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Key Points:
- Different DOC fractions have different radio and stable carbon isotope values
- Large (~25%) fraction of DOC is highly depleted in both ^{13}C and ^{14}C and may be derived from allochthonous sources
- ^{13}C- and ^{14}C-isotopic enrichments in DOC follow the series: HMW DOC > LMW hydrophobic DOC > LMW hydrophilic DOC

Supporting Information:
- Supporting Information S1

Correspondence to:
D. J. Repeta,
drepeta@whoi.edu

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Allochthonous sources and dynamic cycling of ocean dissolved organic carbon revealed by carbon isotopes

Prosper K. Zigah[1], Ann P. McNichol[1], Li Xu[1], Carl Johnson[1], Chiara Santinelli[2], David M. Karl[3], and Daniel J. Repeta[1]

[1]Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA, [2]Consiglio Nazionale delle Ricerche, Istituto di Biofisica, Pisa, Italy, [3]Daniel K. Inouye Center for Microbial Oceanography: Research and Education, University of Hawaii, Honolulu, Hawaii, USA

Abstract We present concentration and isotopic profiles of total, size, and polarity fractionated dissolved organic carbon (DOC) from Station ALOHA (A Long-term Oligotrophic Habitat Assessment), an oligotrophic site in the North Pacific Ocean. The data show that, between the surface and 3500 m, low molecular weight (LMW) hydrophilic DOC, LMW hydrophobic DOC, and high molecular weight (HMW) DOC constitute 22–33%, 45–52%, and 23–35% of DOC, respectively. LMW hydrophilic DOC is more isotopically depleted ($\delta^{13}C$ of −23.9‰ to −31.5‰ and $\Delta^{14}C$ of −304‰ to −795‰; mean age of 2850 to 15000 years) than the LMW hydrophobic DOC ($\delta^{13}C$ of −22‰ to −23‰ and $\Delta^{14}C$ of −270‰ to −568‰; 2470 to 6680 years) and HMW DOC ($\delta^{13}C$ of ~−21‰ and $\Delta^{14}C$ of −24‰ to −294‰; 135–2700 years). Our analyses suggest that a large fraction of DOC may be derived from allochthonous sources such as terrestrial and hydrothermal DOC and cycle on much longer time scales of >10000 years or enter the ocean as preaged carbon.

1. Introduction

Dissolved organic carbon (DOC) is the largest organic carbon pool in the ocean and one of the largest active carbon reservoirs on Earth. The amount of carbon in oceanic DOC (~662 Gt C) is similar to the inventory of carbon in the atmosphere, and therefore, perturbations of oceanic DOC could have implications for the global carbon cycle and the global climate [*Hansell et al.*, 2009]. However, oceanic DOC cycling remains poorly understood. Confounding aspects include the uniform values of total DOC $\delta^{13}C$ of ~−21‰ with depth and across major ocean basins [*Druffel et al.*, 1992], suggesting primarily autochthonous microbial sources with an apparent absence of a quantitatively significant terrestrial component in spite of major terrigenous DOC inputs [*Dai et al.*, 2012] and the millennia ages of DOC that are 2000–3500 years older than dissolved inorganic carbon (DIC) throughout the water column.

The average radiocarbon age of DOC in the deep ocean is 4000–6500 years [*Williams and Druffel*, 1987; *Druffel et al.*, 1992; *Druffel and Bauer*, 2000], but the age distribution within DOC is quite large [*Beaupré et al.*, 2007; *Follett et al.*, 2014]. Linking DOC radiocarbon values with chemical composition may provide better constraints on carbon sources and their fluxes through the DOC pool. A major challenge to understanding the DOC composition is the complex mixture of different compounds that contribute to DOC. A full characterization of these compounds is not currently feasible, but they can be separated into discrete fractions based on molecular size and polarity.

Here we measured the profiles of dissolved organic and inorganic carbon isotopes (DOC $\Delta^{14}C$, $\delta^{13}C$ and DIC $\Delta^{14}C$, $\delta^{13}C$, respectively) in the oligotrophic gyre of the North Pacific Ocean. We also measured the concentrations and isotopic compositions of DOC that had been separated into high and low molecular weight (HMW DOC and LMW DOC) fractions. LMW DOC was further separated by solid phase extraction (SPE) into a hydrophobic (LMW hydrophobic DOC) fraction that was retained by the SPE column and a hydrophilic (LMW hydrophilic DOC) fraction that passed through the column (Figure 1). HMW DOC and LMW hydrophobic DOC fractions were analyzed for their broad chemical compositions by using proton nuclear magnetic resonance (^1H NMR) spectroscopy (Figure S1 in the supporting information). Our measurements were made on samples collected from Station ALOHA (A Long term Oligotrophic Habitat Assessment), an ecological research study site located 100 km north of Oahu, Hawaii. We compared our data to historical measurements made at the Natural Energy Laboratory of Hawaii Authority (NELHA) located 394 km southwest of Station ALOHA just offshore of the Island of Hawaii and from a North Central Pacific (NCP) study site located 924 km northeast of Station ALOHA.

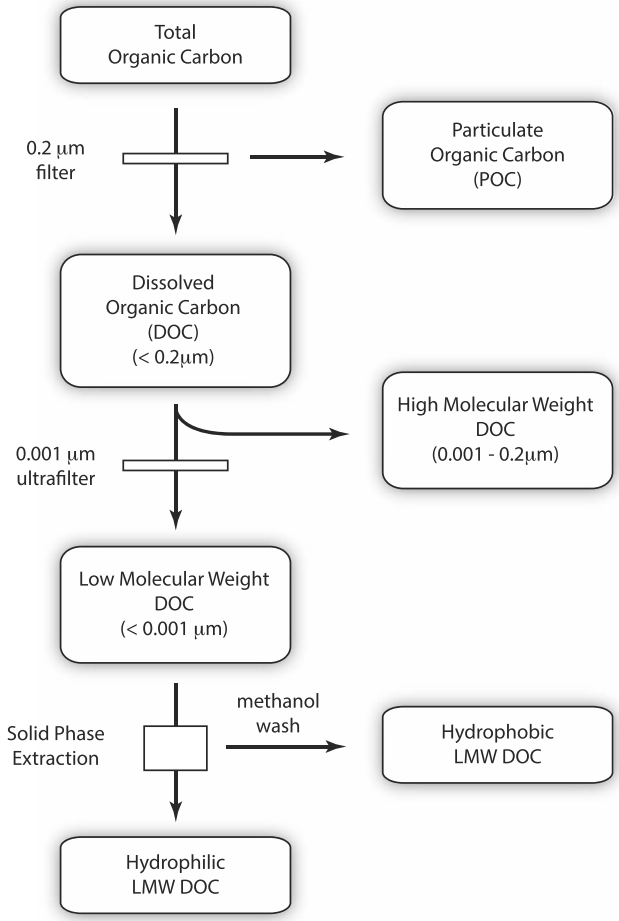


Figure 1. Sampling scheme showing size and polarity-based fractionation of DOC for isotope analyses. Organic carbon in seawater was 0.2 μm filtered into operationally defined particulate organic carbon (POC) and dissolved organic carbon (DOC). POC was not further analyzed. DOC was further separated into high molecular weight (HMW) and low molecular weight (LMW) fractions by ultrafiltration by using a 1000 amu (~1 nm) pore size membrane. Finally, LMW hydrophobic and LMW hydrophilic DOCs were separated by passing the ultrafiltrate through a solid phase extraction column. LMW hydrophobic DOC was retained on the column and recovered by washing the column with methanol, while LMW hydrophilic DOC passed through the column.

2. Methods

Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) samples were collected from 5–4500 m depths at Station ALOHA (22°45′N, 158°00′W) aboard the R/V *Kilo Moana* cruise KM 14–27 in December 2014. Large volume samples (300–445 L) collected by multiple Niskin rosette casts to 1000 m, 2500 m, and 3500 m were separated into high and low molecular weight fractions by ultrafiltration. Seawater was pumped from Niskin bottles into 200 L fluorinated high-density polyethylene (HDPE) reservoirs by using an air-driven diaphragm pump fitted with HDPE tubing and an in-line capsule filter (dual 0.8 μm and 0.2 μm, Whatman Polycap TC capsule filter). Samples were processed as described previously [*Aluwihare et al.*, 2002; *Repeta and Aluwihare*, 2006] to isolate HMW DOC (nominally $>$ 1000 amu). The LMW DOC (nominally $<$ 1000 amu) was acidified to pH 2 with ultrapure 12 N HCl and separated into a LMW hydrophobic DOC fraction defined by retention onto an Agilent Bond Elut ENV column and a LMW hydrophilic DOC fraction that passed through the SPE column. Additional details of the HMW and LMW DOC sampling and processing are provided in the supporting information. We did not have sufficient ship time to complete surface water sampling on our KM 14–27 cruise. Our surface water sample was therefore collected on Hawaii Ocean Time-series cruise KM 15–18 in November 2015. We used an air-driven diaphragm pump to filter-collect 40 L of water from ~20 m which

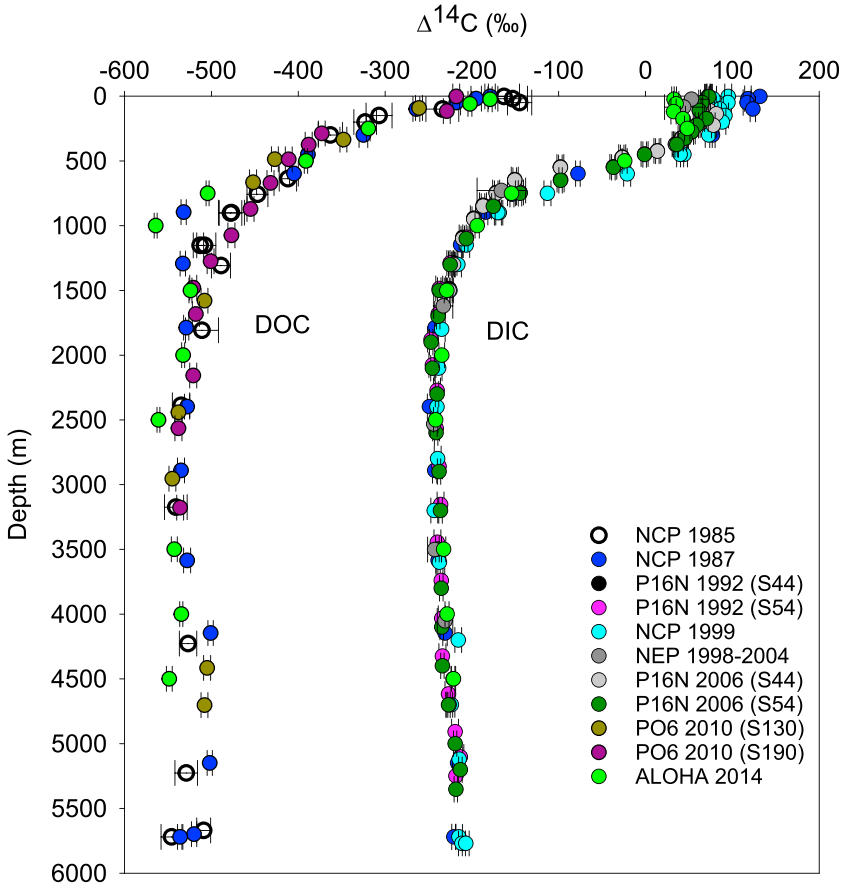


Figure 2. Dissolved inorganic radiocarbon and dissolved organic radiocarbon profiles from Station ALOHA (22°45′N, 158° W) collected in December 2014. For comparison, data from North Central Pacific, NCP (31°00′N, 159°00′W) site from 1985, 1987, and June 1999 [*Druffel et al.*, 1992, 2008]; North Eastern Pacific, NEP (34°50′N, 123°00′W); South Pacific, SP (32°29.99′S, 144°39.39′W and 32°29.96′S, 109°55.63′W) from January to February 2010 [*Druffel and Griffin*, 2015]; data from WOCE line P16N Station 44 (22°00.03′N, 152°00.04′W); and Station 54 (31°99.98′N, 152°00.03′W) from 1992 and 2006 (http://cdiac.ornl.gov/ftp/oceans/GLODAPv2/Data_Products/data_product/). The error bars are 1σ instrumental precisions and, where not visible, are small and embedded within the symbol.

was frozen and returned to Woods Hole for processing. A schematic of our isolation and processing is provided in Figure 1.

DOC concentrations were measured by using a Shimadzu total organic carbon analyzer (total DOC and HMW DOC) or manometrically by measuring the CO_2 evolved after UV oxidation (LMW hydrophilic DOC) and closed tube combustion at 850°C for 5 h (LMW hydrophobic DOC). Carbon recovery was ~90–101% of total carbon determined by measurements of sample volume and DOC concentration. Proton NMR spectra of HMW DOC and LMW hydrophobic DOC samples were acquired as described previously [*Repeta et al.*, 2002; *Repeta and Aluwihare*, 2006]. All radiocarbon and stable isotope measurements were performed at the National Ocean Sciences Accelerator Mass Spectrometry Facility. Further details of sample collection and processing can be found in the supporting information.

3. Results and Discussion

3.1. Carbon Isotopes in DIC and DOC

A comparison of our DIC $\Delta^{14}C$ profile with previously measured DIC $\Delta^{14}C$ profiles from various sites in the Pacific Ocean is presented in Figure 2. At Station ALOHA in 2014, DIC $\Delta^{14}C$ values are high in the surface (33–35‰, <100 m), decrease slowly to a broad minimum at 2500 m (−242‰), then rise slightly with depth to −221‰ at 4500 m. Compared to other North Pacific surface water measurements, our surface value of

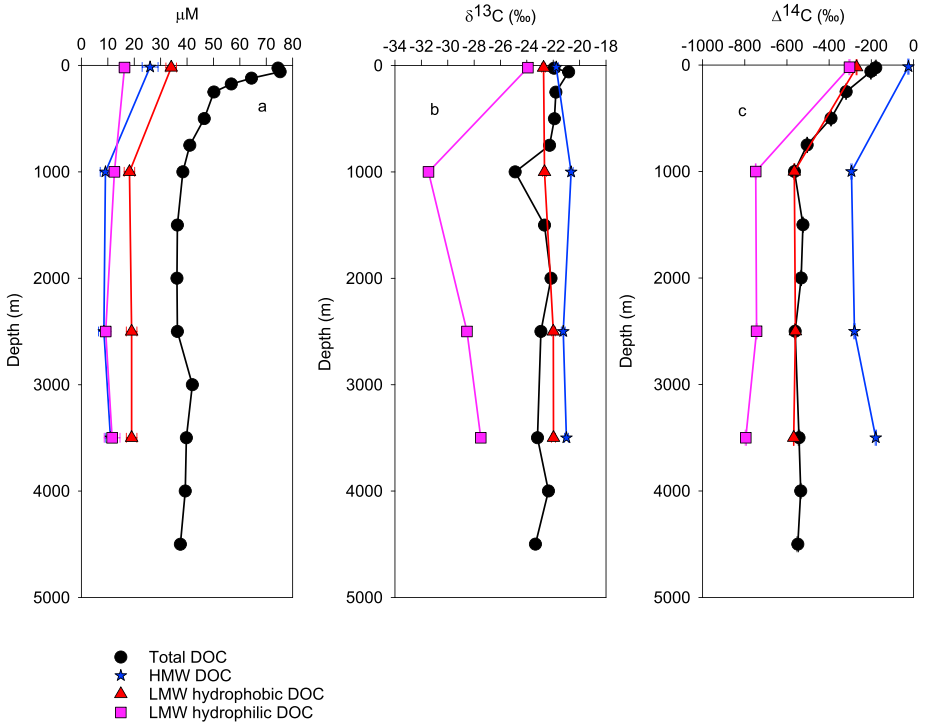


Figure 3. (a) Concentration, (b) stable carbon isotope, and (c) radiocarbon profiles of DOC, high molecular weight (HMW) DOC, low molecular weight (LMW) hydrophobic DOC, and LMW hydrophilic DOC in our Station ALOHA samples.

34‰ clearly reflects the decline of bomb radiocarbon in the atmosphere over the past 27 years (1987–2014), shifting the radiocarbon values of surface DIC by ~100‰ (from +132‰ in 1987 to + 34‰ in 2014). The bomb signal is a spike of ^{14}C that derived from above-ground testing of thermonuclear weapons in the 1950s–1960s and has since been decreasing through equilibration with other carbon reservoirs.

DOC $\Delta^{14}C$ values are also enriched in surface samples and depleted at depth (Figure 3 and Tables S1 and S2 in the supporting information). Bathypelagic (≥1000 m) DOC $\Delta^{14}C$ values range from −564‰ to −532‰ and are −295‰ to −370‰ depleted compared to DIC $\Delta^{14}C$. DOC $\Delta^{14}C$ profiles in the Pacific Ocean over the past three decades are also presented in Figure 2. At the surface (3–100 m), the DOC $\Delta^{14}C$ at the North Central Pacific (NCP) site was −163‰ to −254‰ in 1985 and decreased (became ^{14}C-depleted) slightly to between −179‰ and −264‰ in 1987 [*Druffel et al.*, 1992; *Bauer et al.*, 1992]. At the Natural Energy Laboratory of Hawaii Authority (NELHA), DOC $\Delta^{14}C$ at 21 m was −246‰ in 2005 [*Walker et al.*, 2011, 2016]. At Station ALOHA, DOC $\Delta^{14}C$ at 50 m was −238‰ in 2010 [*Follett et al.*, 2014] and −179‰ to −202‰ in our 25–60 m samples from 2014 (Table S3). Surface water DOC $\Delta^{14}C$ values are influenced by changes in DIC $\Delta^{14}C$ and by the relative proportions and turnover times of different fractions of carbon (labile, semilabile, and refractory) that make up DOC. Temporal shifts in surface DOC $\Delta^{14}C$ values driven by changes in the bomb ^{14}C signal are therefore less evident than for DIC but are nonetheless suggested by the general trend of ^{14}C depletion over the last few decades.

DOC $\delta^{13}C$ values for surface water samples are marine-like, ranging from −21.9‰ to −20.8‰ (Figure 3), reflecting a large contribution of autochthonous microbial carbon. DOC $\delta^{13}C$ values agree well with other reports of DOC $\delta^{13}C$ at NCP, NELHA and Station ALOHA which range from −21.6‰ to −20.4‰ [*Druffel et al.*, 1992; *Walker et al.*, 2011; *Follett et al.*, 2014]. On the other hand, bathypelagic (≥1000 m) DOC $\delta^{13}C$ values at Station ALOHA range from −24.9‰ to −22.2‰, averaging −23.1 ± 0.9‰ (1 SD) (Figure 3). Although we only recovered DOC $\delta^{13}C$ values for two surface samples, we note that the $\delta^{13}C$ values of surface samples are heavier than any value we obtained in the deep waters (student's *t* test, $P < 0.05$), suggesting a trend in DOC $\delta^{13}C$ with DOC concentration.

The highly depleted value (−24.9‰) at 1000 m is anomalous, lying 2 SD outside of the mean deepwater DOC $\delta^{13}C$ value. The DOC $\Delta^{14}C$ value of this sample is also highly depleted (−564‰) compared to the samples

immediately above (−504‰, 750 m) and below (−524‰, 1500 m) and to all other deepwater samples collected at NCP (−489‰ to −546‰). We do not know the exact cause of this anomaly, but the data hint at a local addition of isotopically depleted DOC near this depth. One potential source of isotopically depleted DOC is hydrothermal vent fluids associated with the Lo'ihi Seamount, an active submarine volcano ~500 km southeast of Station ALOHA. The summit of Lo'ihi rises to a depth of 975 m, and a strong subsurface plume of hydrothermal ^{3}He and iron with a maximum at ~1100 m has been reported near Station ALOHA [*Lupton*, 1998; *Boyle et al.*, 2005]. High-temperature vent fluids are characterized by low concentrations (10–15 μm) of isotopically depleted (δ^{13}C to −34.5‰ and Δ^{14}C to −835‰) DOC [*Lang et al.*, 2006; *McCarthy et al.*, 2011]. Adopting McCarthy's isotopic values for hydrothermal DOC and our average carbon isotopic values for deep-sea DOC ($\delta^{13}C = -23.1$ and $\Delta^{14}C = -544$) would require between 6 and 8% of 1000 m water to be of hydrothermal origin to yield the observed isotopic values. ^{3}He and iron measurements suggest that dilutions of hydrothermal fluids at Station ALOHA are $>10^{4}$ greater than this, suggesting other sources for depleted DOC at 1000 m. We observed no anomalies in the CTD hydrographic data (T, S, oxygen, and beam transmission) at 1000 m that might suggest an alternate local source of DOC.

Our bathypelagic DOC δ^{13}C values are significantly depleted compared to values reported by *Druffel et al.* [1992] for the NCP site but similar to values reported for the western North Pacific by *Tanaka et al.* [2010] and the values reported by *Walker et al.* [2011] from the NELHA site. Excluding the anomalous value at 1000 m, DOC δ^{13}C values at Station ALOHA between 750 m and 4500 m range from −22.2‰ to −23.4‰, averaging −22.7 ± 0.5‰, compared to a range of −20.6‰ to −22.3‰ with an average of −21.1 ± 0.4‰ between 756 m and 4227 m at the NCP site. The minimum DOC δ^{13}C isotopic value at NCP is equal to the maximum isotopic value at Station ALOHA. For each data set, gas samples for δ^{13}C measurements were made off-line by isotope ratio mass spectrometry from a subsample of carbon dioxide recovered after UV oxidation of DOC. The average deep-sea concentration of DOC at Station ALOHA (37.8 μM) is comparable to the average values measured in 2005 at the nearby Climate Variability and Predictability P16N Station 43 (37.5 μM; 21°N, 152°W) and Station 53 (37.1 μM; 31°N, 152°W), all of which are somewhat higher than in NCP deepwater DOC (35.2 μM; 31°N, 159°W) (http://cdiac.ornl.gov/ftp/oceans/GLODAPv2/Data_Products/data_product/). If the isotopic difference between NCP and Station ALOHA was due to the additional ~2.6 μM DOC in Station ALOHA deep water, then this DOC would need to have an average δ^{13}C value of −44‰.

3.2. Allochthonous Sources and Dynamic Cycling of Marine DOC Based on Size and Polarity Fractionation

LMW hydrophilic DOC was by far the most ^{14}C-depleted DOC fraction we measured, with Δ^{14}C values of −304‰ in the surface sample and ~−762‰ at depth (Figures 3 and S3 and Table S5). Hydrophilic DOC in the bathypelagic waters was considerably older than DIC and total DOC by ~9000 ^{14}C years and ~5000 ^{14}C years, respectively. The isotope values of hydrophilic DOC in the deep ocean are consistent with a number of potential carbon sources, including terrestrial, black carbon, hydrothermal, and marine microbial lipids. Each year, rivers deliver some ~0.3–0.4 Pg of DOC to the ocean [*Hedges et al.*, 1997], enough to account for the steady-state cycling of oceanic DOC, given the deep-sea radiocarbon values. However, terrestrial organic carbon is isotopically depleted (~−32‰ to −27‰) compared to average deep-sea DOC δ^{13}C values reported for the NCP site (~−22‰ to −21‰) [*Druffel et al.*, 1992]. This difference has been used to infer that terrestrial organic matter contributes only a small fraction of marine DOC, a conclusion supported by the low yields of lignin phenol biomarkers which suggest that only 0.5–2.4% of total DOC is of terrestrial origin [*Meyers-Schulte and Hedges*, 1986; *Opsahl and Benner*, 1997]. The apparent absence of a significant accumulation of terrigenous DOC in the ocean has been framed as a paradox [*Hedges et al.*, 1992; *Opsahl and Benner*, 1997], as having survived remineralization in soils, terrestrial DOC is presumed to be refractory. In contrast, an estimate of δ^{13}C distribution within DOC made by *Follett et al.* [2014] by using serial oxidation suggested that ~25–30% of DOC was more isotopically depleted than −25‰, raising the possibility that allochthonous sources to DOC, including terrestrial organic matter, could represent a major fraction of marine DOC. Our data for hydrophilic DOC are in general agreement with the results from *Follett et al.* [2014] and likewise show that a large reservoir (~25% of total DOC) of isotopically depleted (−24 to −32‰) carbon is present in DOC. Photochemical alterations of terrestrial DOC in surface river and seawater might transform refractory lignins, tannins, cutins, and other forms of terrestrial carbon into smaller hydrophilic components [*Moran and Zepp*, 1997; *Hernes and Benner*, 2003] that

accumulate in the deep ocean [*Medeiros et al.*, 2016]. If hydrophilic DOC is indeed the degradation product of terrestrial DOC, our data could help resolve the paradox of terrestrial DOC in the ocean.

Black carbon (BC), a by-product of fossil fuel combustion and terrestrial biomass burning, is another potential source of isotopically depleted DOC. BC has been measured in hydrophobic and HMW DOC at concentrations of 2–4 μM (5% of total DOC) and $\Delta^{14}C$ values of −450‰ to −945‰ (ages of 4800–23000 years) [*Ziolkowski and Druffel*, 2010; *Coppola and Druffel*, 2016]. $\delta^{13}C$ values for DOC BC have not been reported, but BC in deep-sea (~900 m) sedimentary organic carbon is ^{13}C-depleted ($\delta^{13}C \sim -25‰$) as expected from terrestrial biomass [*Masiello and Druffel*, 2003]. Our sampling protocols would remove HMW and hydrophobic BC from the hydrophilic fraction, but the presence of BC in other DOC fractions suggests that BC could contribute to LMW hydrophilic DOC. Carbon isotopic values of HMW DOC from a ridge-flank hydrothermal system [*McCarthy et al.*, 2011] are similar to those of hydrophilic DOC in the deep sea and suggest that direct production of low molecular weight compounds or degradation of HMW DOC from hydrothermal systems could also be a source of hydrophilic DOC. Estimates of hydrothermal DOC input range from 1 to 3 Tg C per year [*Lang et al.*, 2006; *Druffel and Griffin*, 2015], yielding a steady-state inventory of DOC of ~11–33 Pg C, which is a significant fraction of hydrophilic DOC inventory.

The $\delta^{13}C$ value of hydrophilic DOC also lies within the range of values characteristic of marine microbial lipids. However, unaltered lipids are not expected to be present in the hydrophilic fraction. Lipids are hydrophobic and efficiently retained by solid phase extraction. Indeed, nuclear magnetic and mass spectral analyses of hydrophobic DOC all demonstrate that this fraction is rich in aliphatic organic matter. Microbial or photochemical degradation of lipids could yield small, highly oxidized products that might partition into the hydrophilic fraction, although we expect such products to be readily consumed by microbes [*Miller and Moran*, 1997].

The differential isotopic composition of surface and deep-sea hydrophilic DOC is likely due to inputs of radiocarbon-enriched organic matter in the surface layer. Assuming hydrophilic DOC is a simple mixture of recycled carbon with an isotopic value of deep-sea hydrophilic DOC and newly synthesized carbon with isotopic values of −22‰ and 33‰ (equal to DIC radiocarbon), we calculate that surface hydrophilic carbon is ~7 μM recycled and ~9 μM newly synthesized hydrophilic DOC. Recycled hydrophilic DOC by this calculation is lower than its concentration in deep waters (~9–12 μM), suggesting a potential sink for recycled hydrophilic DOC in surface waters.

Hydrophobic DOC was the largest fraction of DOC isolated by our approach, contributing approximately one half (~46–52%) of the total DOC throughout the water column (Figure 3 and Table S4). The proton NMR spectra of our LMW hydrophobic DOC samples were similar to previous observations [*Hertkorn et al.*, 2006, 2013], showing broad peaks from substituted alkyl carbon protons with major resonances at 0.9–3.0 ppm, 1.3–2.0 ppm, and 1.4–4.5 ppm (Figure S1). The $\Delta^{14}C$ and $\delta^{13}C$ values of surface and deepwater hydrophobic DOCs were −270‰ and −22.7‰, −560‰ to −568‰, and −22.0‰ to −22.7‰, respectively (Figure 3 and Table S4). The $\delta^{13}C$ values are typical of marine humic substances [*Stuermer and Harvey*, 1974; *Druffel et al.*, 1992; *Bauer et al.*, 1992] and suggest autochthonous production of this DOC fraction. The more depleted $\delta^{13}C$ values of LMW hydrophobic DOC compared to HMW DOC may reflect the greater contribution of lipids to LMW DOC compared to isotopically enriched carbohydrates in the HMW DOC fraction. Radiocarbon values of hydrophobic DOC are consistently more depleted than DIC, implying that a majority of the hydrophobic DOC persists (and ages) over multiple deep ocean cycles before complete removal.

The concentration and radiocarbon values of the surface LMW hydrophobic DOC are elevated relative to the deepwater LMW hydrophobic DOC (Figure 3 and Table S4). We used a two-component isotopic model with a $\Delta^{14}C$ value equal to DIC (33‰) and excess DOC concentration of 15 μM ((hydrophobic $DOC_{surface}$) − (hydrophobic DOC_{deep})) for the newly synthesized component, along with the average deep-sea hydrophobic DOC $\Delta^{14}C$ value of −564‰ and 19 μM concentration for the background component (Figure 3 and Table S4) to calculate a value for surface hydrophobic DOC of −301‰. This value is similar to the measured value (−270‰) and suggests that ~40% of the surface hydrophobic DOC could derive from recent photoautotrophy. Although a large fraction of hydrophobic DOC in surface waters contains bomb radiocarbon, a temporal decrease in $\Delta^{14}C$ values is not apparent in existing data. Surface water $\Delta^{14}C$ values for hydrophobic DOC in the middle to late 1980s were −342‰ in the North Pacific [*Druffel et al.*, 1992; *Bauer et al.*, 1992] and −329‰ in the North Atlantic [*Druffel et al.*, 1992; *Bauer et al.*, 1992]. In 2008 the $\Delta^{14}C$ value of hydrophobic DOC from

the eastern Atlantic Ocean was ~−275‰ [*Flerus et al.*, 2012], nearly identical to our value at Station ALOHA in 2014. The smaller data set and differences in collection methods may mask any temporal trends in hydrophobic DOC radiocarbon values.

In both surface and deep waters, HMW DOC concentrated by ultrafiltration consists predominantly of carbohydrate, as shown by ^{1}H NMR spectra that display major resonances at 4.5–3.5 ppm (**H**COH), 2.7 ppm (*N*-methyl amino sugar, C**H**$_3$N(H)C–), 2.0 ppm (*N*-acetyl amino sugar, C**H**$_3$C(O)N–), and 1.3 ppm (6-deoxy sugar, C**H**$_3$–C) (Figure S1). Integration of the ^{1}H NMR spectrum of our surface sample indicates that acyl polysaccharides contribute ~70% of the carbon in the sample. The remaining ~30% are humic substances that appear as a broad, featureless baseline between 0.8 and 3.0 ppm.

HMW DOC represents ~23–35% of total DOC and was enriched in ^{14}C and ^{13}C throughout the water column (Table S3). δ^{13}C values (~−21‰; Figure 3) suggest autochthonous microbial production as the source of this carbon. The surface HMW DOC Δ^{14}C value of −24‰ (135 years) was moderately depleted relative to DIC Δ^{14}C (33‰). This relative depletion can be explained by the mixture of acyl polysaccharides and humic substances in the HMW DOC fraction, as seen in the ^{1}H NMR spectrum. *Repeta and Aluwihare* [2006] treated the HMW DOC recovered from surface water (collected at NELHA in 2002; Δ^{14}C = 10‰) with strong acid to hydrolyze acyl polysaccharides to simple sugars, which were purified for isotopic analyses. Δ^{14}C values of major neutral sugars averaged 57‰, similar to DIC Δ^{14}C (72‰). The humic substance fraction was isolated by anion exchange chromatography and had a Δ^{14}C value of −416‰. This value is more enriched in radiocarbon than our measurements of deep-sea DOC (−544‰), implying that some fraction of humic material was recently produced as well. Based on Δ^{14}C isotopic composition, HMW DOC is a mixture of ~90% newly synthesized carbon (acyl polysaccharides and humic substances) and ~10% refractory (humic substances) carbon ((57‰)(0.9) + (−416‰)(0.1) = 10‰). Our observation of the contemporary origin of a significant fraction of marine surface HMW DOC is consistent with previous studies [*Guo et al.*, 1996; *Aluwihare et al.*, 2002; *Loh et al.*, 2004; *Repeta and Aluwihare*, 2006]. Assuming that our 2014 HMW DOC surface sample is a mixture of newly synthesized DOC with an isotopic value equal to DIC Δ^{14}C (33‰) and refractory DOC with Δ^{14}C = −544‰, we calculate our sample to be a mixture of 90% semilabile DOC and 10% "refractory carbon." The amount of newly synthesized DOC by this calculation is greater than the amount of polysaccharide measured by ^{1}H NMR, again indicating that a significant fraction of humic substances detected by ^{1}H NMR are of recent origin. Polysaccharides are part of the "semilabile" fraction of DOC that is produced by marine microbes and cycles on monthly-to-annual time scales. As such, the radiocarbon value of HMW DOC is expected to decrease in parallel with the temporal decline in surface ocean DIC Δ^{14}C noted above. Our data support this. HMW DOC Δ^{14}C was 46‰ in 1999 at the NCP site (DIC Δ^{14}C < 119‰ [*Key et al.*, 2002]), decreased to 10‰ at the NELHA study site in 2002 (DIC Δ^{14}C = 72‰), and was −24‰ in our 2014 sample (DIC Δ^{14}C = 33‰). In each case, HMW DOC Δ^{14}C was ~60‰ depleted relative to DIC Δ^{14}C.

Bathypelagic HMW DOC Δ^{14}C was −294‰, −280‰, and −179‰ at 1000 m, 2500 m, and 3500 m, respectively, compared to −193‰, −242‰, and −232‰ for DIC Δ^{14}C (Figure 3 and Tables S1 and S3). HMW DOC was moderately depleted in ^{14}C compared to DIC at 1000 m and 2500 m but moderately enriched in the 3500 m sample. The synthesis of acyl polysaccharides by marine microbes yields highly similar values for HMW DOC Δ^{14}C and DIC Δ^{14}C throughout the water column. We attribute the slight depletion in HMW DOC Δ^{14}C at 1000 m and 2500 m to co-isolation of humic substances in our samples. The slight enrichment in HMW DOC Δ^{14}C at 3500 m is most likely due to the incorporation of recently synthesized semilabile DOC released from sinking particles. *Repeta and Aluwihare* [2006] reported a Δ^{14}C value of ~−258‰ for HMW DOC isolated from 600 m NELHA seawater. Δ^{14}C values of four neutral sugars recovered after acid hydrolysis ranged from −108‰ to −133‰, slightly enriched relative to DIC Δ^{14}C (−155‰). This enrichment suggested that ~15% of acyl polysaccharides at the mesopelagic depths are supplied by the dissolution of large, rapidly sinking particles carrying bomb radiocarbon into the deep ocean. Incorporation of bomb radiocarbon into semilabile DOC was also proposed by *Follett et al.* [2014] to explain the distribution of carbon isotopes within deep-sea DOC. Our results support these earlier findings and suggest that bomb radiocarbon could be present at depths up to 3500 m. Our HMW DOC Δ^{14}C values are uniformly enriched compared to the data of *Walker et al.* [2011]. We attribute the relative enrichment of ^{14}C in our samples to a lower retention of humic substances by our ultrafiltration system compared to the system used in the *Walker et al.* [2011] study.

Models of the isotopic time series reported by *Follett et al.* [2014] indicate that a large fraction (~60%) of ALOHA deepwater DOC was significantly depleted in radiocarbon (–1000 to −600‰) relative to total DOC $\Delta^{14}C$, while a smaller fraction (~20%) was isotopically enriched (−50‰ to +150‰). *Follett et al.* [2014] also found that ~25% of deep DOC $\delta^{13}C$ was isotopically depleted (−40 to −30‰) relative to total DOC $\delta^{13}C$. Our measurements showed that at least ~25–33% of deep-sea DOC has a $\Delta^{14}C$ value depleted relative to total DOC, while another ~25% was isotopically enriched. We likewise found ~25–33% of deep-sea DOC $\delta^{13}C$ to be isotopically depleted relative to typical marine $\delta^{13}C$ values of ~−21‰. The isotopic value of HMW DOC at 3500 m suggests some input and accumulation of bomb radiocarbon in deep-sea semilabile DOM, also suggested by the serial oxidation study. Although the very different approaches used in the two studies mean that our measurements are not directly comparable to *Follett et al.* [2014], the results of the two studies are broadly consistent.

A significant component of marine DOC (~22–33%) is hydrophilic and depleted in ^{13}C and ^{14}C. As discussed above, the isotopic values of hydrophilic DOC are consistent with a number of possible sources. Although we cannot rule out degraded microbial lipids as a source of hydrophilic DOC based on isotopic data, most potential sources are allochthonous. Terrestrial DOC, terrestrial black carbon, and DOC derived from hydrothermal inputs could therefore be more important to the marine DOC inventory and cycling than currently recognized. About 46–52% of the autochthonous marine DOC is hydrophobic and humic-like and survives several ocean mixing cycles before removal. In contrast, ~23–35% of the autochthonous marine DOC is polysaccharide-rich HMW DOC and recycles on time scales less than or equal to one ocean mixing cycle. Tandem separation of DOC into size and polarity fractions provides new insights into the sources and fluxes of DOC in the ocean. These new insights will allow for better modeling of DOC cycle, and ultimately, the global carbon cycle.

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