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TEMPORAL VARIABILITY OF DISSOLVED ORGANIC RADIOCARBON IN THE DEEP NORTH PACIFIC OCEAN

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ABSTRACT. We report marine dissolved organic carbon (DOC) $\Delta^{14}C$ from seawater collected from the North central Pacific Ocean (NCP) in 2015. These measurements show DOC $\Delta^{14}C$ values averaged –235 ± 5‰ ($n = 3$) in the mixed layer (24–81 m) and –544 ± 5‰ ($n = 5$) in the deep water (1500–5139 m). A comparison of these data with two previously published DOC $\Delta^{14}C$ profiles from the NCP in 1985 and 1987 reveals that deep DOC $\Delta^{14}C$ values have decreased. We discuss several possible mechanisms that could cause such a shift in DOC $\Delta^{14}C$ values, including spatial inhomogeneity and temporal variability due to changes in the dissolution and $\Delta^{14}C$ value of surface derived particles in the deep sea. We find that forthcoming profiles of DOC $\Delta^{14}C$ results from the NCP will determine the primary mechanisms controlling deep DOC $\Delta^{14}C$ distributions, and changes over the past three decades.

KEYWORDS: ^{13}C , ^{14}C , deep ocean, dissolved organic carbon, variability.

INTRODUCTION

Radiocarbon (^{14}C) is a useful isotope for tracing the flow of deep water in the global ocean, because the transit time of dissolved inorganic carbon (DIC) in seawater from its formation in the North Atlantic to the furthest part of the deep flow in the North Pacific (about 1500 ^{14}C yr) is of the same order of magnitude as its half-life (5730 yr) (Broecker et al. 1960; Bien et al. 1965).

The first measurements of ^{14}C in marine dissolved organic carbon (DOC) were reported by Williams et al. (1969) using gas counting that required 400 L of seawater. When accelerator mass spectrometry (AMS) was available in the early 1980s, measurements required just 5 L of seawater. The DOC was found to be 6000 ^{14}C yr old in the deep North Pacific (Williams and Druffel 1987). This very old age for DOC was surprising because the DOC was thought to be produced in the surface ocean, and should be much younger. Instead, the old ^{14}C age indicated that DOC survived multiple ocean mixing cycles and was circulated, like salt, with the deep water. Our field has been intrigued by these results ever since.

It has been proposed that the surface DOC is composed of a 1:1 mixture of old DOC similar to the $\Delta^{14}C$ value of deep water, and newly produced, post-bomb $\Delta^{14}C$ values (Williams and Druffel 1987). There were few profiles of DOC $\Delta^{14}C$ in the open ocean (Bauer et al. 1992, 1998; Druffel and Bauer 2000; Beaupré and Druffel 2009) until recent studies contributed more data (Griffiths et al 2012; Druffel and Griffin 2015; Tanaka et al. 2010). For example, the presence of bomb ^{14}C was detected in parts of the deep North Atlantic, increasing the pre-bomb ^{14}C age of deep DOC in this region to 4900 ^{14}C yr (Druffel et al. 2016).

The data presented here, combined with previous results from the deep NCP, show that deep DOC $\Delta^{14}C$ values were higher in the past. The possible reasons for this variability include inaccuracies in the data, temporal variability and spatial inhomogeneity.

METHODS

Radiocarbon in DOC ($\Delta^{14}C$) was measured in seawater samples collected from 31°0.047′N 152°0.074′W in the NCP during the P16N cruise (Station 130) on 1 June 2015 aboard the

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NOAA vessel *Ronald H. Brown*. DOC samples shallower than 400 m were filtered using pre-combusted (540°C, 2 hr) GFF (0.7 μm) filters. All DOC samples were collected in pre-combusted, 1 L Amber Boston Round glass bottles with acid cleaned (10% HCl) PTFE caps and frozen at –20°C until analysis.

In the lab, DOC samples were diluted with low carbon (DOC = 0.6 ± 0.3 μM), 18.2 MΩ Milli-Q water, acidified with 1 mL 85% phosphoric acid (HPLC grade), purged with ultrahigh purity helium gas (UHP He), and UV oxidized (UVox) for 4 hr (Beaupré et al. 2007; Griffin et al. 2010). The CO_2 evolved from DOC was then stripped with UHP He and cryogenically purified and quantified. Reported DOC concentrations were corrected for CO_2 lost due to breakthrough from the liquid nitrogen Horibe trap during collection, whose mass was quantified via integration using an infrared CO_2 gas analyzer (LI-COR Inc., model LI-6252) (Walker, Beaupré and Druffel, unpublished data). The breakthrough does not affect the $\Delta^{14}C$ and $\delta^{13}C$ measurements outside of the reported uncertainties. One sample replicate is run for every 14 samples (i.e. one per depth profile).

Samples were converted from CO_2 to graphite, by reduction on an iron catalyst using the closed-tube, zinc method (Xu et al. 2007). $\Delta^{14}C$ measurements were performed at the Keck Carbon Cycle AMS Laboratory at UC Irvine (Southon et al. 2004). ^{14}C results are reported as $\Delta^{14}C$ values that are corrected for date of collection according to convention (Stuiver and Polach 1977). The total uncertainty of the $\Delta^{14}C$ analyses was ± 4‰ (Druffel et al. 2013).

The $\delta^{13}C$ value of each sample was measured on a split of the CO_2 that was produced from the UV oxidation of the DOC sample using a Gas Bench II and Thermo Electron Delta Plus isotope ratio mass spectrometer, with a total analytical uncertainty of ± 0.2‰.

RESULTS

DOC $\Delta^{14}C$ Values

Figure 1 shows new DOC $\Delta^{14}C$ values of samples collected from station 130 in 2015 on the P16N cruise. The $\Delta^{14}C$ values ranged from –239‰ to –229‰ in the upper 81 m of the water column, and decreased monotonically with depth to –487‰ by 901 m (Figure 1a, Table 1). From 1234 m to 5139 m, DOC $\Delta^{14}C$ values ranged from –551‰ to –522‰ (Figure 1b).

Previous DOC $\Delta^{14}C$ values from samples collected in 1985 and 1987 (31°N, 159°W) (Druffel et al. 1992) from a station 670 km to the west of P16N Station 130 were higher in the mixed layer, reflecting higher bomb ^{14}C in surface waters in the 1980s (Andrews et al. 2016). The average of values below 1500 m depth was lower for the 2015 cruise (–544 ± 5‰) than for those from the 1985 (–530 ± 6‰) and 1987 (–522 ± 5‰) cruises (Figure 1b). The physical properties of the water at both sites (potential temperature and salinity) are similar (Figure 2), indicating that similar water masses were sampled below 1500 m (S > 34 psu and potential temperature <6°C) at these two sites.

DOC $\delta^{13}C$ Values

The $\delta^{13}C$ results of DOC samples collected in 2015 on the P16N cruise (Figure 3a) range from –22.1‰ to –21.2‰ throughout the profile. The highest value (–21.2‰) was in surface water (24 m), and the lowest value (–22.1‰) was at both 367 m and 1500 m.

Previous $\delta^{13}C$ values from samples collected in 1985 and 1987 were higher than those from 2015. The average of all values from 2015 was –21.7 ± 0.2‰ ($n = 13$), compared to averages

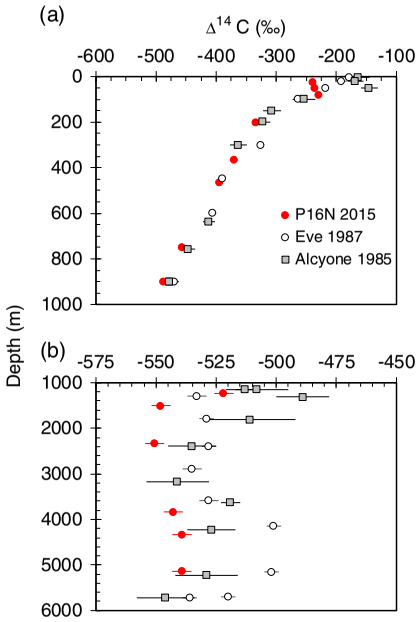

Figure 1 $\Delta^{14}C$ values of DOC collected at station 130 (31° 0.047'N, 152° 0.074'W) during the P16N cruise (June 1, 2015): (a) between 0 and 1000 m depth and (b) deeper than 1000 m depth. Also shown are DOC $\Delta^{14}C$ values for samples collected from 31°0.0′ N, 159°0.0′W for the Alcyone cruise (November 1985) (Williams and Druffel 1987) and the Eve-1 cruise (June/July 1987) (Druffel et al. 1992).

for 1985 and 1987 of –20.9 ± 0.2‰ ($n = 19$) and –21.1 ± 0.2‰ ($n = 16$), respectively. Student's *t*-tests reveal that the values for 1985 and 1987 are significantly different ($p = 0.009$), and that both the 1985 and 1987 results are significantly different than those from 2015 ($p < 0.001$).

DOC Concentrations

In 2015, DOC concentrations ranged from 73.0–38.3 µM (Figure 3b). Values were highest in the upper 81 m (52.7–73.0 µM), and lowest between 2334 m and 5139 m (38.3–38.7 µM).

DOC concentrations reported for the 1985 and 1987 samples, also shown in Figure 3b, show the same general trend from high to low values with depth in the water column. However, these earlier profiles also show an offset in DOC concentrations. The offset of approximately 3–5 µM compared to the 2015 P16N samples is likely due to the "breakthrough" loss of CO_2 from the liquid nitrogen trap during He stripping of evolved CO_2 in samples after UV oxidation (Beaupre, Walker and Druffel, unpublished data). This breakthrough was not quantified in the earlier analyses (Williams and Druffel 1987; Druffel et al. 1992). Unfortunately, there is no way to estimate the amount of CO_2 breakthrough from these early studies. But, if we assume that the same breakthrough occurred in the earlier analyses from the 1985 and 1987 samples as we measured for the 2015 samples (3–5 µM), then the earlier concentrations would be approximately equal to those obtained in 2015. This suggests that DOC concentrations have remained fairly constant in the deep NCP over the past 30 years.

Table 1 Concentration, $\Delta^{14}C$, and $\delta^{13}C$ measurements of DOC in seawater samples collected from station 130 on 1 June 2015 during the P16N cruise.

Niskin #	Stn CTD dbars*	UCID #	[DOC] µM	DOC $\Delta^{14}C$ (‰)	DOC $\delta^{13}C$ (‰)
23	24	19581	71.2	–239	–21.2
22	50	20155	73.1	–236	nd
21	81	19708	52.8	–229	–21.6
19	201	19574	42.3	–333	–22.0
17	367	19575	51.7	–369	–22.1
16	467	19707	47.1	–395	–21.8
14	749	19568	43.8	–457	–21.6
13	901	19580	43.0	–487	–21.7
12	1234	19579	40.7	–522	–21.7
11	1500	19582	40.0	–548	–22.1
9	2334	19567	38.4	–551	–21.8
9	2334	19569	38.6	–550	–21.6
6	3834	19576	38.3	–543	–21.7
5	4333	19570	38.8	–539	–21.7
2	5139	19571	nd	–539	–21.8

nd indicates no data.
*CTD dbars is approximately equal to meters depth.

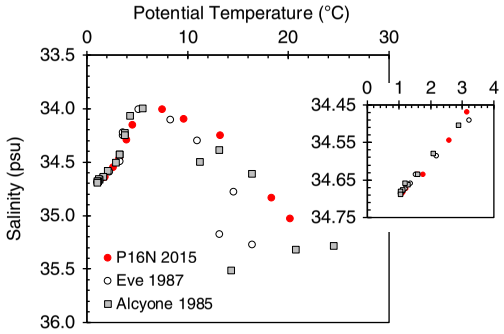

Figure 2 Salinity versus potential temperature of seawater samples collected on the Alcyone cruise in 1985, Eve-1 cruise in 1987 and P16N cruise (station 130) in 2015. Below potential temperature of 4°C (see inset), values are similar for all three cruises, which indicates similar water masses were sampled during the three cruises.

DISCUSSION

Possible Explanations for Variable DOC $\Delta^{14}C$ and $\delta^{13}C$ in the Deep Ocean

Here we discuss several possible reasons for the variability of DOC $\Delta^{14}C$ values observed in the deep NCP, including (1) historical measurement accuracy, (2) spatial inhomogeneity of the DOC $\Delta^{14}C$ signal owing to a variety of reasons (e.g. input of very low $\Delta^{14}C$ hydrothermal DOC), and (3) temporal variability of the DOC $\Delta^{14}C$ signal owing to changes in dissolution of surface-derived particles in the deep sea, and changes in particle bomb ^{14}C and fossil-fuel CO_2 $\Delta^{14}C$ contributions.

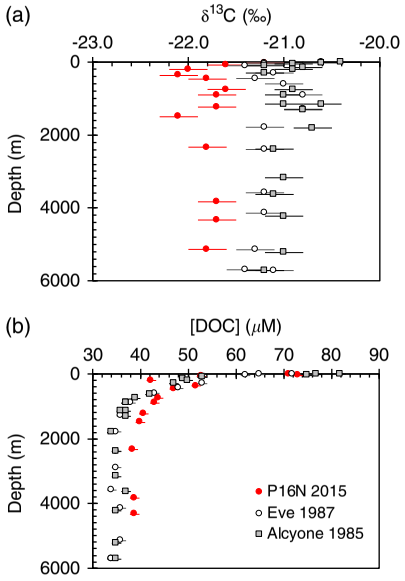

Figure 3 (a) $\delta^{13}C$ values and (b) DOC concentrations of DOC collected at Station 130 during the P16N cruise. Also shown are DOC $\delta^{13}C$ values for samples collected from 31°0.0′N, 159°0.0′W reported for the Alcyone cruise (November 1985) (Williams and Druffel 1987) and the Eve-1 cruise (June/July 1987) (Druffel et al. 1992).

Measurement Accuracy

Methods used to obtain DOC $\Delta^{14}C$ measurements from the three research cruises were similar, albeit the 1980s profile data was produced using a different UV oxidation line from that of the 2015 profile. However, the same UV oxidation methods were used to convert DOC to CO_2, though larger water samples were analyzed for the earlier cruises (5L) than for the 2015 cruise (0.8L). AMS techniques were used to measure the $^{14}C/^{12}C$ ratio in all of the samples, and the same general methods were used to correct for extraneous C, e.g. measuring ^{14}C of oxalic acid I standard. Thus, it is not apparent that the earlier $\Delta^{14}C$ data or those from 2015 are inaccurate. We note that the total uncertainties of the 1985 measurements (±4–19‰) were larger than those from 1987 (±3–9‰), and the uncertainties of both of these earlier measurements were overall larger than those from 2015 (±4‰).

Deep Ocean DOC $\Delta^{14}C$ Spatial Inhomogeneity

There may be spatial variability in DOC $\Delta^{14}C$ in the deep NCP due to a variety of causes. For example, variable fluxes of surface-derived particles and enzymatic hydrolysis, microbial respiration and/or solubilization are sources of DOC from particulate organic carbon (POC) in deep waters. This would make the expectation of obtaining the same *exact* DOC $\Delta^{14}C$ value for a given deep ocean region unreasonable. Duplicate casts from a single station, or within a several hundred km radius, would help to constrain possible inhomogeneity. However, because DOC $\Delta^{14}C$ analyses are so time consuming (9 hr are required to convert and purify DOC to CO_2 gas in a single sample, Milli-Q blank or standard) and expensive, this experiment has not been performed to our knowledge. Thus, we cannot rule out that spatial variability of DOC $\Delta^{14}C$ is present in the deep NCP.

We note that the comparisons presented in Figure 1 are from two sites separated by 670 km. These two sites have similar net primary production and net POC export rates in the surface waters (Falkowski 2014), making it unlikely that there would be differences in the overall input of high $\Delta^{14}C$ surface POC that may dissolve at depth between these two locations.

Another mechanism that could cause regional differences in the DOC $\Delta^{14}C$ value in the deep sea is regional input of DOC produced in hydrothermal ridges and flanks. Studies have shown that DOC emanating from hydrothermal ridges and flanks are altered by chemosynthetic bacteria living in the new seafloor basalt and have low $\delta^{13}C$ and low $\Delta^{14}C$ values (Lang et al. 2006; McCarthy et al. 2011; Hawkes et al. 2015). Other sources of DOC to the deep sea include methane–derived DOC from gas hydrate-bearing seeps (Pohlman et al. 2011), DOC effluxing from pore waters in anoxic sediments (Komada et al. 2013), and chemosynthetic production of organic matter in seawater by microbial populations (Hansman et al. 2009).

Temporal Variability

Temporal changes in the isotopic composition of the DOC is a possible explanation of the DOC $\Delta^{14}C$ variability displayed in data from the three cruises (Figure 1). There were short term differences between the 1985 and 1987 profiles, most notably at 4200 m and 5200 m depths, where $\Delta^{14}C$ values from the 1987 cruise (–501 ± 3‰ and –502 ± 3‰) were significantly higher than those from 1985 (–527 ± 10‰ and –529 ± 13‰, respectively) (Figure 1b). These significant differences (>2 sigma) between deep DOC $\Delta^{14}C$ results at the same station only 19 months apart would argue that there is temporal variability of the isotopic composition of deep DOC. This variability may be seasonal, given that the 1985 samples were collected in November and those in 1987 were collected in June, which may reflect a higher summer particle flux rate (Smith 1989).

Twenty years later, DOC $\Delta^{14}C$ values from the 2015 cruise near 4200 m and 5200 m depths (both –539 ± 4‰) were lower (by 10–38‰). Having data from only three time periods makes it difficult to ascertain whether there is a significant trend that would continue to decrease with time from one ocean region. A seasonal study at Station M in the northeast Pacific (34°50′N 123°00′W) from 1991 to 1993 reported significant variability in DOC $\Delta^{14}C$ from depths below 1500 m (20–30‰) (Bauer et al. 1998). A later study at Station M reports data from 1998–2004 that shows the $\Delta^{14}C$ values at 450 m depth displayed significant short-term variability (20–60‰) (Beaupré and Druffel 2009). In both studies, DOC $\Delta^{14}C$ variability was observed at all depths, and exceeded methodological uncertainty (4–6‰). Therefore, variability seen in the earlier data from the 1985 and 1987 cruises in the NCP appears consistent with these observations at Station M.

The cause(s) of the apparent temporal DOC $\Delta^{14}C$ variability in the deep NCP are not yet identified. A possible candidate is solubilization of surface-derived sinking POC in the deep sea, whose $\Delta^{14}C$ value has decreased during the past 60 years due to both a decrease in atmospheric bomb $^{14}CO_2$ and an increase in fossil fuel CO_2. During the 1980s, the surface DIC $\Delta^{14}C$ value in the NCP was 140 ± 10‰ (Druffel and Griffin 2008), approximately 100‰ higher than that in 2015. This means that DOC produced from sinking POC would have a $\Delta^{14}C$ value that was approximately 100‰ higher in the 1980s than that in 2015. We can estimate the fraction of bomb ^{14}C that would likely be present in the deep DOC pool by 2015. For example, if we assume the production rate of DOC in the deep sea is ~0.14 ± 0.02 GtC/yr (Walker et al. 2016), the size of the deep ocean (>1000 m) DOC reservoir is 477 ± 25 GtC (Hansell et al. 2009), and that 58 ± 1 yr have past between 2015 and when bomb ^{14}C was first introduced (1957), then the

fraction of post-bomb deep DOC would be 1.7 ± 0.3% (= 100 × (58yr × 0.14GtC/yr)/477 GtC). This calculation assumes no remineralization of the post-bomb DOC to CO_2 over the 58 years, and provides a maximum estimate of the fraction of post-bomb carbon in deep ocean DOC.

If we assume that the average $\Delta^{14}C$ value of the surface bomb DOC was +100‰ over the period 1957–2015, based on a Kure Atoll coral $\Delta^{14}C$ record (Andrews et al. 2016), then the $\Delta^{14}C$ value of deep DOC in 58 years would increase by 11‰ [e.g. (0.017) × (+100‰) + (0.983) × (–550‰) = –539‰], increasing from –550‰ to –539‰. This change is similar to the range between the average deep $\Delta^{14}C$ values in our three time periods (–530 ± 5‰, –522 ± 5‰, –544 ± 5). However, we observed a *decrease* in the average values between 1985 and 1987 (–530 ± 5‰ and –522 ± 5‰) and 2015 (–544 ± 5‰), not an increase as this calculation predicts. In order to obtain a change in the deep ocean using the input of post-bomb POC, it would be necessary to increase the export flux to values that exceed an order of magnitude times higher than accepted estimates (Falkowski 2014; Walker et al. 2016). Thus, a clear mechanism for the decrease in deep DOC $\Delta^{14}C$ remains undetermined.

Possible Explanations for Deep Sea DOC $\delta^{13}C$ Variability

Values of DOC $\delta^{13}C$ were significantly lower in 2015 (by 0.6–0.8‰) throughout the water column than those in 1985 and 1987 (Figure 3a). Possible reasons for the variability of DOC $\delta^{13}C$ values observed in the deep NCP are spatial inhomogeneity of the DOC $\delta^{13}C$ signal, seasonal variability, and temporal variability of the DOC $\delta^{13}C$ owing to fossil fuel CO_2. It is not likely that DOC $\delta^{13}C$ values vary spatially, because little variability has been observed in subtropical regions (Druffel et al. 1992; Bauer et al. 1998), though this explanation cannot be eliminated.

It is possible that the lower DOC $\delta^{13}C$ values in 2015 are influenced by the presence of fossil fuel CO_2 ($\delta^{13}C = -28 \pm 1$‰), whose concentration has continued to increase over the last century. Measurements of DIC $\delta^{13}C$ in NCP surface waters decreased by about 0.6‰ from 1972 to 1987 (McNichol and Druffel 1992), and subtropical surface waters have continued to decrease by ~0.16‰ per decade (Sonnerup et al. 2000). However, the low values from the 2015 cruise were likely not caused by fossil fuel derived CO_2 from particles produced in the surface ocean. For example, input of 0.9 ± 0.1% DOC to the deep ocean [= 100 × (30 yr × 0.14 GtC/yr)/477 GtC] from 1985 to 2015 would cause a lowering of deep DOC (–21.0‰) by only 0.06‰ [e.g. 0.01 × –28) + (0.99 × –21) = –21.06 ± 0.20‰], an order of magnitude smaller than the observed decrease of 0.6–0.8‰. At this time, a clear mechanism for the decrease in deep DOC $\delta^{13}C$ also remains undetermined.

FUTURE DIRECTIONS

Completion of six additional profiles of DOC $\Delta^{14}C$ results from the P16N cruise along 152°W from 14°S–57°N in 2015 will improve our understanding of the mechanism(s) responsible for the trends in deep DOC $\Delta^{14}C$ and $\delta^{13}C$ in the NCP. These new data will help to determine whether the DOC $\Delta^{14}C$ trend in the deep ocean was primarily controlled by aging during deep circulation (as revealed by DIC $\Delta^{14}C$ measurements), or by other mechanisms, such as input of DOC from POC or from hydrothermal sources.

Additional time series of DOC $\Delta^{14}C$ and $\delta^{13}C$ are necessary to adequately evaluate the temporal and spatial shifts in oceanic DOC cycling, especially given continued global change of the carbon cycle and warming of the Earth.

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