevated DOC, I did not observe locally added DOC to persist
in the deep layers nor did I observe any local sinks. Instead, observed DOC distributions in the SO result from linear mixing of the Atlantic, Indian, and Pacific deep waters.

In the original study reported in Chapter 3 (Bercovici and Hansell, 2016), the scarcity of radiocarbon data of DOC prevented a complete and quantitative assessment of the radiocarbon in the Southern Ocean using $^{14}$C data from all the major ocean basins. However, in Chapter 4, I report the first $^{14}$C data for DOC in the SIO. In these data, the observed $^{14}$C age of IDW (~5600 years) reflected the estimated $^{14}$C age of DOC in Chapter 3. These results from Chapter 2 and 3 suggest that in addition to DOC concentrations, the age distributions in the deep Southern Ocean are due to the mixing of the major deep water masses (NADW, IDW, PDW).

In the SIO, the $^{14}$C age distributions of DOC largely reflect a conserved system with no local sources. Age gradients between IDW and CDW water masses are consistent with the gradients that are expected due to overturning circulation. Additionally, the high-salinity NADW core in the SIO holds younger $^{14}$C ages of DOC, consistent with observations in the South Atlantic. My findings in these two chapters suggest that DOC and the $^{14}$C age of DOC in the deep SO and the SIO both reflect a conserved system.

6.3. Behavior of DOM in the FNP

In Chapter 5, I report that the DOC concentrations are ~10 $\mu$mol kg$^{-1}$ lower and the $^{14}$C ages of SPE-DOM in PDW are ~1700 $^{14}$C years older than those in NADW, similar to the ~2000 $^{14}$C year offset between the bulk $^{14}$C ages between NADW and PDW (Druffel et al., 1992). Additionally, the molecular composition of SPE-DOM in PDW indicates that the DOM in PDW is molecularly more recalcitrant than that in NADW.
Specifically, in PDW, intrinsically stable ultra-refractory compounds make up a higher relative proportion of deep waters in PDW than in NADW.

As I report in Chapter 2 that the deep DOC pool of CDW/AABW is not being renewed by Antarctic shelves, the DOC in PDW is likely a derivative of deep, northward flowing CDW that has been out of contact with the atmosphere for centuries. The molecular composition of DOM in PDW supports this claim; it is highly degraded and lower in reactivity as compared to the NADW, implying removal of compounds in DOM with higher reactivity without any subsequent renewal of material in the SO.

6.4. Assessing the behavior of deep DOM cycling

In this dissertation, I show that gradients in DOC concentrations and $^{14}$C-DOC ages in the SO and SIO reflect water mass mixing. I find that DOC produced on Antarctic shelves is remineralized upon export into AABW, thus leaving no local DOC input to the SO deep water formation cell. Instead, I show that DOC in the deep SO waters is allochthonous with lower latitude sources, reflecting a mixture of NADW, IDW, and PDW. The $^{14}$C-DOC age of the circumpolar waters in the SO also represents this allochthonous mixture. The $^{14}$C age of DOC in the SO is further supported by the $^{14}$C – DOC distributions in the SIO. Lastly, DOM in the FNP has an old $^{14}$C age and molecularly degraded characteristic, implying that it has not been renewed for millenia. Since I show here that the Antarctic shelf systems are not important in bringing DOM into the ocean’s deep waters, then the main source of the deep DOM pool is via AMOC and NADW formation.
NADW, with its subtropical surface water characteristics, has the highest DOC concentrations of all the ocean’s deep waters upon formation: (~48 µmol kg\(^{-1}\)) at around 60°N (Chapter 3; Fig. 3.3) and the youngest deep \(^{14}\)C age at ~4500 \(^{14}\)C years in the Sargasso Sea (Druffel et al., 1992). However, DOC concentrations in NADW reach ~40-42 µmol kg\(^{-1}\) by 20°N, showing a loss of ~6-8 µmol kg\(^{-1}\) (Fig. 3.3) and the \(^{14}\)C ages become ~5000 \(^{14}\)C years by the South Atlantic. Whether this concentration loss and \(^{14}\)C ageing is due to conserved mixing of newly formed NADW with underlying AABW with lower DOC concentrations, or whether modern DOC is removed due to biological respiration remains largely unexplored. Beyond the North Atlantic, DOC concentrations in the deep Indian and Southern oceans are uniformly ~40 µmol kg\(^{-1}\) and reflect conserved mixing. In addition, the \(^{14}\)C age gradients of DOC between different water masses (CDW, IDW, NADW) are consistent with gradients in water masses.

However, the components and reactivity of DOM as it transits the deep ocean’s conveyer belt have resulted in multiple interpretations of its cycling. In several interpretations, the nature of DOM is highly dynamic as opposed to conserved. A general consensus in recent studies on DOM structure and reactivity is that it exhibits a size-age continuum in which small, dissolved, hydrophobic molecules are the most highly aged forms of organic matter and have much older \(^{14}\)C ages than the larger components of the DOM pool, which exhibit younger \(^{14}\)C ages than the majority of total DOM (Druffel et al., 1992; Loh et al., 2004; Walker et al., 2011; 2016, Repeta and Aluwihare, 2006; Zigah et al., 2017). Molecular composition techniques suggest that bulk DOM represents a continuum of thousands of different molecular formulae, and that each one of those molecular formulae has a distinct lifetime in the bulk pool of DOM (Chapter 5; Flerus et
There are reportedly multiple sources of organic matter, including old, allochthonous terrestrial or hydrothermal material, surviving on timescales of 10,000 years (Medeiros et al., 2016; Druffel et al., 2015; Zigah et al., 2017).

In addition, DOC concentrations remain relatively constant (between \( \sim 37 \) and \( 40 \) \( \mu \text{mol kg}^{-1} \)) in CDW, IDW, and PDW (Hansell et al., 2009; Chapter 3; Bercovici and Hansell, 2016). It is still unclear why DOC concentrations in the deep ocean reach \( \sim 37-40 \) \( \mu \text{mol kg}^{-1} \) and don’t go much lower, yet have ages that reflect the ocean’s conveyer belt (i.e. DOC is oldest in PDW, youngest in NADW, and somewhere in the middle in IDW and CDW). Processes that limit further drawdown of DOC while allowing this ageing could include intrinsic recalcitrance of deep DOC (Hansell, 2013) or dilution (Arrieta et al., 2015), in which deep heterotrophs can only draw DOC down to a certain level before it is unattainable.

With the fundamental ideas behind these previously described studies, Follett et al (2014) used \(^{14}\)C fractionation experiments to suggest that the DOC pool is renewed on decadal timescales by solubilized sinking particulate organic material. They suggest that DOC in the SO is not conserved and that the \(^{14}\)C age there is too old because of dynamic processes renewing the DOC pool with aged material. However, I find through observing both large scale distributions and smaller scale isotopic and molecular composition work that DOC concentrations and the \(^{14}\)C age of DOC in the SO largely reflect those expected from water mass mixing. I indirectly show in this dissertation (by eliminating the SO deep water cell as a source of DOM to the deep) that AMOC plays a fundamental role in renewing DOM to the deep ocean. As such, I believe that studying both large scale
mixing of NADW and coupling that with molecular composition and isotopic work is important in further understanding the behavior of deep DOC.

6.5. Future directions

As a next step, I hope to conduct research that works to unite the many different interpretations of the dynamics of deep DOC cycling and uncover why DOM is comprised of thousands of different molecular formulae, and parts of different sizes and polarity, yet in the deep it appears to be conserved.

Furthermore, the process of how DOC is introduced into NADW via AMOC remains largely unexplored. As we suggest here that the main source of DOC to the deep is through AMOC, it is important to understand the mechanisms that bring DOC to depth in NADW and the mechanisms that cause the ~6 µmol kg\(^{-1}\) concentration gradient from the far North Atlantic to the equatorial Atlantic. Finally, the ~3 µmol kg\(^{-1}\) gradient between DOC concentration in PDW versus CDW should be explored in future work. Previous observations on DOC in the deep ocean suggest that slow removal over time is what causes concentration gradients over large scales. As the Pacific basin is massive, the transit of CDW to the formation of PDW would take place over hundreds of years and thus the slow removal of DOC over these large time scales could explain why concentrations are slightly older. However, Hansell et al (2009) suggested that localized sinks in the Pacific are what cause DOC concentrations to be ~3 µmol kg\(^{-1}\) lower in PDW than in CDW. Some processes that cause these sinks include removal via hydrothermal vents (Druffel et al., 2015), photo-oxidation (Mopper et al., 1991), priming (Carlson et al., 2002; Bianchi et al., 2011), gel formation (Verdugo et al., 2004), and conserved
mixing with lower salinity waters (Hansell and Carlson, 2013). However, the origin of the DOC gradient in the deep Pacific is largely unexplored. In our current state of knowledge, it is impossible to infer whether the low DOC in the Pacific is due to localized sinks or slow, continuous degradation. Future research should be focused on understanding the mechanism behind this removal.

Here, the conservative behavior of DOC can be explained if the removal of DOC is slower than the time it takes for one meridional overturning circulation. We show that DOC concentration and $^{14}$C age in the Southern Ocean exhibit conserved behavior. We additionally demonstrate that a likely reason why DOC behaves conservatively in CDW is because the DOC concentrations in IDW, PDW, and NADW have removal rates that are slower than the time it takes for meridional overturning circulation. Finally, by showing that DOC in the CDW pool in the Southern Ocean is not enhanced by any lasting local organic material, we can infer that the main lasting source of DOC to the deep ocean is via NADW formation. However, whether the DOC in the NADW pool itself behaves conservatively is still largely unknown.
References


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