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Constraining the propagation of bomb-radiocarbon through the dissolved organic carbon (DOC) pool in the northeast Pacific Ocean

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ABSTRACT

This study extends the 1991–1995 records of marine dissolved organic carbon (DOC) concentrations and $\Delta^{14}\text{C}$ values at hydrographic Station M (34°50'N, 123°00'W) with new measurements from a frozen (−20 °C) archive of samples collected between April 1998 and October 2004. The magnitudes and synchronicity of major $\Delta^{14}\text{C}$ anomalies throughout the time-series imply transport of DOC from the surface ocean to depths of at least 450 m on the timescale of months. Keeling plots of all measurements at Station M predict a continuum of possible background DOC compositions containing at least 21 μM of −1000‰ (i.e., $\geq 57,000$ ^{14}C years) DOC, but are more consistent with mean deep DOC (38 μM , −549‰; i.e., $\sim 6,400$ ^{14}C years). These results and coral records of surface dissolved inorganic carbon (DIC) $\Delta^{14}\text{C}$ were used to estimate pre-bomb DOC $\Delta^{14}\text{C}$ depth profiles. The combined results indicate that bomb- ^{14}C has penetrated the DOC pool to depths of ≥ 450 m, though the signal at that depth is obscured by short-term variability.

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1. Introduction

Dissolved organic carbon (DOC) is the largest reservoir of reduced carbon in seawater with a global abundance of $\sim 685 \times 10^{15}$ gC (Hansell and Carlson, 1998) and is approximately equal in size to atmospheric CO_2 (Hedges, 1992). Despite its importance in the oceanic carbon cycle and more than a century of research (Natterer, 1892), DOC biogeochemical fluxes are poorly constrained. For example, the estimated global riverine input of ~ 0.25 Gt DOC per year (Cauwet, 2002; Meybeck, 1982) is sufficient to support its radiocarbon (^{14}C) based oceanic residence time. Yet molecular composition (Meyers-Schulte and Hedges, 1986; Opsahl and Benner, 1997) and stable carbon ($\delta^{13}\text{C}$) isotopic (Williams and Gordon, 1970) signatures indicate that the majority of marine DOC is autochthonous, ultimately originating from primary production in

the euphotic zone. Furthermore, while 4,000–6,000 year ^{14}C ages reported for deep DOC suggests a major proportion cycles on long time scales and ages during deep water transit (Bauer et al., 1992; Williams and Druffel, 1987), the removal processes necessary to produce these ages remain unknown.

As a tracer of time (Arnold and Libby, 1949; Libby, 1955, 1961; Libby et al., 1949) and carbon sources (Bauer and Druffel, 1998; Mortazavi and Chanton, 2004; Trumbore and Druffel, 1995), the ^{14}C content of marine DOC is a powerful tool for potentially constraining many of these uncertainties. However, significant analytical challenges have limited the number of bulk marine DOC $\Delta^{14}\text{C}$ observations to five regions globally (Fig. 1). Long-term measurements of DOC $\Delta^{14}\text{C}$ have been reported for only two of these locations: the central North Pacific (CNP) in 1985 and 1987 (Bauer et al., 1992; Williams and Druffel, 1987), and Hydrographic Station M off the coast of California from July 1991 to June 1995 (Bauer et al., 1998a, 1998b). Therefore, the global data set of DOC $\Delta^{14}\text{C}$ observations is significantly limited in spatiotemporal range and resolution.

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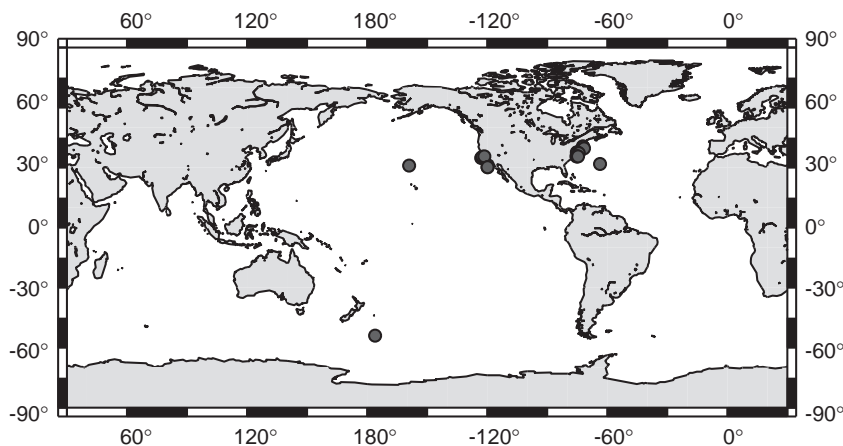


Fig. 1. Map of locations of previously published bulk marine DOC $\Delta^{14}\text{C}$ measurements (Bauer and Druffel, 1998; Bauer et al., 1998a, 2002, 1992; Beaupré et al., 2007; Druffel and Bauer, 2000; Druffel et al., 1992, 1989; Williams and Druffel, 1987; Williams et al., 1969, 1978).

Similar $\Delta^{14}\text{C}$ depth profiles of DOC and dissolved inorganic carbon (DIC) suggest that the DOC pool in the CNP contains bomb- ^{14}C (McNichol and Aluwihare, 2007; Williams and Druffel, 1987) created by thermonuclear weapons testing in the 1950s and 1960s (Nydal, 1963; Nydal et al., 1980). Since bulk DOC $\Delta^{14}\text{C}$ values are weighted averages of the radiocarbon contents of DOC constituents, knowledge of bomb- DO^{14}C distributions would constrain the spatiotemporal scales over which DOC is reactive. The long time-series at Station M is the most promising data set for observing such changes in the marine DO^{14}C inventory.

This study extends the previously published record of DOC concentrations and $\Delta^{14}\text{C}$ values at Station M (Bauer et al., 1998a, 1998b) with new measurements of archived samples from April 1998 to October 2004. In addition, Keeling plots (Keeling, 1958; Mortazavi and Chanton, 2004) from each depth profile throughout this time-series were used to constrain the isotopic composition of bulk marine DOC at Station M. These analyses were combined with coral records of surface DIC $\Delta^{14}\text{C}$ (Druffel, 1987) to construct pre-bomb DOC $\Delta^{14}\text{C}$ depth profiles and constrain the propagation of bomb-carbon through the DOC pool at Station M.

2. Materials and procedures

Seawater samples were collected during a series of cruises (Pulse-34, 37, 38, 40, and 45; Table 1) to hydrographic Station M ($34^{\circ}50'\text{N}$, $123^{\circ}00'\text{W}$), a long-term abyssal study site (maximum depth of $\sim 4100\text{ m}$) located 220 km west of Point Conception, CA (Smith and Druffel, 1998). Samples from $\sim 25\text{ m}$, $\sim 85\text{ m}$, and $\sim 450\text{ m}$ depth were analyzed for the period of April 1998 to June 2002. Additional samples from seven depths (one surface, three mesopelagic, and three $> 1000\text{ m}$ depth) were collected during October 2004. Samples collected from the Southern Ocean (54°S , 176°W) in December 1995 (Druffel and Bauer, 2000) were also analyzed as a test of isotopic

fidelity during long-term frozen storage. Except where noted, the time-series (Table 1) represents single measurements of individual samples from discrete bottle or CTD rosette casts.

All samples from April 1998 to June 2002 were gravity filtered directly from Go-Flo bottles into 1-liter glass bottles using pre-combusted (525°C) GF/C glass fiber filters ($1\ \mu\text{m}$ nominal pore size). Samples from October 2004 were gravity filtered directly from Go-Flo bottles into 3.8-liter glass jugs using Whatman Polycap AS filter capsules ($0.2\ \mu\text{m}$ nominal pore size) that were pre-rinsed with acetonitrile and Milli-Q water. Filters were connected to the bottles using Nalgene 50 platinized silicone tubing that was previously washed with 10% HCl and Milli-Q water. All filters and silicone tubing were flushed with sample for several minutes prior to dispensing into glass bottles. The bottles were then sealed with polytetrafluoroethylene (PTFE) Teflon lined caps that were pre-rinsed with 10% HCl, Milli-Q water, and seawater sample. Lastly, the sealed sample bottles were wrapped in clean polypropylene bags, and stored frozen at -20°C until laboratory analysis.

DOC concentrations and $\Delta^{14}\text{C}$ values were measured via an ultraviolet-oxidation procedure described in detail elsewhere (Beaupré et al., 2007). Briefly, each seawater sample was transferred into a quartz reaction vessel, then acidified with 1 ml of 85% H_3PO_4 , sparged with ultra high purity (UHP) helium to remove DIC, and irradiated with UV-light from a 1200 Watt medium pressure mercury arc lamp for a total of 4 hours. Samples archived before October 2004 ranged in volume from 347 – 552 ml and were diluted to ~ 1 liter with pre-irradiated Milli-Q water prior to UV-oxidation. The resulting CO_2 was then extracted from the residual seawater via sparging with UHP helium and collected in a dedicated vacuum line. DOC concentrations were calculated via manometric quantification of the CO_2 collected and measurements of the seawater volumes that were irradiated.

Following reduction of CO_2 to graphite (Vogel et al., 1987), DOC $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values were concurrently

Table 1
DOC and DIC $\Delta^{14}\text{C}$, and DOC concentration measurements from Station M.

Depth (m)	DOC UCID# ^a	[DOC] ^b (μM)	DOC $\Delta^{14}\text{C}$ ^c (‰)	DIC UCID# ^a	DIC $\Delta^{14}\text{C}$ ^d (‰)
<i>Pulse-34, April 1998</i>					
25	9264	76.5 \pm 0.9	-260.1 \pm 1.6	3054	58.9
85	9339	64.5 \pm 0.8	-275.8 \pm 1.4	3055	73.1
450	9343	41.3 \pm 0.6	-416.3 \pm 1.4	3056	-111.3
<i>Pulse-37, June 2001</i>					
25	9263	63.7 \pm 0.7	-283.9 \pm 1.5	6261	25.8
85	9340	55.5 \pm 0.7	-326.1 \pm 1.4	4951	29.6
450	9283	39.8 \pm 0.5	-469.3 \pm 1.4	6253 & 6255	-112.2
<i>Pulse-38, October 2001</i>					
25	9262	77.4 \pm 1.4	-302.9 \pm 1.4	6306	42.0
85	9341	50.1 \pm 0.6	-374.6 \pm 1.5	6311B	18.2
450	9282	42.9 \pm 0.6	-509.2 \pm 1.2	6305	-117.2
<i>Pulse-40, June 2002</i>					
25	9226	61.1 \pm 0.5			
85	9342	55.7 \pm 0.7	-276 \pm 1.3	6356	24.6
450	9281	40.8 \pm 0.5	-435 \pm 1.3	6357A & B	-115.0
2500	9296	38.5 \pm 0.5	-546.4 \pm 1.5	6363	-246.7
<i>Pulse-45, October 2004</i>					
21	^e	71.8 \pm 1.2	-300.6 \pm 1.4	9355	31.0
206	8308	48.2 \pm 0.2	-402.0 \pm 1.4		
458	8307	43.7 \pm 0.2	-467.1 \pm 1.1		
690	8306	41.7 \pm 0.2	-511.9 \pm 1.1		
2013	8305	38.9 \pm 0.2	-579.0 \pm 1.1	9356	-246.9
3478	8300	39.2 \pm 0.2	-568.4 \pm 1.1		
4059	8299	42.8 \pm 0.2	-584.3 \pm 1.1		
<i>Mean values for depth bins from all Pulse cruises, July 1991–October 2004^f</i>					
24 \pm 2		71 \pm 4.8	-272 \pm 24		53 \pm 20
85 \pm 1		58 \pm 4.8	-309 \pm 33		44 \pm 22
455 \pm 9		42.5 \pm 1.6	-453 \pm 28		-117 \pm 13
728 \pm 35		39.3 \pm 1.4	-495 \pm 18		-166 \pm 28
1619 \pm 23		37.3 \pm 2.4	-552 \pm 10		-233 \pm 11
2532 \pm 89		37.3 \pm 1.1	-553 \pm 12		-244 \pm 4
3502 \pm 46		38.2 \pm 1.2	-556 \pm 12		-243 \pm 8
4052 \pm 45		38.3 \pm 2.9	-552 \pm 17		-231 \pm 9
> 1000		37.9 \pm 1.8	-549 \pm 20		-237 \pm 10

^a Laboratory sample identification number.^b Errors propagated from uncertainty in manometry.^c Errors propagated from AMS measurement statistics and blank corrections.^d Methodological errors for DIC $\Delta^{14}\text{C}$ measurements were ca. $\pm 5\%$ (Masiello et al., 1998).^e [DOC] and DOC $\Delta^{14}\text{C}$ are reported as the mean values from measurements of four separate aliquots at this depth (UCID 8253, 8270, 8271, 8276), ± 1 standard deviation of the mean.^f Includes previously published data (Bauer et al., 1998a, 1998b; Masiello et al., 1998).

measured via accelerator mass spectrometry (AMS) at the UCI Keck Carbon Cycle Accelerator Mass Spectrometry (KCCAMS) laboratory. While machine-induced fractionation is proportional among carbon isotopes during AMS measurements and permits precise $\delta^{13}\text{C}$ corrections for $\Delta^{14}\text{C}$ values, it does not provide reliable, independent $\delta^{13}\text{C}$ data (Santos et al., 2007). Since DOC abundances in the smaller volume samples (ca. < 0.5 L) were insufficient for complimentary $\delta^{13}\text{C}$ measurements by isotope ratio mass spectrometry (IRMS), $\delta^{13}\text{C}$ measurements are not reported. However, $\Delta^{14}\text{C}$ values are still reported according to the conventions of Stuiver and Polach (1977).

All concentrations and $\Delta^{14}\text{C}$ values were corrected for the methodological blank of the UV-extraction procedure. The mass of blank carbon, $2 \pm 1 \mu\text{g C}$, was determined by reanalysis of previously oxidized seawater and Milli-Q water. The small mass of carbon in the blank precluded direct analysis by AMS. Therefore, the radiocarbon content

of the methodological blank was determined by observing the deviations in $\Delta^{14}\text{C}$ measurements of UV oxidized ^{14}C standards [IAEA C-6 (Rozanski et al., 1992), IAEA C-7, and IAEA C-8 (Le Clercq et al., 1998)] from their consensus values.

Lastly, DIC $\Delta^{14}\text{C}$ values ($\pm 5\%$, Masiello et al., 1998) were measured in separate archived samples (Table 1) according to published methods (McNichol et al., 1994, 1995).

3. Results and discussion

3.1. Sample storage

The effects of long-term storage (≤ 12 years) on DOC concentrations and $\Delta^{14}\text{C}$ values were determined by measuring Southern Ocean samples collected and frozen

in December 1995. These were the only available samples stored prior to the onset of the Station M DOC archive and quantified prior to frozen storage (Druffel and Bauer, 2000). Seven samples containing less than 100 ml of seawater were available from 25 m, 85 m, 250 m, 450 m, and 4200 m depth, and required dilution to ~1 liter for UV-oxidation of DOC. These volumes and the associated total masses of DOC extracted from each sample were nearly an order of magnitude smaller than the undiluted seawater typically used in this extraction procedure, resulting in significantly larger uncertainties for both concentration and $\Delta^{14}\text{C}$ measurements. Upon thawing, five of the seven samples revealed the presence of a persistent white crystalline precipitate, as well as a crystalline film on the inner walls of their glass bottles. Elemental analysis (EA) coupled with IRMS of lyophilized crystals revealed that the precipitate was $6.4 \pm 0.1\%$ carbon by mass with a $\delta^{13}\text{C}$ value of $-0.6 \pm 0.2\text{‰}$. These values are consistent with the precipitation of barium carbonate but may contain other constituents. The limited mass of crystals did not permit further elemental characterization.

Concentrations and $\Delta^{14}\text{C}$ values of the two samples that did not possess crystals were within 2 standard deviations of previously published values (Fig. 2, gray data points), whereas those of the five samples with precipitated crystals were not (Fig. 2, white data points). Since the crystals did not dissolve prior to analysis, both high and low yields could have resulted from transferring non-uniform slurries into the reactor. Despite originating from the same Go-Flo bottle, two out of three

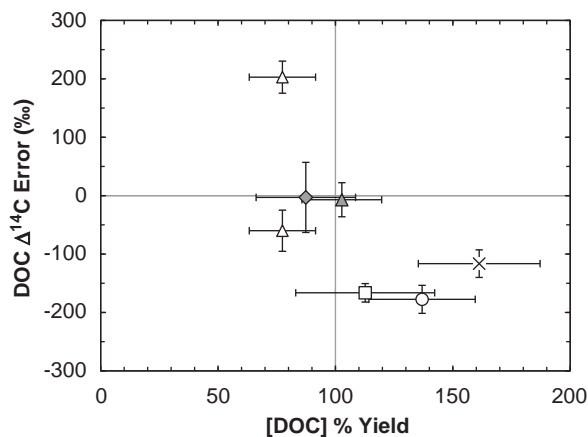


Fig. 2. The effects of long term (≥ 11 years) frozen storage on DOC concentration and isotopic fidelity in small aliquots of seawater collected from 25 m (circle), 85 m (square), 250 m (triangles), 450 m (\times), and 4200 m (diamond) depth in the Southern Ocean, December 1995. $\Delta^{14}\text{C}$ error is defined here as the difference between $\Delta^{14}\text{C}$ measurements performed in 2007 and those performed at the time of collection in 1995 (Druffel and Bauer, 2000). Percent yield is the ratio of concentration measurements performed in 2007 to those performed at the time of collection in 1995 (Druffel and Bauer, 2000), expressed as a percentage. The concentration and $\Delta^{14}\text{C}$ value of the previously published 4200 m sample was taken as the average of all measurements below 1000 m to accommodate the large scatter in the original data. Error bars on the data points represent ± 2 standard deviations. The gray data points correspond to the only samples in this test that did not contain a crystalline precipitate when thawed in 2007.

250 m deep samples developed a precipitate and exhibited concentration and isotopic inconsistency (Fig. 2, triangles). Therefore, the crystallization observed here might be an artifact of sampling procedures coupled with frozen storage rather than an intrinsic property of the seawater samples.

Only one of the 24 archived Station M time-series samples (UCID 9288, Pulse-34 cruise, April 1998, 450 m) developed persistent crystals and possessed a DOC concentration ($58.9 \mu\text{M}$) that was inconsistent at this depth of the time-series. This sample was presumed compromised and therefore excluded from the present analysis. Fine white precipitates developed in the three samples from Pulse-34 and the 450 m sample from Pulse-38 that are presented in Table 1. However, these crystals dissolved readily upon shaking and were attributed to turbidity in the thawed samples. All measurements reported here (Table 1) were performed on samples that did not develop a persistent crystalline precipitate during storage.

Although the physicochemical connection between the precipitate and DOC fidelity is not yet understood, their association has several practical implications. Analytically, samples can be frozen for at least 12 years with DOC concentration and isotopic fidelity within the present methodological uncertainty as long as precipitation has not occurred. However, the unpredictable occurrence of precipitation in this Southern Ocean sample set preliminarily limits the viability of long term frozen storage of seawater for DOC analyses. Geochemically, if an inverse relationship exists between fidelity and crystal formation in frozen samples, then a natural mechanism may exist for altering the native characteristics of DOC. Additional analyses are required to confirm this relationship and its potential for coupling the biogeochemistry of DOC to sea-ice formation.

3.2. DOC time series data

This work extends the previously published Station M DOC time-series that began July 1991 and ended July 1993 (Bauer et al., 1998a). An additional depth profile of DOC concentration and $\Delta^{14}\text{C}$ at Station M from June 1995 (Bauer et al., 1998b) has been included in this assimilation (Table 1, Fig. 3). The literature values were reported with precisions of 3–6‰ and approximately $\pm 1 \mu\text{M}$ for replicate $\Delta^{14}\text{C}$ and concentration measurements (Bauer et al., 1998a), respectively, and are comparable with the method employed here (Beaupré et al., 2007). Therefore, the complete time-series (Fig. 3) is assumed to be free of instrumental artifacts.

The collection depths of previously published (Bauer et al., 1998a, 1998b) and archived DOC samples varied with each cruise. Thus, concentrations and $\Delta^{14}\text{C}$ values were grouped into “depth bins” (Table 1) with average depths (and associated ranges) of 24 m (20–25 m), 85 m (83–85 m), 455 m (449–475 m), 728 m (690–767 m), 1619 m (1595–1649 m), 2532 m (2379–2703 m), 3502 m (3459–3582 m), and 4052 m (3966–4096 m). Standard deviations of mean concentrations and $\Delta^{14}\text{C}$ values were

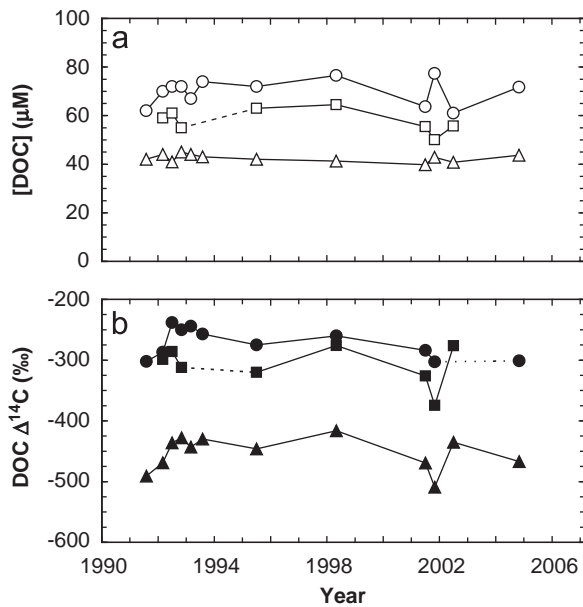


Fig. 3. Time-series measurements of DOC (a) concentrations and (b) $\Delta^{14}\text{C}$ values for ~25 m (circles), ~85 m (squares), and ~450 m (triangles) depth bins. Dashed lines indicate gaps in the time-series data with respect to other depths. Error bars (± 1 standard deviation) are smaller than the individual data points. DOC concentrations and $\Delta^{14}\text{C}$ values prior to 1996 are previously published values (Bauer et al., 1998a, 1998b). Major tick marks on the “Year” axis denote the first day of January.

not positively correlated with the number of samples or range of depths per bin (Beupr , 2007). Therefore, variability within each depth bin throughout the time-series was not an artifact of data organization.

On average, depth profiles of DOC concentrations and $\Delta^{14}\text{C}$ values from each depth bin were typical of marine DOC (Fig. 4a, b). Both were enriched in surface waters and decreased monotonically until becoming practically invariant below ~1000 m. DOC concentrations varied significantly in the upper ~450 m (Fig. 3a), with maximum variability ($1\sigma = \pm 4.8 \mu\text{M}$) at 24 m and 85 m depth (Table 1). With the exception of ~1600 m ($\pm 2.4 \mu\text{M}$) and 50 m above bottom ($\pm 2.9 \mu\text{M}$) the magnitudes of variability at all other depths ($\leq \pm 1.6 \mu\text{M}$) were on the order of methodological precision ($\leq \pm 1.5 \mu\text{M}$) for concentration measurements via UV-oxidation (Beupr  et al., 2007). Furthermore, daily variability at Station M ($1\sigma \approx \pm 4.4 \mu\text{M}$, $n = 8$, 85 m, Oct 1992; Bauer et al., 1998a) exceeded that of monthly and interannual variability at depths greater than 100 m. Therefore, the time-series concentration measurements alone are insufficient to resolve short-term variability at Station M.

In contrast, long-term DOC $\Delta^{14}\text{C}$ variability (Table 1, Fig. 3b) exceeded methodological precision ($\pm 1.5 - 6\text{‰}$; Bauer et al., 1998a; Beupr  et al., 2007) and daily variability ($1\sigma \approx \pm 7\text{‰}$, $n = 7$, 85 m, Oct 1992; Bauer et al., 1998a) at all depths. Monthly to inter-annual variations in DOC at Station M were primarily discernible in $\Delta^{14}\text{C}$ values from the upper ~450 m where variability was greatest ($1\sigma = \pm 24 - 33\text{‰}$).

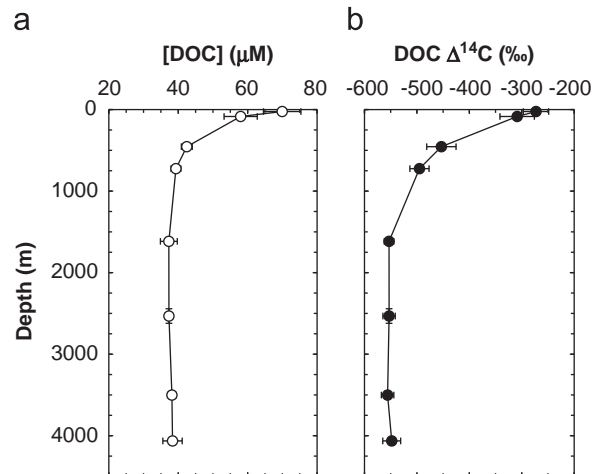


Fig. 4. Profiles of mean (a) DOC concentrations and (b) $\Delta^{14}\text{C}$ values at Station M as a function of mean depth for each depth bin (24 m, 85 m, 455 m, 728 m, 1619 m, 2537 m, 3502 m, and 4052 m). Error bars represent $\pm 1\sigma$ of the mean values. The data set includes previously published measurements from July 1991 through June 1995 at Station M (Bauer et al., 1998a, 1998b); the 2500 m depth bin excludes the anomalous sample collected during February 1992 (41 μM , -510‰), as noted by Bauer et al. (1998a).

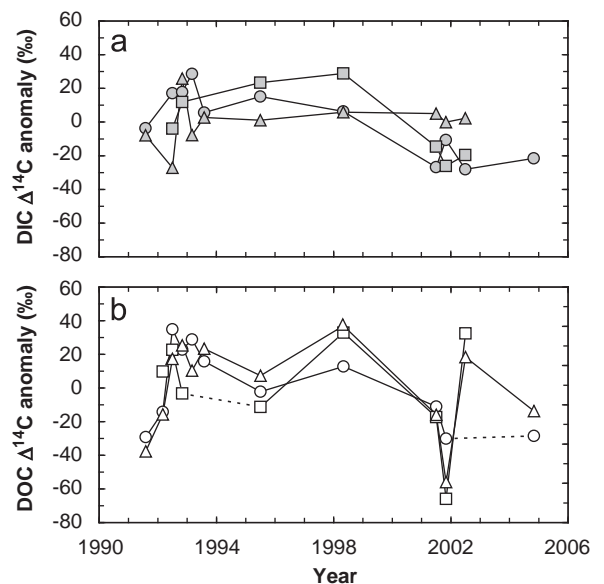


Fig. 5. Anomalies in $\Delta^{14}\text{C}$ of (a) DIC and (b) DOC at mean depths of 24 m (circles), 85 m (squares), and ~455 m (triangles) depth. Dashed lines indicate gaps in the time-series data with respect to other depth bins. $\Delta^{14}\text{C}$ anomalies for each depth bin are defined here as the difference between individual $\Delta^{14}\text{C}$ values and the mean $\Delta^{14}\text{C}$ value during the time-series. Major tick marks on the “Year” axis denote the first day of January.

3.3. DOC and DIC variability at Station M

The magnitude of DOC $\Delta^{14}\text{C}$ variability exceeded that of DIC $\Delta^{14}\text{C}$ at 25 m, 85 m, and 450 m throughout the time-series (Fig. 5). Major DOC $\Delta^{14}\text{C}$ features included rising $\Delta^{14}\text{C}$ values from 1991 to 1993, a slight elevation

during 1998, and a decrease during October 2001 (Figs. 3b and 5b). Synchronicity between features in $\Delta^{14}\text{C}$ values of DOC at these three depths and DIC above 85 m indicates oceanographic processes as their cause rather than methodological artifacts. The dissimilarity between these series and 450 m DIC (Fig. 5) suggests that the sources of DOC $\Delta^{14}\text{C}$ variability are tightly coupled throughout the upper 450 m to the surface layer DIC. This is consistent with photosynthesis as the principle source of marine DOC.

Variability during 1991–1992 and June 2001–June 2002 (Figs. 3 and 5) implies a rapid (e.g., ~months) propagation of the near-surface $\Delta^{14}\text{C}$ signal to depth. One possible mechanism may be seasonal convective overturn, as has been observed to vertically redistribute DOC in the Sargasso Sea (Carlson et al., 1994). However, limited temporal resolution in the time-series did not permit conclusive analyses of seasonal or climatological influences on these events. The strong signal at 455 m during various times of year (Figs. 3 and 5) may also have developed hydrographically via water movement and spatial gradients near Station M (e.g., Hansell and Carlson, 2009; Hansell et al., 2002), or geochemically by any processes that transport ^{14}C -enriched organic carbon through the operationally-defined DOC pool. For example, sinking particulate organic carbon (POC) dissolution (Repeta and Aluwihare, 2006) or POC mediated transport of DOC from the surface ocean (Beaupré, 2007; Druffel et al., 1996) may have influenced the $\Delta^{14}\text{C}$ values at depth.

The vertical distribution of DOC $\Delta^{14}\text{C}$ was directly related to DIC $\Delta^{14}\text{C}$ throughout the entire water column ($r^2 = 0.952$; Fig. 6) suggesting tightly coupled long-term (> months) processes that redistribute both carbon pools at Station M. However, none of the individual depth bins exhibited robust correlations between DOC and DIC $\Delta^{14}\text{C}$ values (Fig. 6). The highest correlation, $r^2 = 0.635$, was

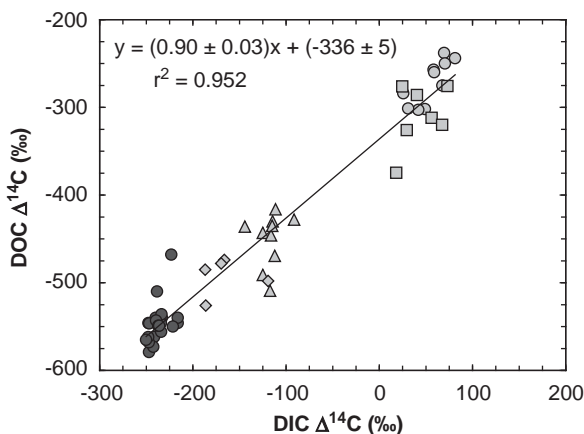


Fig. 6. DOC $\Delta^{14}\text{C}$ versus DIC $\Delta^{14}\text{C}$ at mean depths of 24 m (gray circles), 85 m (gray squares), 455 m (gray triangles), 728 m (gray diamonds), and >1000 m (black circles) for all available data. The black line is the least-squares fit to all data points. Linear regressions of all DOC and DIC $\Delta^{14}\text{C}$ values within each depth bin [i.e., the clusters of points from each depth; lines not shown] produced r^2 values of 0.635, 0.173, 0.033, 0.008, and 0.228 for measurements from mean depths of 24 m, 85 m, 455 m, 728 m, and >1000 m, respectively.

observed at 24 m, while coefficients of determination from all other depths were ≤ 0.228 . Therefore, the physical controls on short-term DIC variability below ~85 m (Masiello et al., 1998) did not likely dominate the observed short-term variability in DOC $\Delta^{14}\text{C}$.

3.4. Keeling plot models of Station M DOC

Mortazavi and Chanton (2004) have demonstrated that covariance between DOC concentrations and $\Delta^{14}\text{C}$ values with depth (Fig. 4) can be explained by Keeling plot models. Under this model, DOC consists of a background (bg) component of constant concentration and isotopic composition throughout the water column to which a second, isotopically distinct component is added in excess (xs) (Keeling, 1958; Pataki et al., 2003). This model makes no assumptions about the composition of background DOC and is consistent with previous descriptions of an isotopically-depleted DOC fraction that is uniformly distributed with depth (Williams and Druffel, 1987). The model can be expressed by the following equations for conservation of mass,

$$[\text{DOC}] = [\text{DOC}_{\text{bg}}] + [\text{DOC}_{\text{xs}}] \quad (1)$$

and isotopic mass-balance

$$\Delta^{14}\text{C} \times [\text{DOC}] = \Delta^{14}\text{C}_{\text{bg}} \times [\text{DOC}_{\text{bg}}] + \Delta^{14}\text{C}_{\text{xs}} [\text{DOC}_{\text{xs}}] \quad (2)$$

Substituting Eq. (1) into Eq. (2) and rearranging produces the standard Keeling plot model equation relating DOC concentrations to $\Delta^{14}\text{C}$ values throughout the water column.

$$\Delta^{14}\text{C} = (\Delta^{14}\text{C}_{\text{bg}} - \Delta^{14}\text{C}_{\text{xs}}) \times \frac{[\text{DOC}_{\text{bg}}]}{[\text{DOC}]} + \Delta^{14}\text{C}_{\text{xs}} \quad (3)$$

Thus, a plot of DOC $\Delta^{14}\text{C}$ versus $[\text{DOC}]^{-1}$ from a depth profile should produce a straight line with a slope (m) equal to $(\Delta^{14}\text{C}_{\text{bg}} - \Delta^{14}\text{C}_{\text{xs}}) \times [\text{DOC}_{\text{bg}}]$ and a y-intercept equal to the $\Delta^{14}\text{C}$ value of the excess component. Slopes and intercepts have been determined by geometric mean Model-II linear regressions for all depth profiles of the time-series (Table 2, Fig. 7), and are in agreement with

Table 2

Keeling plot regression parameters for depth profiles from Station M between July 1991 and October 2004.

Cruise	Date	Slope ^a ($\mu\text{M} \text{‰}$)	$\Delta^{14}\text{C}_{\text{xs}}$ ^a (‰)	r^2	n
Pulse-7	July 1991	-19100 ± 3000	-11 ± 78	0.861	8
Pulse-11	February 1992	-25500 ± 2500	105 ± 58	0.932	8
Pulse-12	June 1992	-26700 ± 2500	152 ± 61	0.929	10
Pulse-15	October 1992	-24500 ± 1400	111 ± 33	0.977	9
Pulse-16	February 1993	-24600 ± 2100	125 ± 52	0.970	6
Pulse-17	July 1993	-20800 ± 1400	31 ± 33	0.987	5
Pulse-26	June 1995	-21600 ± 2500	44 ± 61	0.883	11
Pulse-34	April 1998	-14700 ± 1700	-59 ± 31	0.986	3
Pulse-37	June 2001	-19800 ± 400	28 ± 8	1.000	3
Pulse-38	October 2001	-19800 ± 7400	-26 ± 140	0.865	3
Pulse-40	June 2002	-31800 ± 7900	310 ± 180	0.939	3
Pulse-45	October 2004	-26000 ± 4400	94 ± 99	0.864	7
all Pulse data		-23100 ± 900	74 ± 22	0.885	76

^a Errors are presented as ± 1 standard error of regression.

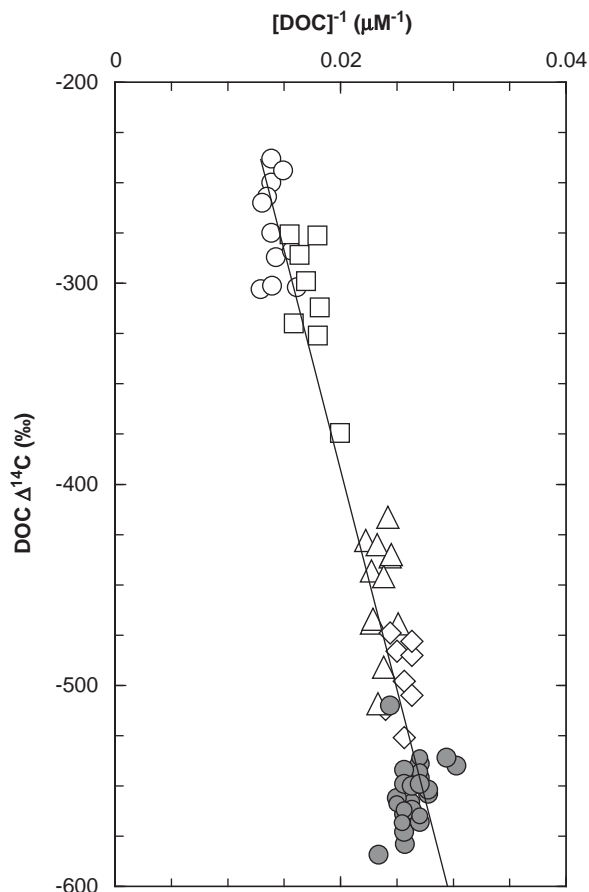


Fig. 7. Keeling plot of all Station M [DOC] and $\Delta^{14}\text{C}$ data at mean depths of 24 m (white circles), 85 m (squares), 455 m (triangles), 728 m (diamonds) and all depths below 1000 m (gray circles). The black line represents the least-squares fit to all data points ($r^2 = 0.885$, $n = 76$).

values determined by [Mortazavi and Chanton \(2004\)](#) for the period of July 1991 to July 1993.

3.5. Concentration and isotopic composition of background DOC

The Keeling plot model does not presume a concentration or isotopic signature for the background component of DOC. The only constraint is conservation of mass. That is, the background DOC must not exceed the minimum observed concentration and $\Delta^{14}\text{C}$ values. Uniform concentrations and $\Delta^{14}\text{C}$ values below ~ 1000 m ([Figs. 4a, b](#)) suggest an upper limit equal to mean values for deep DOC ($38 \pm 2 \mu\text{M}$ and $-549 \pm 20\text{‰}$). Since all $\Delta^{14}\text{C}$ values must be greater than -1000‰ , the $\Delta^{14}\text{C}$ value of background DOC must lie between -1000‰ and $-549 \pm 20\text{‰}$. Based on the Keeling plot of all time-series data ([Table 2](#)), this corresponds to a continuum of potential background compositions that range from $21 \pm 1 \mu\text{M}$ with a $\Delta^{14}\text{C}$ of -1000‰ to $38 \pm 2 \mu\text{M}$ with a $\Delta^{14}\text{C}$ of $-549 \pm 20\text{‰}$ ([Fig. 8a](#)). Therefore, the concentration of background DOC present

throughout the water column is at least $21 \mu\text{M}$. Likewise, the concentration of surface-derived excess DOC in deep water at Station M is at most $17 \mu\text{M}$ (i.e., $38 \mu\text{M} - 21 \mu\text{M}$). In addition, the significant variability in mean deep DOC ($\pm 2 \mu\text{M}$, $\pm 20\text{‰}$) may be explained by assuming a background composition along this continuum and propagating the variabilities in [Eqs. \(1\) and \(2\)](#) introduced by the presence of DOC_{xs} in the deep ocean. For example, adding $2 \pm 2 \mu\text{M}$ of $53 \pm 20\text{‰}$ DOC_{xs} (e.g., mean 24 m DIC, [Table 1](#)) to a background of $36 \pm 0 \mu\text{M}$ and $-564 \pm 0\text{‰}$ would lead to mean bulk values of $38 \pm 2 \mu\text{M}$ and $-548 \pm 32\text{‰}$.

Since the Keeling plot model ([Eq. \(3\)](#)) assumes an invariant concentration and $\Delta^{14}\text{C}$ signature of background DOC, variations in slope are theoretically produced by variations in the $\Delta^{14}\text{C}$ -signature of the excess component, $\Delta^{14}\text{C}_{\text{xs}}$.

$$\text{Keeling slope} = (\Delta^{14}\text{C}_{\text{bg}} - \Delta^{14}\text{C}_{\text{xs}}) \times [\text{DOC}_{\text{bg}}] \quad (4)$$

Rearranging [Eq. \(4\)](#) predicts a linear relationship for a set of unique $\Delta^{14}\text{C}_{\text{xs}}$ and slope values from multiple Keeling plots with a common background.

$$\Delta^{14}\text{C}_{\text{xs}} = \Delta^{14}\text{C}_{\text{bg}} - \frac{1}{[\text{DOC}_{\text{bg}}]} \times \text{Keeling slope} \quad (5)$$

The relationship observed for all depth profiles from the Station M time-series based on [Eq. \(5\)](#) is shown in [Fig. 8b](#). The data lie closely to the line predicted from the concentration and $\Delta^{14}\text{C}$ of mean, deep DOC. The data do not align with the trend predicted by the Keeling limit composition of $21 \mu\text{M}$ and -1000‰ (dashed line). This suggests that, on average, background DOC at Station M is compositionally similar to mean deep DOC with a $\Delta^{14}\text{C}$ value of ca. -549‰ .

Linear regression of the data points ($r^2 = 0.923$) shown in [Fig. 8b](#) produced a slope and intercept equivalent to $46 \pm 4 \mu\text{M}$ of background DOC with a $\Delta^{14}\text{C}$ value of $-421 \pm 45\text{‰}$. These values deviate from the Keeling plot model in exceeding minimum concentration and $\Delta^{14}\text{C}$ measurements observed at Station M ([Fig. 4](#)). The possibility of a multiple component model cannot be excluded. For example, varying DOC $\Delta^{14}\text{C}_{\text{xs}}$ values faster than DOC_{xs} can be redistributed and removed is one possible mechanism by which the water column could be populated with multiple, unique components. Although the persistently high $\Delta^{14}\text{C}_{\text{xs}}$ and rising r^2 values for Keeling plots from Feb 1991 to Feb 1993 are consistent with this hypothesis, finer temporal resolution and measurement uncertainty are required to confirm this mechanism.

3.6. Pre-bomb DOC $\Delta^{14}\text{C}$ depth profiles

Although propagation of the bomb-transient through the DOC pool has been modeled ([Repeta and Aluwihare, 2006](#)), there are currently no known proxies for reconstructing historical marine DOC. However, the strong correlation between DOC and DIC $\Delta^{14}\text{C}$ ([Fig. 6](#)), coupled with proxy DIC data ([Druffel, 1989](#); [Druffel and Griffin, 1995](#); [Druffel et al., 2004](#)) and Keeling plot analyses, can be used to estimate historical profiles of DOC $\Delta^{14}\text{C}$.

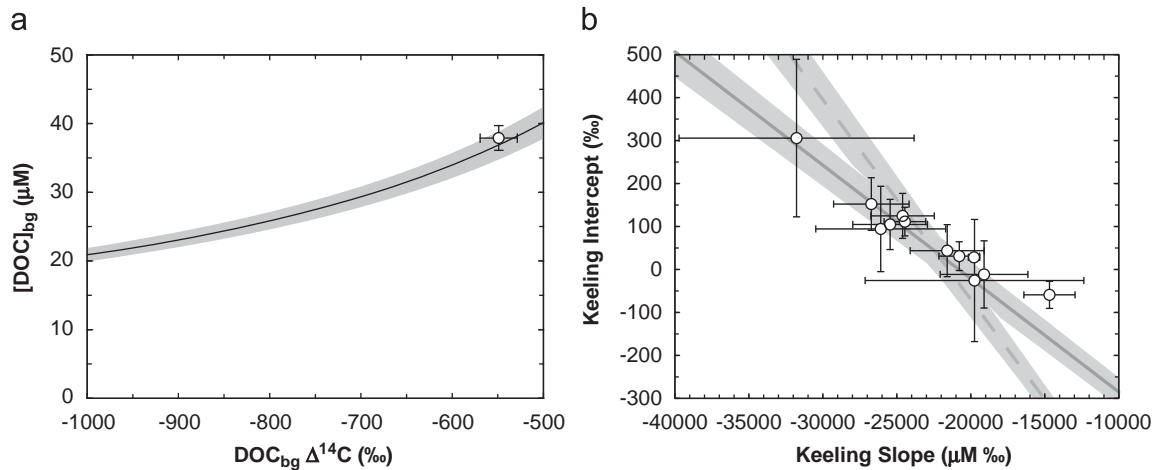


Fig. 8. (a) The range of possible concentrations and $\Delta^{14}\text{C}$ values of background DOC at Station M predicted by a Keeling-type two component mixing model (black line). The concentration and $\Delta^{14}\text{C}$ value of mean, deep (≥ 1000 m) DOC at Station M (white circle) represents the upper boundary for $[\text{DOC}]_{\text{bg}}$ and $\Delta^{14}\text{C}_{\text{bg}}$, with error bars represent ± 1 standard deviation of the mean. Error in the Keeling model predictions of $[\text{DOC}]_{\text{bg}}$ (gray shaded area) represent ± 1 standard deviation propagated from the standard errors of regression and an assumed uncertainty of $\pm 5\%$ for prescribed $\Delta^{14}\text{C}$ values. (b) Intercepts versus corresponding slopes determined from Keeling plots of each DOC depth profile (white circles) from Station M. Error bars represent ± 1 standard error of regression. The solid gray line is the relationship predicted assuming the background component of DOC has a concentration ($38 \pm 2 \mu\text{M}$) and $\Delta^{14}\text{C}$ value ($-549 \pm 20\text{‰}$) equal to mean, deep DOC based on Eq. (5) (i.e., $\Delta^{14}\text{C}_{\text{xs}} = -549\text{‰} - (1/38 \mu\text{M}) \times \text{Keeling slope}$); it is not the least-squares fit to the data points. Error in $\Delta^{14}\text{C}_{\text{xs}}$ predicted by this equation (gray shaded area) represents ± 1 standard deviation propagated from standard deviations of mean deep DOC and the standard error of the slope ($\pm 900 \mu\text{M}\text{‰}$) of a Keeling plot of all Station M data (i.e., Fig. 7, Table 2). The dashed gray line is the relationship predicted by Eq. (5) assuming the background component of DOC has a concentration ($21 \mu\text{M}$) and $\Delta^{14}\text{C}$ value (-1000‰) equal to the Keeling plot limit (i.e., Fig. 8a). The point lying outside the gray shaded area ($-14700 \mu\text{M}\text{‰}$, -59‰) is from the April 1998 depth profile.

Without additional information, depth-dependent reconstructions must assume the historical marine carbon cycle did not differ significantly from contemporary observations. Therefore, the average vertical distribution of DOC concentrations immediately prior to thermonuclear weapons testing is assumed to have been the same as observed during this time series (Fig. 4a). Since the conventional radiocarbon ages of deep DOC in the Eastern North Pacific (6,400 years) are orders of magnitude greater than the time elapsed since thermonuclear weapons testing (~ 50 years), we further assume that the pre-bomb composition of background DOC has not changed and is equal to mean, deep DOC ($38 \mu\text{M}$ and -549‰). Finally, assuming that $\Delta^{14}\text{C}_{\text{xs}}$ is equal to pre-nuclear estimates of surface DIC at Station M [ca. -60‰ , (Berger et al., 1966; Druffel and Williams, 1991)] the pre-bomb $\Delta^{14}\text{C}$ profile is calculated by substitution into Eq. (3):

$$\Delta^{14}\text{C} = (-549\text{‰} + 60\text{‰}) \times (38 \text{ M}) / [\text{DOC}] - 60\text{‰} \quad (6)$$

The depths at which $\Delta^{14}\text{C}$ values are assigned in this pre-bomb profile (Fig. 9), gray diamonds) are based on the depth profile of contemporary DOC concentrations (Fig. 4a). The pre-bomb profile is isotopically depleted in the upper ~ 1000 m compared to the contemporary profile and suggests that significant amounts of bomb- ^{14}C have not penetrated the DOC pool below this depth. Representing background carbon as mean, deep DOC therefore generates a conservative estimate of the persistence and re-distribution of bomb- ^{14}C throughout the water column. Alternatively, assuming background DOC is compositionally similar to the Keeling limit ($21 \mu\text{M}$ and -1000‰ ,

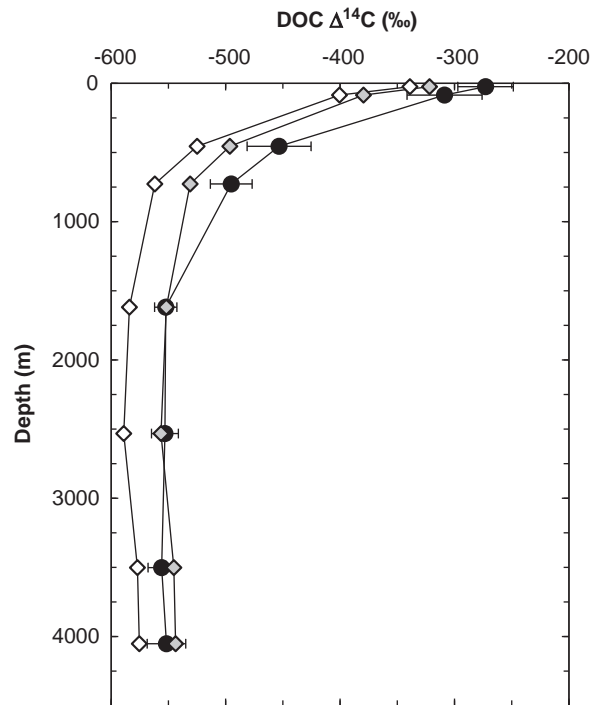


Fig. 9. Depth profiles of contemporary (circles) and pre-bomb (diamonds) DOC $\Delta^{14}\text{C}$ at Station M. Contemporary values are the mean $\Delta^{14}\text{C}$ values from each depth bin of the time series (i.e., Fig. 4b). Pre-bomb $\Delta^{14}\text{C}$ values were calculated using a pre-bomb estimate of the surface DIC $\Delta^{14}\text{C}$ value [ca. -60‰ , (Berger et al., 1966; Druffel and Williams, 1991)] and assuming DOC_{bg} is compositionally similar to mean deep DOC ($38 \mu\text{M}$, -549‰ ; gray diamonds) and the Keeling limit ($21 \mu\text{M}$, -1000‰ ; white diamonds).

Eq. (7)) implies significant bomb carbon has been distributed to the deep waters of Station M.

$$\Delta^{14}\text{C} = (-1000\% + 60\%) \times (21 \mu\text{M}) / [\text{DOC}] - 60\% \quad (7)$$

The majority of DOC in this pre-bomb profile possessed a ^{14}C -based turnover time \geq ca. 57,000 years (i.e., -1000‰), considerably longer than the 6,400 year turnover assuming a background equal to mean, deep DOC (i.e., -59‰; Eq. (6)). The true pre-bomb profile is constrained between the two estimates derived from Eqs. (6) and (7) (Fig. 9), and therefore substantiates DOC as a long-term carbon reservoir. However, similarity between mean deep DOC and the background component (Fig. 8b) implies that the pre-bomb profile is more closely represented by Eq. (6).

4. Conclusions

The synchronicity, magnitude, and rate of variability in DOC and DIC $\Delta^{14}\text{C}$ in the upper 450 m at Station M imply rapid redistribution of recently produced DOC from the surface at Station M. Coupled with Keeling plot analyses, these results suggest that bomb- ^{14}C has penetrated the DOC pool to at least 1000 m at Station M. Data uncertainties do not permit unambiguous identification of the background component along the continuum of potential compositions (Fig. 8) and therefore cannot presently exclude the possibility of bomb- DO^{14}C in the deep ocean. However, the better fit of Keeling plots to a $38 \pm 2 \mu\text{M}$, $-548 \pm 20\%$ background component suggest the amount of bomb- DO^{14}C below 1000 m is at most a small fraction of total DOC.

The mechanisms giving rise to variability in the concentrations and $\Delta^{14}\text{C}$ values of DOC_{xs} remain unconstrained. Continued observations with increased spatio-temporal resolution and precision may refine the relative importance of particle transport, hydrography, and climatology in this system. In addition, an augmented, high-precision time-series will help constrain the isotopic composition of DOC and validate the two-component model at this site. The global DOC data set (Fig. 1) may be similarly augmented via analyses of modern proxies (e.g., DIC and banded corals), contemporaneous DOC $\Delta^{14}\text{C}$ measurements, and quantification of regional variability in the relationship between deep DIC and DOC $\Delta^{14}\text{C}$. Coupled with simple-box models, these reconstructions may be used to determine the global impact of bomb- ^{14}C on marine DOC, the turnover time and fate of long-lived deep DOC, and the fluxes between oceanic carbon reservoirs.

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