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Radiocarbon distributions in Southern Ocean dissolved and particulate organic matter

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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±2 µM) 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 µM in the Greenland Sea to 34 µM 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 [Deuse 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$_{>1}$ > 1 µm 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 $^{8}$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 (1 σ) for individual AMS $\Delta^{14}$C measurements ranged from +5 to ±7‰, the total uncertainty for DIC $\Delta^{14}$C values was ±6‰, and for DOC and POC $\Delta^{14}$C was ±13‰.

Results

The DOC $\Delta^{14}$C values from the S. Ocean samples (Fig. 1a) ranged from -366‰ at 3 m depth to -517‰ at 2876 m depth. These $\Delta^{14}$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...
Figure 1. a) $\Delta^{13}C$ of DOC and DIC in samples collected from Station FLUSH (54°S, 176°W) in the S. Ocean from December 1995 - January 1996 (filled and open circles, respectively), from the N. Central Pacific site (31°N, 159°W) from June - July 1987 (open and filled triangles, respectively) [Druffel et al., 1992] and from the Sargasso Sea site (33°50’N 63°30’W) in May - June 1989 (open and filled diamonds, respectively) [Bauer et al., 1992; Druffel et al., 1992]. The dashed line shows the $\Delta^{13}C$ values for seawater DIC collected during the GEOSECS expedition, Stn 290 (near the FLUSH site) at 58°S, 174°W on 25 February 1974 [Ostlund and Stuiver, 1980]. The DOC samples (0.65 liters seawater) were from seawater that was acidified to remove DIC and oxidized using high energy, UV-oxidation [Bauer et al., 1992; Williams and Druffel, 1987]. The recovery of DOC using high-energy UV oxidation has been compared to other methods (e.g., high-temperature catalytic oxidation, HTCO), and the two methods have been found to yield identical DOC concentrations for deep Pacific waters [Peltzer and Hayward, 1996; Sharp et al., 1995]. In addition, recent results from a global survey of deep ocean DOC using HTCO [Hansell and Carlson, 1998] show that concentrations obtained by this method are within 1µM of our values obtained by UV oxidation for latitudes matching those of our three sites. The analytical precision of the UV method is ±1 µM DOC, and independent replicate sample analyses typically agree to within 2 µM [Bauer et al., 1998; Bauer et al., 1992]. The DIC samples (0.5 liters seawater) were acidified and stripped of CO$_2$ by recirculated nitrogen gas [Masiello et al., 1998; McNichol et al., 1994].

b) $\Delta^{13}C$ of POC$_{susp}$ in samples collected from the S. Ocean (filled circles), the N. Central Pacific site (open triangles) [Druffel et al., 1992] and the Sargasso Sea (open triangles) [Bauer et al., 1992; Druffel et al., 1992]. Suspended POC was collected using in situ pumps which pumped seawater for 2-8 hours through 4 quartz fiber filters (0.8 µm pore diameter) mounted in PVC holders [Williams et al., 1980]. The filters with POC$_{susp}$ were acidified, dried and combusted in double quartz tubes at 850°C [Druffel et al., 1992]. The concentrations of POC (µg/l) at each depth were determined from the manometric measurement of CO$_2$ gas obtained after combustion of each filter and the liters of water filtered. Radiocarbon measurements for all samples are reported as $\Delta^{13}C$ in per mil [Stuiver and Polach, 1977]. $\Delta^{13}C$ values are corrected for blank CO$_2$ added during combustion of POC$_{susp}$ and production of graphite [Druffel et al., 1996]. Stable carbon isotope results ($\delta^{13}C$) for all samples in this study were performed on splits of CO$_2$. The $\delta^{13}C$ measurements of all CO$_2$ samples were made by C. E. Franks on the VG Micromass 602E isotope ratio mass spectrometer in the laboratory of L. Keigwin at WHOI.

constant density into the surface waters. This range in DOC $\Delta^{13}C$ values from surface to deep in the S. Ocean (151%) is similar to that observed for the DIC $\Delta^{13}C$ values (201%) [Fig. 1a], though the DOC $\Delta^{13}C$ values are 340-390% lower. The similarities in the shapes of the DOC and DIC $\Delta^{13}C$ profiles show that bomb $^{13}C$, produced in the stratosphere in the late 1950s and early 1960s, has penetrated both dissolved carbon pools to a depth of $\geq$ 1000 m (pre-bomb, DIC $\Delta^{13}C$ values in surface and deep waters was $\sim$ -160% [Linick, 1980]).

In contrast, POC$_{susp}$$\Delta^{13}C$ values (Fig. 1b) ranged from 32% at 16 m (= surface DIC $\Delta^{13}C$ values) to -111% at 5391 m (50 m above bottom), indicating that even the deepest POC$_{susp}$
samples contained some post-bomb carbon. Concentrations of POC_{sup} 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^{14}C of POC_{sup} with depth may be due to incorporation of 'old' DOC onto POC_{sup} by heterotrophic uptake or sorption [Druffel and Williams, 1990] (Figure 1b). This scenario requires ~14% of POC_{sup} in the mid-water column (2800 m, Δ^{14}C = -38‰) to consist of old DOC (with a Δ^{14}C = -500‰). Other combinations of phases and Δ^{14}C values can produce the observed reduction in Δ^{14}C of POC_{sup}.

The quantitative importance of DOC sorption onto POC_{sup} while unknown, has been speculated to have a significant impact on the Δ^{14}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^{14}C of -500‰ ≥ 1500 m depth) and modern, surface-produced DOC (51 µM minus 41 µM = 10 µM, with an average Δ^{14}C value = surface DOC = surface DIC = +20‰), then the total surface DOC (51 µM) would have a Δ^{14}C value of -398‰ (41/51(-500) + 10/51(20)). This agrees with the average of three observed DOC Δ^{14}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^{14}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^{14}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^{14}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^{14}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 (4C yrs) appears too large compared to the water transit time determined from DIC 14C age differences (700 (4C 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.

An important clue is the small but significant lowering of the mean deep DOC Δ^{14}C between the S. Ocean and N. Pacific (25% or 400 (4C yrs), which is close to the shift observed in the DIC 14C age for S. Ocean-Pacific deep water transit [Fiadeiro, 1982; Stuiver et al., 1983]. Thus, constant remineralization or sorptive losses in this sector, with aging and non-fractionation of 13C during remineralization, would be consistent with our observations.

The lower Δ^{14}C values in N. Atlantic DOC (-21 to -22‰) compared to starting planktonic organic matter (-18 to -20‰)[unlike the N. Pacific or S. Ocean] remain enigmatic, but may reflect a relatively larger contribution of terrigenous C3 plant material (δ^{13}C = -28 to -30‰) to the Atlantic. This material carries with it a significantly elevated Δ^{14}C signature [Hedges et al., 1986; Raymond and Bauer, 1998].

Alternatively, the Δ^{14}C of S. Ocean DOC could be too low, and explained either by a 3 µM (~8 %) addition of 'dead' DOC (Δ^{14}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^{14}C carbon to the S. Ocean could include black (elemental) carbon whose Δ^{14}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^{14}C values in the S. Ocean [Masiello and Druffel, 1998]. Inputs from the Antarctic continental margin may also significantly influence the Δ^{14}C of DOC and POC in the S. Ocean, because low Δ^{14}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^{14}C measurements and mass balance calculations off the east and west coasts of the U.S. suggest that 'old' DOC and POC_{sup} 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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