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Radiocarbon in dissolved organic carbon of the South Pacific Ocean

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Abstract

Marine dissolved organic carbon (DOC) originates mainly from primary production using dissolved inorganic carbon (DIC) that has young 14C ages. Paradoxically, the 14C age of deep DOC ranges from 4000 to 6400 14C years, indicating that a portion of DOC survives multiple, deep ocean mixing cycles. Here we show that 14C ages of DOC from the deep South Pacific are equal to those from the deep north central Pacific. This is contrary to DIC 14C ages that increase from south to north in the deep Pacific. We hypothesize that DOC in the South Pacific is influenced by input of ancient DOC from hydrothermal flanks and ridges of the East Pacific Rise. We show that DOC Δ14C values in the deep Pacific are not controlled by aging during northward transport of deep waters, indicating that the deep oceanic carbon cycle needs reassessment.

1. Introduction

Dissolved organic carbon (DOC) is the largest pool of reduced carbon in the oceans, approximately 200 times larger than the living biomass [Hansell et al., 2009]. Measurements of DOC Δ14C are available for only a few locations in the deep ocean (Figure 1a, inset). Values decrease from the Sargasso Sea in the North Atlantic (−393‰ 4000 14C years), to the Southern Ocean (−500‰ 5600 14C years) [Druffel and Bauer, 2000], to the north central Pacific (NCP) (−522‰ 6000 14C years) [Druffel et al., 1992; Williams and Druffel, 1987] and are lowest in the northeastern Pacific (−550‰ 6400 14C years) [Beaupré and Druffel, 2009]. This pattern is in contrast to the DIC Δ14C values that show a 700 14C year difference between the Sargasso Sea and Southern Ocean (compared to a 1600 year difference for DOC) and a 700 14C year difference between the Southern Ocean and NCP (compared to a 400 year difference for DOC). It was suggested that bomb 14C was present in the Sargasso Sea, making the DOC too young there [Druffel and Bauer, 2000]. A companion study reporting DOC Δ13C values for the Atlantic Ocean addresses this issue.

Additionally, ocean margins are a source of old DOC to the deep northeast Pacific and northwest Atlantic [Bauer and Druffel, 1998] and a source of young DOC to the deep subpolar Pacific [Tanaka et al., 2010]. It appears that the bulk DOC Δ14C values near ocean margins are significantly influenced by additional inputs of DOC. The South Pacific data we report are indicative of ocean basin locations and have very low deep DOC concentrations (35 µM), whereas those near ocean margins are higher by 3–4 µM.

We report DOC Δ14C results of samples from the South Pacific that show deep Δ14C values are equal to those in the deep NCP. This result indicates that deep DOC is not controlled by northward circulation of Lower Circumpolar Deep Water. This presents a conundrum in the present understanding of the DOC cycle in the deep sea.

2. Methods

Radiocarbon in DOC was measured in seawater samples collected from two to 14 depths at six stations along 32.5°S, between 145°W and 71°W on the Repeat Hydrography P06 cruise in January/February 2010. The mixed layer depths at these stations were 30–40 m. Subsurface water masses are Antarctic Intermediate Water (AAIW) (500–1200 m), southward Pacific Deep Water (PDW 1500–3000 m, low oxygen, high silica), northward Lower Circumpolar Deep Water (LCDW 2500–4500 m, high salinity, low silica) and Antarctic Bottom Water (within a few hundred meters of the bottom, cold, and dense) [Reid, 1986] (Figure 1b).

Samples were diluted with 18.2 MΩ Milli-Q water, acidified, purged with helium gas, and UV oxidized according to previously described techniques [Beaupré et al., 2007; Griffin et al., 2010]. The resultant CO2 was converted to graphite on iron catalyst for 14C analysis at the Keck Carbon Cycle Accelerator Mass...
Spectrometry Laboratory at University of California Irvine [Druffel et al., 2013]. Total uncertainties for individual $\Delta^{14}C$ values of approximately $-500\%$ are $\pm 4\%$ as determined from analyses of duplicate seawater samples and secondary standards [Druffel et al., 2013]. DOC concentrations are determined from the manometric measurement of CO$_2$ obtained from the UV oxidation of acidified seawater, with uncertainties of $\pm 0.9$ μM. Stable carbon isotopes ($\delta^{13}C$) were measured on equilibrated splits of the CO$_2$ samples using a Gas Bench II and Thermo Electron Delta Plus mass spectrometer with an uncertainty of $\pm 0.1\%$.

3. Results and Discussion

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

The DOC $\Delta^{14}C$ values were highest in the surface (3–92 m depth) along 32.5°S ranging from $-210\%$ at Station 218 to $-259\%$ at Station 248 in the Peru coastal upwelling region (Figure 1a). There was a rapid decrease to $-500\%$ by 1200 m at the base of AAIW. Values were constant ($-524 \pm 3\%$ standard error, $n = 10$) between 1400 and 2200 m and lowest between 2400 and 3200 m depth (average $-538 \pm 2\%$, $n = 6$) in the southward PDW. In northward LCDW, values were significantly higher (>3200 m, $-519 \pm 3\%$, $n = 8$). Results from all stations were similar, with the exception of two depths (739 m and 1042 m) from Station 228 where $\Delta^{14}C$ values were 17–28% lower than those from the other stations.

A comparison of the South Pacific DOC $\Delta^{14}C$ values with those of the NCP from 1987 [Druffel et al., 1992] (Figure 1a) reveals that values were similar below 1400 m (see Table S2 in the supporting information) and their averages were equal within error ($-526 \pm 2\%$, $n = 24$; $-522 \pm 5\%$, $n = 8$, respectively). Values were higher in the South Pacific from 800 to 1300 m and lower between 200 and 500 m than those at the NCP, indicating circulation differences, or that bomb $^{14}C$, produced in the 1950s and 1960s, may have penetrated deeper in the 23 years between the collections. This would complicate comparisons between the two data sets in the upper water column, but not below 1300 m.

Also shown in Figure 1a are the DOC $\Delta^{14}C$ values for a site in the Southern Ocean (SOce) [Druffel and Bauer, 2000] that had a higher average value ($-500 \pm 3\%$, $n = 14$) for samples below 1400 m (i.e., LCDW) than those from the

Figure 1. (a) DOC $\Delta^{14}C$ (this work, left) and DIC $\Delta^{14}C$ [Druffel and Bauer, 2000; Druffel et al., 1992; Wanninkhof et al., 2010] measurements plotted versus depth from samples collected in the South Pacific at six stations occupied during the P06 cruise in January/February 2010; errors are $\pm 4\%$ (smaller than sizes of the points) and were determined from duplicate analyses of seawater samples [Druffel et al., 2013]. Values for samples from the NCP [Druffel et al., 1992] and Southern Ocean (SOce) [Druffel and Bauer, 2000] cruises are shown for comparison (lines), with uncertainties of $\pm 10\%$ for DOC $\Delta^{14}C$ (not shown) and $\pm 4\%$ for DIC $\Delta^{14}C$. Inset map shows locations of the P06 stations (see Table S1 in the supporting information for exact locations) and other DOC $\Delta^{14}C$ profiles [Beaupré and Druffel, 2009; Druffel and Bauer, 2000; Druffel et al., 1992]; (b) DOC concentrations (μmol kg$^{-1}$) along 150°W (colors as per legend above); arrows show water mass renewal and circulation, where PDW is Pacific Deep Water, LCDW is Lower Circumpolar Deep Water, AAIW is Antarctic Intermediate Water, and SAMW is Subantarctic Mode Water; white lines indicate isopycnal surfaces $\sigma_0$ [after Hansell et al., 2009].
Paciﬁc. In contrast, all of the SOce values shallower than 600 m were lower than the corresponding Paciﬁc values, because of intense mixing of low Δ14C deep waters up to the surface in the Southern Ocean.

The δ13C values in the South Paciﬁc ranged from −19.5‰ to −23.2‰ (both at Station 190), with values higher than −21‰ generally found for samples shallower than 200 m (Figure 2a). A comparison of the South Paciﬁc DOC δ13C values with those of the NCP [Druffel et al., 1992] (Figure 2a) reveals lower values for most South Paciﬁc samples. Values from the deep South Paciﬁc and deep SOce were similar.

3.2. Comparison of DOC and DIC Δ14C Values

Comparison of the South Paciﬁc DOC Δ14C values with the DIC Δ14C values [Wanninkhof et al., 2010] from the same water samples reveals that both are high in the upper 1000 m due to the presence of bomb 14C (Δ14C > −50‰) (Figure 1a). The lowest DIC Δ14C values are in PDW, which overlap with the lowest DOC Δ14C values. The DIC Δ14C values in the South Paciﬁc >1500 m (average −205 ± 2‰, n = 51) [Wanninkhof et al., 2010], however, are signiﬁcantly higher than those in the NCP [Druffel et al., 1992] (average −234 ± 5‰, n = 7). An earlier study [Stuiver et al., 1983] used measurements of DIC Δ14C [Ostlund and Stuiver, 1980] to calculate an approximate 510 year replacement time of deep waters in the Paciﬁc.

In sharp contrast, our DOC Δ14C values from the deep South Paciﬁc (−522‰) are identical to those from the deep NCP. Whereas DIC Δ14C values decreased from the South Paciﬁc to the NCP, demonstrating aging of about 300 14C year as LCDW ﬂowed from 32°S to 31°N, no such trend exists in the DOC Δ14C data. We had expected to ﬁnd DOC Δ14C values that were intermediate between those in the SOce and the NCP, or approximately −512‰. We based our original expectation on three assumptions: (1) the transport of deep DOC is northward from the South Paciﬁc to the North Paciﬁc, (2) 14C decay is the primary cause of the difference between the Δ14C values at the two locations, and (3) no patchiness exists in the Δ14C ﬁeld of the deep Paciﬁc that would cause an anomaly. Because we see no difference between the Δ14C values in the deep South Paciﬁc and the deep NCP, we conclude that one or more of these assumptions is incorrect.

3.3. DOC Concentrations

Concentrations of DOC in the South Paciﬁc are similar at each depth for all stations (Figure 2b and Table S2 in the supporting information). The average DOC concentration (and range) for samples below 1200 m is 35.0 ± 1.0 μM (standard deviation (sd)) (32.6–37.0 μM, n = 27), equal to that in the NCP (35 ± 1 μM sd, 34–36 μM, n = 9).
In contrast, DOC concentrations in the SOce (41.4 ± 1.4 μM, sd, 39.1–43.7 μM, n = 14) are higher than those in the NCP and South Pacific.

A localized sink of refractory DOC was reported in the subtropical South Pacific at 150°W [Hansell and Carlson, 2013]. However, our DOC concentration data show that low DOC concentrations extend throughout the South Pacific basin from 145°W to 72°W.

3.4. Differences Between DIC and DOC Cycles

To understand why DOC Δ¹⁴C values and DOC concentrations are equal in both the North and South Pacific deep waters, while DIC Δ¹⁴C values are not, it is important to note their relative pool sizes. The DOC concentration (35 μM) is much lower than the DIC concentration (~2300 μM) [Wanninkhof et al., 2010], making the DOC reservoir more sensitive to small changes in DOC production and removal. Also, the sources and sinks (or removal) of DIC in seawater are relatively well understood (gas exchange with the atmosphere, photosynthesis, and remineralization of organic matter and calcium carbonate), whereas those of DOC in seawater are complex and not well understood (e.g., photosynthesis, remineralization, microbial transformations [Jiao et al., 2010], particle solubilization [Smith et al., 1992], river input, chemosynthesis [Hansman et al., 2009], and hydrothermal processes [McCarthy et al., 2011]).

The above considerations make DIC Δ¹⁴C gradients an approximate measure of the transport time of seawater from the deep Southern Ocean to the deep North Pacific. However, our results illustrate that DOC Δ¹⁴C values in the deep Pacific are not controlled by aging during transport, considering the assumptions stated above. Instead, selective remineralization or input of fractions of DOC with Δ¹⁴C values that are significantly different from the bulk DOC value may be key for understanding why deep South Pacific DOC Δ¹⁴C values are equal to those in the deep NCP.

3.5. Possible Mechanisms for Low Δ¹⁴C Values in the South Pacific

Possible explanations for the low Δ¹⁴C values include (i) enhanced remineralization of DOC whose Δ¹⁴C value is higher than that of the bulk value, (ii) hydrothermal alteration at ridges and flanks where DOC is stripped from inflowing water and old, chemosynthetic DOC is added to outflowing water, and (iii) enhanced input of young DOC to the NCP.

First, enhanced remineralization of DOC may be occurring during transport from the SOce (41.4 μM, ~500‰) to the South Pacific (35 μM, ~526‰). A mass balance calculation reveals that 6.4 μM (41.4–35.0 μM) of the DOC with a Δ¹⁴C value of ~380‰ would have been remineralized to achieve the average concentration and Δ¹⁴C value in the deep South Pacific. The rate of remineralization required for this scenario is 0.015 ± 0.003 μmol C kg⁻¹ yr⁻¹ (6.4 μmol C kg⁻¹/430 years). This does not agree with a previous study that showed refractory DOC is generally conserved during much of its circulation in the deep Pacific [Hansell and Carlson, 2013].

A second mechanism that would explain low DOC concentrations and lower Δ¹⁴C values in the South Pacific is hydrothermal venting of ocean water through porous ocean crust. Ridge-flank systems have been shown to strip out oceanic DOC onto porous basalts [Lang et al., 2006] and deliver chemosynthetic DOC (Δ¹⁴C = ~140‰, δ³¹C = ~26 to ~34.5‰ [McCarthy et al., 2011]) to the deep northeast Pacific. A linear regression of DOC Δ¹⁴C values and excess δ³¹He content of seawater (a tracer of hydrothermal activity) below 1000 m depth in the South Pacific is inversely correlated (r = −0.93, p < 0.0001, n = 30) (Figure S1b in the supporting information). The linear correlation between DOC Δ¹⁴C and δ³¹He in the deep ocean does not necessarily demonstrate a causal link. However, the DOC δ¹⁴C values of samples closest to the East Pacific Rise (Station 190) and all South Pacific values >3000 m are lower than those in the NCP (Figure 2a and Table S2 in the supporting information), which could indicate that there is more chemosynthetic DOC in the South Pacific than in the NCP. An estimate of the mass of hydrothermal DOC that is admitted to the deep ocean, assuming a DOC concentration of 12 μM [Lang et al., 2006; McCarthy et al., 2011] and a total ridge-flank fluid input to the world ocean of 7.1 × 10¹² m³ yr⁻¹ [Johnson and Pruis, 2003] to 2 × 10¹³ m³ yr⁻¹ [Mottl, 2003], is 1–3 × 10¹² g C yr⁻¹. This is 1–3% of the input of DOC to the global deep ocean based on mass and Δ¹⁴C age (6.0 × 10¹⁷ g C/6000 Δ¹⁴C years) [Williams and Druffel, 1987]. This means that approximately 1–3% of the deep DOC could be replaced each year by hydrothermal venting, assuming the lability of the hydrothermal DOC is similar to that of average deep DOC. A 3% input of hydrothermal DOC (Δ¹⁴C = ~800‰ [McCarthy et al., 2011]) would lower the deep DOC
Δ¹⁴C value in the South Pacific from our expected value of −512‰ to −521‰ (0.03 · (−800‰) + 0.97 · (−512)), which is within error of the average observed value of −526‰. A similar calculation of the deep DOC δ¹³C value (0.03 · (−30‰) + 0.97 · (−21.2)) reveals a decrease from the NCP value of −21.2‰ to −21.5‰, close to the average observed value of deep DOC for the South Pacific (−21.6‰).

A third scenario that may explain the DOC Δ¹⁴C values in the Pacific involves the assumption that, instead of South Pacific values being too low, the values in the NCP are too high. Enhanced delivery of fresh DOC from surface production to the deep NCP, or chemosynthetic production of DOC using deep DIC (whose Δ¹⁴C value is several hundred ‰ higher than that of DOC [Hansman et al., 2009]) would be potential sources of high Δ¹⁴C DOC that could make NCP values higher than expected. This does not appear likely, however, because net primary production in the NCP and the South Pacific are similar [Falkowski, 2014].

Of the three processes discussed as possible explanations for the low DOC Δ¹⁴C values in the South Pacific, the input of ancient DOC at hydrothermal ridges and flanks appears to be the most plausible. This effect is likely higher in the Pacific than in other oceans because the spreading rates of ridges in the Pacific are the highest of all ocean ridge systems [Lupton, 1998].

### 4. Implications for the Ocean Carbon Cycle

It appears that there is a small, but significant amount of preaged DOC entering the deep Pacific from hydrothermal ridges and flanks, which contributes, in small part, to the great age of oceanic DOC. The implications of this DOC input on our understanding of the oceanic carbon cycle are in two areas: (1) the distribution of DOC and (2) its residence time in the deep sea.

First, understanding of the distribution of DOC in the deep ocean is based on thousands of measurements of DOC concentrations in waters from the major ocean basins over the past two decades [Hansell and Carlson, 1998, 2013; Hansell et al., 2012, 2009]. Recent work suggests that there is a DOC deficit at 30°–34°S along 150°W, though a mechanism has not yet been identified [Hansell and Carlson, 2013]. This DOC deficit may, in part, be the result of hydrothermal stripping of deep DOC in porous basalts and input of water with low DOC concentrations into the deep sea.

Second, the residence time of DOC in the deep sea has been estimated using ¹⁴C measurements, assuming that the DOC originates from photosynthetic production in the surface ocean. A source of ancient DOC produced by chemosynthesis would mean that the residence time of DOC in the deep ocean is shorter than originally estimated.

Additional data from the Pacific, including DOC alteration at hydrothermal ridges and flanks, are needed to nail down the process or processes responsible for controlling deep DOC concentrations and Δ¹⁴C values in the Pacific. Measurements from other oceans are also required to establish the global extent of the process(es) and the implications for the oceanic carbon cycle.

### References


