Radiocarbon distributions in Southern Ocean dissolved and particulate organic matter

ERM Druffel

JE Bauer
Virginia Institute of Marine Science

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Abstract. Dissolved organic carbon (DOC) is the largest actively exchanging pool of organic carbon in the ocean, yet its sources and sinks are not well constrained. The average $^{14}$C ages of DOC in the deep N. Atlantic and N. Pacific Oceans are 4,000 [Bauer et al., 1992; Druffel et al., 1992] and 6,000 years [Williams and Druffel, 1987], respectively, and represent the beginning and end of the deep ocean conveyor [Broecker, 1991]. Here we report that the deep Southern Ocean DOC has a $^{14}$C age (5,600 y) much closer to that of the deep N. Pacific, but its concentration in seawater ($41 \pm 2 \mu M$) is nearly equal to that of the deep N. Atlantic. The radiocarbon and concentration data indicate that most, but not all, deep DOC is transported conservatively with the ocean's conveyor. A younger (post-bomb) source of DOC to the N. Atlantic is the most likely explanation for the large age difference we observe between deep DOC in the Atlantic and Southern Oceans. Other possibilities are a source of older DOC or a smaller microbial sink in the S. Ocean, or perhaps a possible slowdown of S. Ocean deep water formation during the past century [Broecker et al., 1999].

Introduction

The $^{14}$C ages of DOC are significantly older (by 3300-3800 $^{14}$C y) than those of dissolved inorganic carbon (DIC) in the same waters of the deep (> 1500 m depth) N. Atlantic and N. Pacific Oceans. This is due to recycling of DOC on century-to-millennial timescales [Druffel et al., 1992; Williams and Druffel, 1987]. Most deep DOC is believed to be utilized at extremely low rates by free-living bacteria [Barber, 1968], which likely accounts for the decrease in DOC in the deep sea from about 48 $\mu M$ in the Greenland Sea to 34 $\mu M$ in the N. Pacific (49°N) [Druffel et al., 1992; Hansell and Carlson, 1998]. Global riverine inputs alone could account for observed $^{14}$C residence times of DOC in the world oceans [Hedges et al., 1997], however, lignin content [Meyers-Schulte and Hedges, 1986; Opsahl and Benner, 1997], molecular composition [Hedges et al., 1992] and $^{87}$C signatures [Williams and Gordon, 1970] indicate that oceanic DOC contains only small amounts of identifiable terrestrial organic matter. Instead, autochthonous marine production in surface waters is believed to be the primary source of the standing DOC pool in the oceans [Williams and Druffel, 1987]. The ultimate sinks of DOC are even more poorly defined, but include bacterial utilization [Carlson and Ducklow, 1996; Cherrier et al., 1996; Williams and Carlucci, 1976], photochemical degradation [Mopper et al., 1991] and sorption to particles [Druffel and Williams, 1990; Santachi, 1991].

The 2000-year $^{14}$C age difference between deep N. Pacific and deep N. Atlantic DOC is larger than the 1500 year $^{14}$C age difference for DIC, possibly owing to excess 'young' DOC from higher river inputs to the Atlantic [Opsahl and Benner, 1997] or higher fluxes of 'young' (post-bomb) organic matter from the euphotic zone in the Atlantic [Deuser et al., 1988; Druffel et al., 1992]. It has been hypothesized that most deep DOC is transported conservatively between the N. Atlantic and the N. Pacific via the deep conveyor belt [Druffel et al., 1992]. Measurements of the $^{14}$C age and concentration of deep DOC in the S. Ocean, located between these two end members, are essential to test this hypothesis.

Methods

Radiocarbon in DOC, DIC and suspended particulate organic carbon (POC$_{\text{dep}} > 1 \mu m$ diameter) was measured in samples collected from 22 - 24 depths between 3 and 5441 meters in the S. Ocean in December 1995 - January 1996. This area is dominated by westward flowing surface waters that have a weak thermocline, even in summer. Deep waters include Pacific Deep Water (1000-2500 m, low oxygen, high silica), the core of the N. Atlantic Deep Water (2500-4500 m, high salinity, low silica) and Antarctic Bottom Water found within a few hundred meters of the bottom (cold and dense) [Reid, 1986]. Samples were treated and oxidized according to previously described techniques (see Figure 1a,b caption) and the resultant CO$_2$ extracted and purified. The CO$_2$ from these samples was split ~ 1:10, with the small fraction for $^{87}$C analysis and the large fraction converted to a graphite target [Vogel et al., 1987] on cobalt catalyst for $^{14}$C analysis using accelerator mass spectrometry (AMS) at the Center for AMS Res. at the Lawrence Livermore National Laboratory. Statistical uncertainties (1σ) for individual AMS $^{14}$C measurements ranged from $\pm 5 to \pm 7\%_o$; the total uncertainty for DIC $^{14}$C values was $\pm 6\%_o$, and for DOC and POC $^{14}$C was $\pm 13\%_o$.

Results

The DOC $^{14}$C values from the S. Ocean samples (Fig. 1a) ranged from -366%o at 3 m depth to -517%o at 2876 m depth. These $^{14}$C values are the lowest yet observed for surface waters. The weak thermocline at high latitudes [Gille, 1999] allows $^{14}$C-poor, deep DOC to mix vertically along surfaces of
constant density into the surface waters. This range in DOC
$\Delta^{14}C$ values from surface to deep in the S. Ocean (151%) is
similar to that observed for the DIC $\Delta^{14}C$ values (201%) (Fig.
1a), though the DOC $\Delta^{14}C$ values are 340-390% lower. The
similarities in the shapes of the DOC and DIC $\Delta^{14}C$ profiles
show that bomb $^{14}C$, produced in the stratosphere in the late
1950s and early 1960s, has penetrated both dissolved carbon
pools to a depth of ≥ 1000 m (pre-bomb, DIC $\Delta^{14}C$ values in
surface and deep waters was ~ -160% [Linick, 1980]).

In contrast, POC$_{sup}$ $\Delta^{14}C$ values (Fig. 1b) ranged from 32%
at 16 m (= surface DIC $\Delta^{14}C$ values) to -111% at 5391 m (50 m
above bottom), indicating that even the deepest POC$_{sup}$
samples contained some post-bomb carbon. Concentrations of POC<sub>susp</sub> in surface (3-85 m) waters (2.6 - 10 μM) were the highest we have observed in the open ocean and were non-trivial compared to the surface DOC pool (51 μM). Deep values, however, averaged 0.08μM which are similar to other open ocean sites [Druffel et al., 1992].

Analysis

The decrease in Δ<sup>14</sup>C of POC<sub>susp</sub> with depth may be due to incorporation of 'old' DOC onto POC<sub>susp</sub> by heterotrophic uptake or sorption [Druffel and Williams, 1990] (Figure 1b). This scenario requires ~14% of POC<sub>susp</sub> in the mid-water column (2800 m, Δ<sup>14</sup>C = -38‰) to consist of old DOC (with a Δ<sup>14</sup>C = -500‰). Other combinations of phases and Δ<sup>14</sup>C values can produce the observed reduction in Δ<sup>14</sup>C of POC<sub>susp</sub>. The quantitative importance of DOC sorption onto POC<sub>susp</sub> while unknown, has been speculated to have a significant impact on the Δ<sup>14</sup>C of the POC pool [Druffel et al., 1996; Druffel and Williams, 1990].

Vertical mixing between the local surface and deep reservoirs adequately describes mass and isotope balances of DOC in the three oceans. For example, if surface DOC in the S. Ocean is comprised of a mixture of deep DOC (41 μM with average Δ<sup>14</sup>C of -500‰ ≥ 1500 m depth) and modern, surface-produced DOC (51 μM minus 41 μM = 10 μM, with an average Δ<sup>14</sup>C value = surface POC ≈ surface DIC = +20‰), then the total surface DOC (51 μM) would have a Δ<sup>14</sup>C value of -398‰ (41/51*(-500) + 10/51*(20)). This agrees with the average of three observed DOC Δ<sup>14</sup>C values in the upper 30 m of the mixed layer, -372 ± 5 (sd) ‰. Similar calculations reported previously for the N. Atlantic and N. Pacific revealed Δ<sup>14</sup>C values for surface DOC of -214‰ and -206‰, compared to measured surface values of -210‰ and -179‰, respectively [Druffel et al., 1992] (Fig. 1a).

When deep DOC Δ<sup>14</sup>C values are plotted as a function of DOC concentrations for our three sites (Fig. 2), it appears that either the S. Ocean values depart from the curve (shown) that links the deep N. Atlantic and N. Pacific values, or that the N. Atlantic values depart from a curve (not shown) that links the deep N. Pacific and the deep S. Ocean. Either DOC concentrations in the S. Ocean are high, or those in the N. Atlantic are low.

On one hand, if remineralization and aging alone of deep DOC had occurred during its transport via the deep conveyor, we would have expected the DOC concentrations in the deep S. Ocean to have been lower (and perhaps the Δ<sup>14</sup>C values to have been higher) than those observed, i.e., closer to the curve shown in Fig. 2. Bacterial consumption lags phytoplankton production of organic matter in the S. Ocean water column [Kari, 1993], which argues for DOC concentrations that are too high in the S. Ocean.

On the other hand, deep N. Atlantic DOC Δ<sup>14</sup>C values may be high because of riverine inputs of DOC to the Atlantic that are 4- and 6-fold greater per unit volume than to the Pacific or S. Oceans [Sverdrup et al., 1942], respectively. Aging of DOC during its transit from the N. Atlantic to the S. Ocean (1600 ¹⁴C yrs) appears too large compared to the water transit time determined from DIC ¹⁴C age differences (700 ¹⁴C yrs) [Stuiver et al., 1983]. Selective replacement of younger DOC, removed by remineralization, photo-oxidation or some other process(es), with older DOC could account for the large age decrease, but would require a nearly 1:1 exchange of DOC in order to maintain similar concentrations.

Figure 2. Δ<sup>14</sup>C of deep (>1500m) DOC versus concentration of DOC in the Sargasso Sea (open diamonds), N. Central Pacific (open triangles) [Druffel et al., 1992] and the S. Ocean (filled circles, this work). The curve is the calculated relationship between DOC concentration and Δ<sup>14</sup>C, assuming that DOC ¹⁴C ages at a constant rate from the average N. Atlantic value (-390‰, 4000 ¹⁴C years) to the average N. Pacific value (-525‰, 6000 ¹⁴C years). The line is slightly curved due to the natural log relationship between Δ<sup>14</sup>C and ¹⁴C age. The low DOC concentration for the S. Ocean point obtained from the water sample at 1700m shows a value of 35.5 μM and a Δ<sup>14</sup>C = -483‰, and probably represents less than 100‰ yield.

An important clue is the small but significant lowering of the mean deep DOC Δ<sup>14</sup>C between the S. Ocean and N. Pacific (25‰ or 400 ¹⁴C yrs), which is close to the shift observed in the DIC ¹⁴C age for S. Ocean-Pacific deep water transit [Fiedeiro, 1982; Stuiver et al., 1983]. Thus, constant remineralization or sorptive losses in this sector, with aging and non-fractionation of ¹⁴C during remineralization, would be consistent with our observations.

The lower Δ<sup>14</sup>C values in N. Atlantic DOC (-21 to -22‰) compared to starting plankton organic matter (-18 to -20‰) (unlike the N. Pacific or S. Ocean) remain enigmatic, but may reflect a relatively larger contribution of terrigenous C<sub>3</sub> plant material (Δ<sup>14</sup>C = -28 to -30‰) to the Atlantic. This material carries with it a significantly elevated Δ<sup>14</sup>C signature [Hedges et al., 1986; Raymond and Bauer, 1998].

Alternatively, the Δ<sup>14</sup>C of S. Ocean DOC could be too low, and explained either by a 3 μM (~8 %) addition of 'dead' DOC (Δ<sup>14</sup>C =-1000‰) to S. Ocean deep water (originally -460‰, 39 μM) or a >8-17% addition of a very 'old' fraction of the DOC (>1000 to -700‰) (Fig. 2). Sources of low Δ<sup>14</sup>C carbon to the S. Ocean could include black (elemental) carbon whose Δ<sup>14</sup>C values (-500 to -900‰) are significantly lower than the bulk organic carbon (-200 to -700‰) in the same sediment horizons (0-50 cm) from our S. Ocean site [Masiello and Druffel, 1998]. Some black carbon is submicron in size, thus it could contribute to the low DOC Δ<sup>14</sup>C values in the S. Ocean [Masiello and Druffel, 1998]. Inputs from the Antarctic continental margin may also significantly influence the Δ<sup>14</sup>C of DOC and POC in the S. Ocean, because low Δ<sup>14</sup>C values were found in organic carbon from surface sediments of the continental slope in the Ross Sea (<500 to -700‰)[DeMaster and Ragueneau, 1996]. Recent Δ<sup>14</sup>C measurements and mass balance calculations off the west and east coasts of the U.S suggest that 'old' DOC and POC<sub>susp</sub> inputs from ocean margins to the open ocean interior may be greater than inputs of...
recently produced organic carbon derived from the surface ocean [Bauer and Druffel, 1998]. Another possibility may be related to the recent report involving the possible slowdown of S. Ocean deep water formation during the 20th-century suggesting that ventilation of this deep water mass is episodic rather than in steady state [Broecker et al., 1999]. That DOC in this region could be aged longer at depth over the past few hundred years may be the reason for the old DOC (Druffel and Bauer, in prep).

Further studies, including compound specific 14C analysis [Eglinton et al., 1997], will help to determine the relative importance of selective replacement of young DOC by old DOC between the N. Atlantic and S. Ocean, inputs of old DOC in the S. Ocean and net remineralization losses between the S. Ocean and N. Pacific in the deep ocean.

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References


J. Bauer, School of Marine Sciences, College of William and Mary, Gloucester Point, VA 23062, (bauer@vims.edu)

E. Druffel, Department of Earth System Science, U. C. Irvine, Irvine, CA 92697-3100, (edruffel@uci.edu)

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