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Key Points:

- More than 10% of DOC in the deep North Atlantic contains bomb ^{14}C
- DOC decreases in concentration and increases in ^{14}C age along the deep ocean conveyor
- DOC in the deep ocean is surprisingly dynamic both temporally and spatially

Supporting Information:

- Supporting Information S1
- Movie S1

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Radiocarbon in dissolved organic carbon of the Atlantic Ocean

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Abstract Marine dissolved organic carbon (DOC) is produced in the surface ocean though its radiocarbon (^{14}C) age in the deep ocean is thousands of years old. Here we show that $\geq 10\%$ of the DOC in the deep North Atlantic is of postbomb origin and that the ^{14}C age of the prebomb DOC is ≥ 4900 ^{14}C year, ~ 900 ^{14}C year older than previous estimates. We report ^{14}C ages of DOC in the deep South Atlantic that are intermediate between values in the North Atlantic and the Southern Ocean. Finally, we conclude that prebomb DOC ^{14}C ages are older and a portion of deep DOC is more dynamic than previously reported.

1. Introduction

Marine DOC is the largest pool of reduced carbon (C) in the oceans, about equal to the atmospheric CO_2 reservoir. Though most DOC is produced from photosynthetic uptake of modern DIC in the surface ocean, estimates of the bulk ^{14}C ages in deep open ocean DOC ranged from 4000 ^{14}C years in the Sargasso Sea to 6000 ^{14}C years in the North and South Pacific [Druffel and Griffin, 2015; Druffel et al., 1992; Williams and Druffel, 1987]. Previous work suggested that the average ^{14}C age of DOC in the deep Southern Ocean (5600 ^{14}C years) was much closer to that in the deep Pacific, suggesting that the deep North Atlantic DOC contained bomb ^{14}C , that there was a source of old DOC to the Southern Ocean [Druffel and Bauer, 2000] or that there were diverse isotopic sources of DOC [Follett et al., 2014; Loh et al., 2004; McCarthy et al., 2011; Walker et al., 2011; Ziolkowski and Druffel, 2010]. In the ocean margins, there is evidence of inputs of old DOC in the deep northeast Pacific and the mid-Atlantic Bight off the U.S. coast [Bauer and Druffel, 1998; Ziolkowski and Druffel, 2010] and young DOC to the deep subpolar North Pacific [Tanaka et al., 2010]. Terrestrially derived DOC was found in the deep Arctic Ocean [Griffith et al., 2012].

We find here that the DOC $\Delta^{14}\text{C}$ values in the deep Sargasso Sea in 2012 are lower than those in 1989, indicating that bomb ^{14}C levels have decreased over a period of two decades, similar to the decrease of surface dissolved inorganic C (DIC). Implications for the C cycle in the ocean include the presence of a labile pool of DOC in deep water.

2. Setting and Methods

Water samples were collected from the North and South Atlantic Ocean during the Repeat Hydrography Climate Variability and Predictability program. Sampling included surface and subsurface water, northward Antarctic Intermediate Water (AAIW ~ 700 – 1200 m, low salinity, high silica) and Upper Circumpolar Deep Water (1000–2000 m), southward North Atlantic Deep Water (NADW 1500–4000 m, high oxygen, low silica), and Antarctic Bottom Water (within a few hundred meters of the bottom, cold and dense) [Jenkins et al., 2015a; Reid, 1989]. A data-constrained, ocean circulation model was used to show that in the South Atlantic, Antarctic water penetrates the NADW in volume-weighted averages that vary from 20 to 40% [DeVries and Primeau, 2011].

Radiocarbon in DOC was measured in seawater samples collected from three stations along 32°S on the A10 cruise in October 2011, four stations along 20°W on the A16N cruise in July/August 2013, and four stations along 65°W on the A22 cruise in March/April 2012 (Figure 1 and Table S1 in the supporting information). Samples shallower than 400 m were filtered using precombusted glass fiber (0.7 μM) filters, and all samples were collected in 1 L Amber Boston Round glass bottles and frozen at -20°C at an angle to avoid breakage until analysis at University of California, Irvine (UCI). Samples were diluted with 18.2 M Ω Milli-Q water (DOC concentration 0.5–0.9 μM), acidified to pH 2 with 85% phosphoric acid, purged with ultra high purity helium gas and UV-oxidized (UVox) [Beaupré et al., 2007; Druffel et al., 2013; Griffin et al., 2010]. Samples for DIC $\Delta^{14}\text{C}$ analyses were prepared according to standard methods [McNichol et al., 1994].

The resultant CO_2 from UVox was converted to graphite on iron catalyst for ^{14}C analysis at the Keck carbon cycle accelerator mass spectrometry (AMS) laboratory at UCI [Southon et al., 2004; Xu et al., 2007]. Total uncertainties for

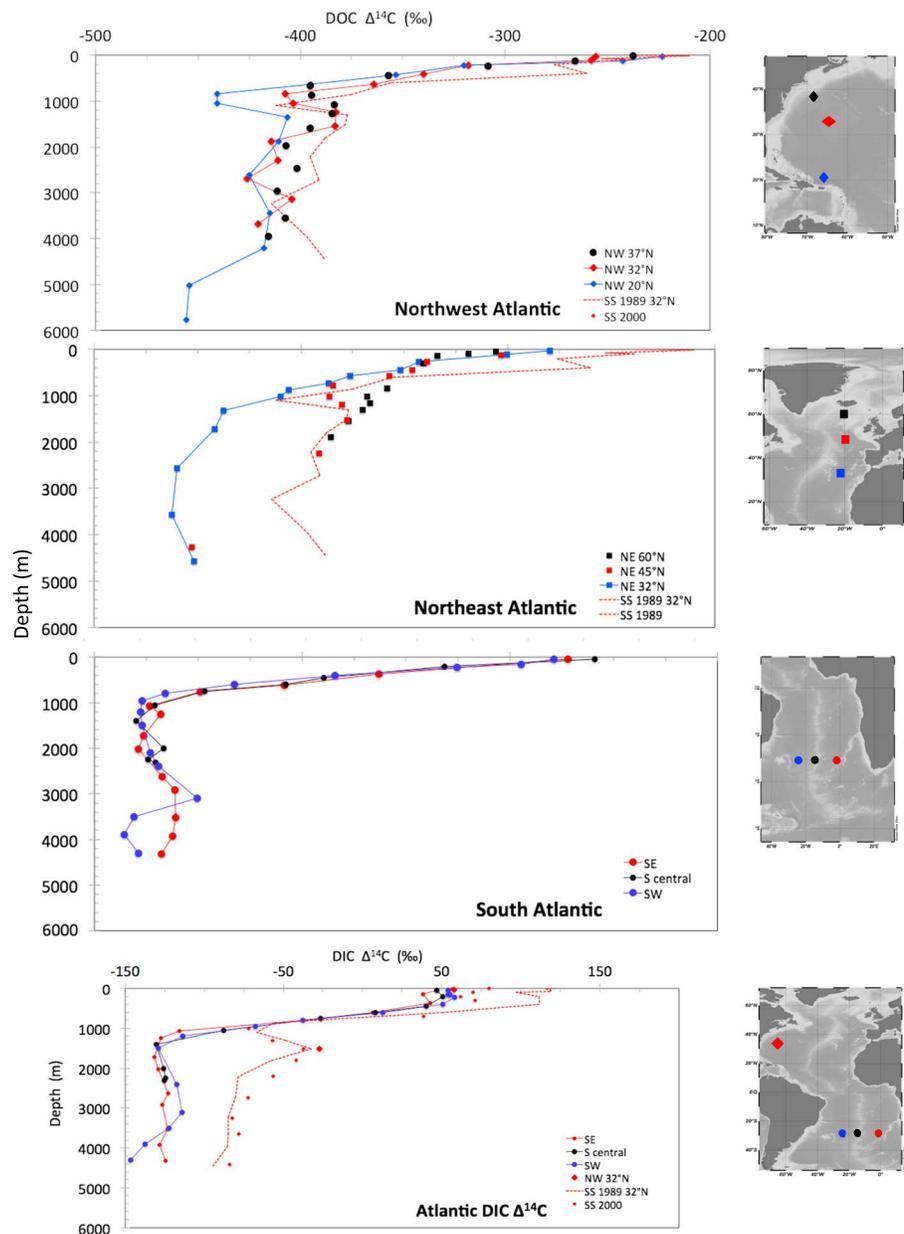


Figure 1. DOC $\Delta^{14}\text{C}$ values in samples collected from (a) the northwest Atlantic along $\sim 65^\circ\text{N}$ (A22 cruise in 2012), (b) the northeast Atlantic along $\sim 20^\circ\text{W}$ (A16N cruise in 2013), and (c) the South Atlantic along 32°S (A10 cruise in 2011). (d) DIC $\Delta^{14}\text{C}$ values in samples collected from the South Atlantic along 32°S (A10 cruise) and the SS (A22 cruise in 2012 large red diamonds). DOC and DIC $\Delta^{14}\text{C}$ values from the SS (in 1989 [Druffel et al., 1992] red dashed line and in 2000 [Druffel et al., 2008], small red diamonds) are shown for comparison.

individual DOC $\Delta^{14}\text{C}$ values of approximately -500‰ are $\pm 4\text{‰}$ as determined from analyses of numerous duplicate seawater samples and secondary standards [Druffel et al., 2013]. Total uncertainty for DIC $\Delta^{14}\text{C}$ values are $\pm 3\text{‰}$. Total uncertainties for DOC concentrations are $\pm 1.0 \mu\text{M}$. Stable C isotopes were measured on splits of the CO_2 samples using a Thermo Electron Delta Plus mass spectrometer; the total uncertainty of $\delta^{13}\text{C}$ values are $\pm 0.2\text{‰}$.

3. Results

3.1. DOC $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ Values

In the North Atlantic, the surface DOC $\Delta^{14}\text{C}$ values ranged from -306‰ at 60°N to -223‰ at 20°N (Figures 1a and 1b and Table S2 in the supporting information). Surface values ranged from -279‰ to -259‰ in the

South Atlantic (Figure 1c). Minimum $\Delta^{14}\text{C}$ values were reached by ~800–1100 m depth (AAIW) in the North (–441‰ to –395‰) (Figures 1a and 1b) and South (–477‰ to –466‰, Figure 1c) Atlantic. Generally, the DOC $\Delta^{14}\text{C}$ values below 1200 m in the North Atlantic decreased with depth. Two values from 2569 and 3576 m depth in the northeast Atlantic (32°N) were the lowest (–460‰ and –462‰, respectively) and a value (–370‰) from 1313 m depth at the farthest north site (60°N) was the highest (Figure 1b). The average of (>1800 m) deep DOC $\Delta^{14}\text{C}$ values from the same location (within 145 km) in the Sargasso Sea are 19‰ higher in 1989 ($-396 \pm 10\text{‰}$ ($n=6$)) than those in 2012 ($-415 \pm 8\text{‰}$ ($n=5$)) (Figure 1a).

The DOC $\Delta^{14}\text{C}$ values from the South Atlantic below 1200 m averaged $-471 \pm 8\text{‰}$ ($n=19$) and were significantly lower than those in the North Atlantic. Values below 3500 m depth were significantly higher in the southeast basin ($-464 \pm 4\text{‰}$ ($n=3$)) than those in the southwest basin ($-482 \pm 3\text{‰}$ ($n=3$)) (Figure 1c).

Stable C isotope ($\delta^{13}\text{C}$) DOC values ranged between –20.5 and –23.0‰, typical of marine-produced organic matter (Figure S1 in the supporting information). Values were higher in the deep South Atlantic ($-21.3 \pm 0.4\text{‰}$ ($n=13$)) and Sargasso Sea ($-20.8 \pm 0.6\text{‰}$ ($n=4$)) than those in the rest of the deep North Atlantic ($-22.3 \pm 0.4\text{‰}$ ($n=19$)).

3.2. DOC Concentrations

Concentrations of DOC ranged from 58 to 76 μM in the upper 40 m of the water column (Figure S2 and Table S2 in the supporting information). Values decreased to about 1000 m depth at all stations, and average values in the deep Atlantic were significantly lower in the south ($38.1 \pm 1.1 \mu\text{M}$ ($n=22$)) than in the north ($40.9 \pm 1.3 \mu\text{M}$ ($n=23$)) (Figure S2 in the supporting information).

3.3. DIC $\Delta^{14}\text{C}$ Values

New DIC $\Delta^{14}\text{C}$ values are reported for the South Atlantic samples (2011) and two depths from the Sargasso Sea station (2012) (Figure 1d). Surface DIC $\Delta^{14}\text{C}$ values ranged from +47 to 54‰ in the South Atlantic and was +58‰ in the Sargasso Sea. Values in the South Atlantic decreased steadily to ~1000 m depth and averaged –127‰ below 1200 m. Values in the southwest basin were higher at 2400 m and 3100 m and lower at 3900 and 4300 m than those in the southeast basin, which did not vary with depth below 2000 m.

4. Discussion

We address four major trends in the DOC $\Delta^{14}\text{C}$ data. First, values in the deep North Atlantic vary both temporally and spatially, indicating the presence of bomb ^{14}C . Second, the difference between prebomb DOC $\Delta^{14}\text{C}$ values of the deep North and deep South Atlantic is discussed as possible aging of DOC during the southward transport of NADW. Third, we discuss the possible reasons for the dissimilarity of the deep DOC $\Delta^{14}\text{C}$ values in the southwest and southeast basins of the Atlantic. Fourth, the global trends of DOC $\Delta^{14}\text{C}$ values in the open ocean are presented, and reasons for the decrease in both $\Delta^{14}\text{C}$ and DOC concentration are discussed.

4.1. Bomb ^{14}C in North Atlantic DOC and Decadal Variability

There was a wide range of DOC $\Delta^{14}\text{C}$ values (–462‰ to –370‰) in the deep North Atlantic below 1200 m (Figures 1a and 1b). Values were highest in the northernmost station (60°N) and lowest in the northeast station at 32°N. This pattern is not surprising because NADW forms by surface-to-deep convection in the Labrador and the Nordic Seas, incorporating bomb ^{14}C into DIC of the Deep Western Boundary Current [Key *et al.*, 2004; Stuiver and Ostlund, 1980]. It stands to reason that bomb ^{14}C would also be present in DOC in the deep North Atlantic. Notwithstanding, there were six very low DOC $\Delta^{14}\text{C}$ values, the three deepest samples from 32°N (–460, –462‰, and –452‰) and the deepest sample from 45°N (–453‰) in the northeast Atlantic (Figure 1b), and the two deepest samples from 20°N in the Puerto Rican Trench (–454‰ and –456‰) in the northwest Atlantic (Figure 1a). The DOC concentrations of these six samples (average $38.9 \pm 2.1 \mu\text{M}$) are not significantly different from the remaining deep samples at these sites (average $40.5 \pm 1.9 \mu\text{M}$ ($n=9$)). We hypothesize that the average of the six low $\Delta^{14}\text{C}$ values (–456 \pm 4‰) represents an upper bound estimate of the prebomb DOC $\Delta^{14}\text{C}$ value in the deep North Atlantic. This is supported by minimal bomb-produced tritium ($\delta^3\text{H} < 0.08$ tritium unit) measured at these deep locations [Jenkins, 2007; Jenkins *et al.*, 2015b]. This DOC $\Delta^{14}\text{C}$ value is 60‰ lower than the previous estimate for the deep North Atlantic samples collected in 1989 (–396‰) [Druffel *et al.*, 1992], indicating that bomb ^{14}C was present in the Sargasso Sea at this time.

Using this prebomb DOC $\Delta^{14}\text{C}$ estimate, we calculate the fraction of bomb DOC in the deep north Atlantic in 2012–2013 using a mass balance approach. Assuming that the source of bomb ^{14}C to the deep water was from solubilization of particulate organic C (POC) produced in the surface (DIC in the surface waters during the period of 1992–2012 averaged 70‰ (Druffel, unpublished data)) and the deep average DOC $\Delta^{14}\text{C}$ value was -415‰ ($>1800\text{ m}$, excluding the six prebomb values), there was 92% prebomb DOC (-456‰) and 8% bomb DOC from organic particles ($-415\text{‰} = 0.92 \cdot -456\text{‰} + 0.08 \cdot 70\text{‰}$). Thus, the input of bomb DOC to the deep north Atlantic was $\geq 8\%$ of the standing stock of the deep DOC because our prebomb $\Delta^{14}\text{C}$ value is a maximum estimate. A similar calculation for the Sargasso Sea site in 1989, assuming that the DIC $\Delta^{14}\text{C}$ in the surface waters during the previous two decades was $+140\text{‰}$ [Druffel, 1989], reveals that there was $\leq 90\%$ prebomb DOC and $\geq 10\%$ bomb DOC from surface POC ($-396\text{‰} = 0.90 \cdot -456\text{‰} + 0.10 \cdot 140\text{‰}$).

We observed a temporal shift in DOC $\Delta^{14}\text{C}$ values in the deep Sargasso Sea. Here the average deep value was 19‰ higher in 1989 than in 2012. This decrease was likely not the result of a change in the production of NADW, which has not changed in the last decade [Fischer *et al.*, 2010]. Also, seasonal variability of the deep-sea DOC pool is unlikely, because deep ocean DOC $\Delta^{14}\text{C}$ time series have not shown temporal changes [Bauer *et al.*, 1998; Beaupré and Druffel, 2009]. Input of aged DOC from hydrothermal systems is also not likely the cause of the decrease in deep DOC $\Delta^{14}\text{C}$ in the Atlantic given low $\delta^3\text{He}$ values in these waters (Figure S3 in the supporting information). We hypothesize that the 19‰ higher average DOC $\Delta^{14}\text{C}$ value in 1989 represents a higher relative contribution of bomb ^{14}C to the DOC pool than was present in 2012–2013.

To test this hypothesis, we compare the amount of bomb DOC in the deep Sargasso Sea in 1989 to net production of organic C exiting the surface ocean. If we assume that a minimum of 20% of the C exported from the mixed layer at the Bermuda Atlantic Time-series Study site ($32^\circ 10' \text{N } 64^\circ 30' \text{W}$) was converted to DOC ($0.20 \cdot 3 \pm 1 \text{ mol C m}^{-2} \text{ yr}^{-1} = 0.60 \text{ mol C m}^{-2} \text{ yr}^{-1}$) [Emerson, 2014], then the replacement time of the DOC in a 1 m^2 area of the deep ocean ($2500 \text{ m}^3 \cdot 0.043 \text{ mol m}^{-3} = 108 \text{ mol C}$) (see Table S2 in the supporting information) would have been 180 years ($108 \text{ mol C m}^{-2} / 0.60 \text{ mol C m}^{-2} \text{ yr}^{-1}$). To replace 20% of the DOC in a 1 m^2 area of the deep ocean would have taken about 36 years ($0.20 \cdot 180$ years), which is approximately equal to the time that bomb ^{14}C had been in the ocean from the time of the first sampling of DOC in the Sargasso Sea (1989–1957 = 32 years). This rough calculation indicates that DOC in the deep Sargasso Sea is likely a heterogeneous mixture that contains distinct $\Delta^{14}\text{C}$ signatures with different cycling rates. We determine that $\geq 4 \mu\text{M}$ DOC has ages of a few decades (postbomb) and $\leq 39 \mu\text{M}$ has ages of centuries or longer. This has important implications for the role of DOC in the oceanic C cycle of the Atlantic (see section 5).

Evidence that DOC is a heterogeneous, isotopic mixture in the surface ocean is shown by a Keeling plot (Figure S4 in the supporting information), which identifies the $\Delta^{14}\text{C}$ value of an excess component added to a background pool [Mortazavi and Chanton, 2004]. Keeling plots of $(\text{DOC concentration})^{-1}$ versus DOC $\Delta^{14}\text{C}$ value were linear, and suggested rapid export out of the upper 85 m, and advection between 100 and 1000 m [Beaupré and Aluwihare, 2010]. Keeling plots of the Atlantic data reveal y -intercepts that were similar to the DIC $\Delta^{14}\text{C}$ values of the surface waters at each site (Figure S4 and Table S3 in the supporting information), indicating that the excess DOC originated from recent production in the surface ocean. Similar results were obtained from Keeling plots of South Pacific data [Druffel and Griffin, 2015].

Additionally, DOC $\delta^{13}\text{C}$ values in the North Atlantic (1989–2013) were generally lower than those in the South Atlantic (Figure S1 in the supporting information), which may indicate that there is a larger ^{13}C Suess effect (presence of mostly fossil fuel-derived CO_2) in the deep North Atlantic than in the South Atlantic. This would support the premise that bomb ^{14}C was present in the North Atlantic, however, it is also possible that input of fossil C may have contributed to a significant decrease in DOC $\Delta^{14}\text{C}$ values in the North Atlantic.

4.2. Aging of DOC in North Atlantic Deep Water

Our upper bound estimate for the prebomb DOC $\Delta^{14}\text{C}$ value in the deep North Atlantic ($-456 \pm 4\text{‰}$) corresponds to a ^{14}C age of 4900 ± 60 ^{14}C year. This means that the prebomb ^{14}C ages of the deep basins of the North Atlantic and North Pacific have decreased from 4000 and 6000 ^{14}C years in 1989 to 4900 and 6000 ^{14}C years in 2012.

The difference between the prebomb ^{14}C ages of the North and South (5120 ± 35 ^{14}C year) Atlantic DOC is 220 ± 95 ^{14}C years. This difference is equal to the estimated replacement time (250 ^{14}C years) determined

from the deep DIC ^{14}C ages in the Atlantic [Stuiver *et al.*, 1983]. However, this may be fortuitous due to the presence of bomb (and prebomb) DOC from the dissolution of surface POC [Smith *et al.*, 1992] in the deep waters. This similarity may indicate that DOC has been transported with NADW as it traveled southward, but we cannot demonstrate this because DOC is not an isolated C pool.

4.3. Spatial Variability of $\Delta^{14}\text{C}$ in the Deep South Atlantic

Comparison of the DOC and DIC $\Delta^{14}\text{C}$ values from the South Atlantic in 2011 reveals that both were high in the upper 1000 m indicating the presence of bomb ^{14}C (Figures 1c and 1d). It appears that bomb ^{14}C penetration was several hundred meters deeper in the DIC pool. In the two deepest samples (3900 and 4300 m), the DIC $\Delta^{14}\text{C}$ values in the southwest basin were 9‰ and 22‰ lower than those in the southeast basin (Figure 1d). Older waters in the west suggest that they may be less well ventilated than those in the east. The DOC $\Delta^{14}\text{C}$ values from the west were also lower (by 11–24‰) in the deepest three samples (3500–4300 m) than those in the east (Figure 1c).

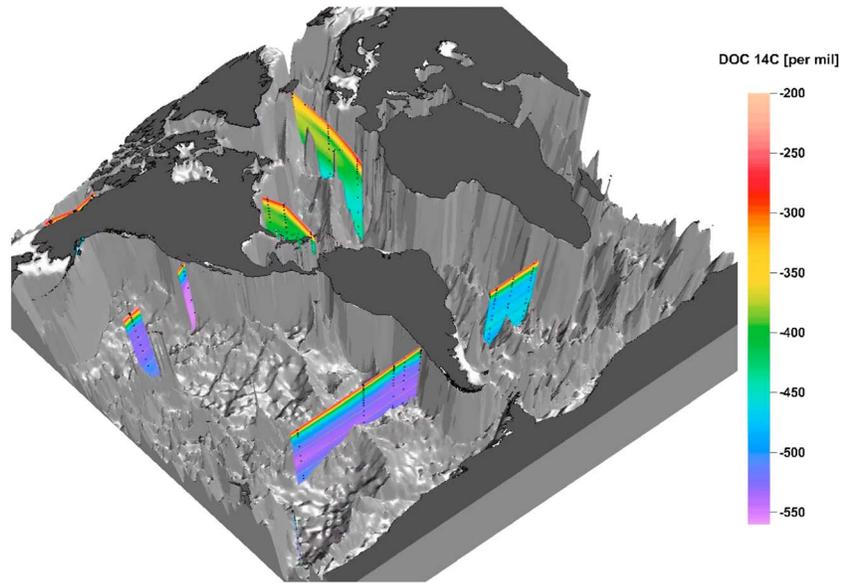
Differences in the $\Delta^{14}\text{C}$ values of DIC and DOC in the deep south basin could be the result of (1) dissolution of high $\Delta^{14}\text{C}$ POC from the surface, (2) mixing of Southern Ocean waters into the deep South Atlantic, or (3) both of these processes. The amount of surface POC (prebomb $\Delta^{14}\text{C}$ value of -65‰ [Druffel, 1996]) required to increase the deep DOC $\Delta^{14}\text{C}$ value from -483‰ (west basin average) to -463‰ (east basin average) is 5% of the DOC pool. This value would be 4% if the surface POC $\Delta^{14}\text{C}$ value contained bomb ^{14}C ($+70\text{‰}$). Because the net primary production is higher in the southeast Atlantic than that in the southwest Atlantic [Falkowski, 2014], this would cause a higher input of surface-derived POC to the deep southeast basin and provide a mechanism for the higher DOC $\Delta^{14}\text{C}$ values. Additionally, DeVries and Primeau [2011] used a data-constrained ocean circulation model to characterize the distribution of water masses and their ages in the global ocean and showed that the ratio of Southern Ocean to NADW at 32°S in the South Atlantic was about 1:3. There was no evidence that this ratio was different in the southeast and southwest basins (F. Primeau, personal communication). Thus, we suggest, but are not able to determine definitively, that dissolution of POC to DOC is a likely reason for the DIC and DOC $\Delta^{14}\text{C}$ offsets we observe between the southwest and southeast basins of the Atlantic.

4.4. Global Trends of DOC $\Delta^{14}\text{C}$ Values

There are 17 DOC $\Delta^{14}\text{C}$ profiles available for the Pacific and Atlantic Ocean basins, including the nine new profiles presented here. Though the number of profiles is limited, they improve our understanding of the global ocean DOC $\Delta^{14}\text{C}$ cycle. To portray the global DOC $\Delta^{14}\text{C}$ trends better, a three-dimensional animation is presented that displays the $\Delta^{14}\text{C}$ profiles in these basins (Figure 2) [Schlitzer, 2015] (DOC ^{14}C animation S1). The animation shows the gradual decrease of DOC $\Delta^{14}\text{C}$ values in the deep water from high values in the subpolar North Atlantic (-410‰ green) to lower values in the South Atlantic (-470‰ aqua). There are areas of low $\Delta^{14}\text{C}$ values (-456‰ light green) in the northwest at 20°N and the northeast Atlantic, portraying the water masses we hypothesize as near prebomb DOC in these slower ventilated regions.

The $\Delta^{14}\text{C}$ values decreased further at the Southern Ocean site (-500‰ blue) and fell to an even lower value (-525‰ purple) in the South and North Pacific basins. As noted above, the lack of an apparent gradient in $\Delta^{14}\text{C}$ values in the Pacific basin indicates that processes other than ^{14}C decay during northward transport are at work [Druffel and Griffin, 2015]. Values were lowest (-550‰ fuchsia) off California in the northeast Pacific and were believed to have been influenced by sources of old C from the continental margin [Bauer and Druffel, 1998]. The surface waters at all locations were similar (average $-255 \pm 35\text{‰}$ ($n = 18$)), with the exception of the Southern Ocean ($-372 \pm 5\text{‰}$ ($n = 3$)), where surface-to-deep mixing bring lower $\Delta^{14}\text{C}$ water to the surface.

The gradual decrease of deep DOC $\Delta^{14}\text{C}$ values from the North Atlantic to the South Atlantic, and on into the Southern Ocean and Pacific, is shown in a plot of average deep DOC concentrations and ^{14}C ages for each of our open ocean sites in the world ocean (Figure 3). The regression is significant ($r^2 = 0.97$ $p < 0.0001$). The decrease in DOC concentration and ^{14}C ages from the North Atlantic to the Pacific mimics the flow of NADW along the deep ocean conveyor, and both quantities are lowest in the Pacific basin. This pattern likely suggests that (1) DOC ages as it is transported within NADW along the deep conveyor, (2) DOC with a higher $\Delta^{14}\text{C}$ value than that of the bulk is selectively remineralized during transport, or (3) there is a combination of aging and selective remineralization. However, because the basin-scale increase in DOC age is also



Data: Alysha Coppola and Ellen Druffel
Graphics: Reiner Schlitzer

Figure 2. DOC $\Delta^{14}\text{C}$ animation. Three-dimensional animation produced by Reiner Schlitzer using Ocean Data View software and the DOC $\Delta^{14}\text{C}$ measurements from our group [Bauer et al., 1998; Beaupré and Druffel, 2009; Druffel and Bauer, 2000; Druffel and Griffin, 2015; Druffel et al., 1992].

matched by a concomitant decrease in DOC concentration, we believe that both aging and remineralization processes are responsible for the broader trend. Our observations agree with previous studies of global deep DOC concentrations along the deep ocean conveyor [Hansell et al., 2012]. The Southern Ocean value lies off of this relationship suggesting an additional source of DOC [Druffel and Bauer, 2000] or potentially different DOC isotopic signatures within deep DOC [Follett et al., 2014; Loh et al., 2004; McCarthy et al., 2011; Walker et al., 2011; Ziolkowski and Druffel, 2010].

A recent study shows that DOC concentrations in the Southern Ocean reflect the conservative mixing of water masses in this region [Bercovici and Hansell, 2015].

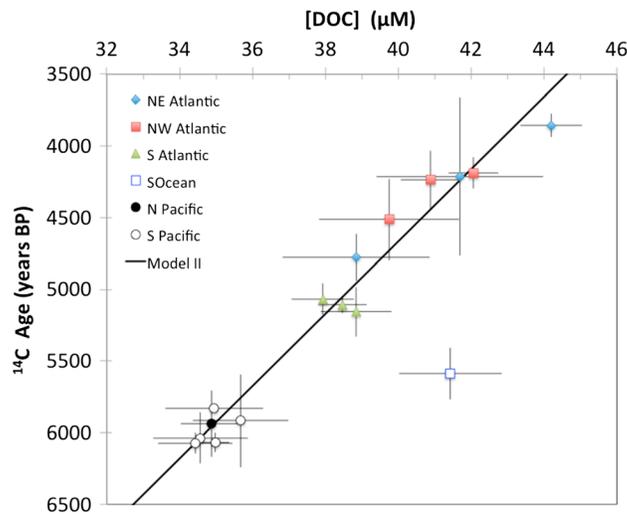


Figure 3. Average DOC concentrations versus average DOC ^{14}C ages for each site >1500 m depth. Data are from the Atlantic (this work), North Pacific [Druffel et al., 1992], SOcean (Southern Ocean) [Druffel and Bauer, 2000], and South Pacific [Druffel and Griffin, 2015]. The solid line is the Model II geometric mean regression of all points (except SOcean); the equation is $y = (-252.2x - 14760)$ with a slope of -252.2 ± 11.6 and y -intercept of 14760 ± 447 , $r^2 = 0.97$, and $p < 0.0001$.

5. Implications for the DOC Cycle in the Ocean

Though the bulk DOC ages in the deep sea are thousands of ^{14}C years old, we show that a portion of this DOC is post-bomb and that the $\Delta^{14}\text{C}$ values in the deep Sargasso Sea have changed on decadal time scales. We estimate that the prebomb age of DOC in the North Atlantic (≥ 4900 ^{14}C years) is older than previously reported (4000 ^{14}C years [Druffel et al., 1992]). These results influence our current understanding of labile versus refractory DOC in the deep ocean.

Whereas $\geq 10\%$ of the DOC in the deep North Atlantic is of postbomb origin, $\leq 90\%$ of the DOC has an older

^{14}C ages of ≥ 4900 ^{14}C years. There is a fraction of the prebomb DOC that has ^{14}C ages much greater than the time scale of meridional overturning circulation. Black C in DOC has been identified and has ages of 18000 to 23000 ^{14}C years [Coppola and Druffel, 2016; Ziolkowski and Druffel, 2010]. Whether this ancient DOC was put into the ocean preaged (e.g., hydrothermal sources), or had aged by decay within the deep sea, is an open question.

Though the average ^{14}C age of prebomb DOC in the North Atlantic was ≥ 4900 ^{14}C years, the turnover time of DOC was much shorter. This is because ^{14}C age and turnover time ($1/k$, where $k = \Sigma(1/^{14}\text{C age})$) are equal only for a homogeneous C pool. For DOC composed of two pools with different ^{14}C ages (e.g., 30 and 4900 ^{14}C years), the turnover time ($284 \text{ years} = 1/(0.1/30 + 0.9/4900)$) is much less than its ^{14}C age due to dominance of the quickly cycled DOC term [Loh et al., 2004; Trumbore and Druffel, 1995].

The differences between the Atlantic DOC $\Delta^{14}\text{C}$ profiles presented here reveal that the deep DOC cycle is far more dynamic, both spatially and temporally, than previously believed, particularly in the North Atlantic. DOC $\Delta^{14}\text{C}$ values for samples collected from the Southern Ocean in 1995 [Druffel and Bauer, 2000] have a lower average value ($-500 \pm 12\%$) below 1500 m depth than those in the North or South Atlantic and are more variable. More measurements are needed from the Southern Ocean to constrain the cycling of DOC in the global ocean. We note that the biogeochemical cycling of DOC is more clearly resolved when isotopic measurements are included versus when concentration measurements are considered alone. A more complete global picture of DOC cycling will be further illuminated with future $\Delta^{14}\text{C}$ and compound-specific $\Delta^{14}\text{C}$ measurements.

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