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Title

Pacific carbon cycling constrained by organic matter size, age and composition relationships

Permalink

<https://escholarship.org/uc/item/1gd6f7b1>

Journal

Nature Geoscience, 9(12)

ISSN

1752-0894

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Publication Date

2016-12-01

DOI

10.1038/ngeo2830

Peer reviewed



RESEARCH LETTER

10.1002/2016GL070359

Key Points:

- Marine dissolved organic carbon (DOC) molecular size is closely linked to its radiocarbon age
- Modern and “bomb” radiocarbon are prevalent in the largest DOC molecules
- Molecular size and chemical composition control DOC biological reactivity and oceanic residence time

Supporting Information:

- Supporting Information S1

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Citation:

Walker, B. D., F. W. Primeau, S. R. Beaupré, T. P. Guilderson, E. R. M. Druffel, and M. D. McCarthy (2016), Linked changes in marine dissolved organic carbon molecular size and radiocarbon age, *Geophys. Res. Lett.*, *43*, doi:10.1002/2016GL070359.

Received 8 JUL 2016

Accepted 30 SEP 2016

Accepted article online 2 OCT 2016

Linked changes in marine dissolved organic carbon molecular size and radiocarbon age

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Abstract Marine dissolved organic carbon (DOC) is a major global carbon reservoir, yet its cycling remains poorly understood. Previous work suggests that DOC molecular size and chemical composition can significantly affect its bioavailability. Thus, DOC size and composition may control DOC cycling and radiocarbon age (via $\Delta^{14}\text{C}$). Here we show that DOC molecular size is correlated to DOC $\Delta^{14}\text{C}$ in the Pacific Ocean. Our results, based on a series of increasing molecular size fractions from three depths in the Pacific, show increasing DOC $\Delta^{14}\text{C}$ with increasing molecular size. We use a size-age distribution model to predict the DOC and $\Delta^{14}\text{C}$ of ultrafiltered DOC. The model predicts both large and small surface DOC with high $\Delta^{14}\text{C}$ and a narrow range (200–500 Da) of low $\Delta^{14}\text{C}$ DOC. Deep model offsets suggest different size distributions and/or $\Delta^{14}\text{C}$ sources at 670–915 m. Our results suggest that molecular size and composition are linked to DOC reactivity and storage in the ocean.

1. Introduction

With ~662 Pg C, marine dissolved organic carbon (DOC) represents one of the largest active pools of carbon on Earth [Hansell *et al.*, 2009], comparable in size to atmospheric CO₂. The controls on ocean DOC production and remineralization are therefore of primary importance in regulating the global carbon cycle. Despite the importance of DOC to biogeochemical cycles, and its potential for impacting global climate [Peltier *et al.*, 2007; Ridgwell, 2011; Sexton *et al.*, 2011], explicit controls governing the cycling of marine DOC are not fully understood.

Radiocarbon (¹⁴C) measurements represent a central tool for determining the persistence and cycling rate of oceanic DOC. Deep ocean DOC has a ¹⁴C age of ~4000–6000 years, suggesting a mean ocean residence time of ~2000 years [Bauer *et al.*, 1992; Williams and Druffel, 1987]. These results are commonly interpreted in the context of a “two-pool” model, whereby recently produced (semilabile) surface DOC is added to an older, chemically and isotopically homogenous, “background” pool of recalcitrant DOC (RDOC) [Williams and Druffel, 1987].

Multiple DOC cycling mechanisms are present in the global ocean. DOC production by phytoplankton excretion, bacterial/viral mediated release and particle solubilization is balanced by DOC removal through bacterial and photochemical oxidation and sorption to sinking particles [Carlson, 2002]. However, there is a growing consensus that bacterial activity known as the “microbial carbon pump” (MCP) plays a central role in transforming labile DOC into increasingly refractory molecules, which accumulate in the background DOC pool. A number of mechanisms have been suggested for the functioning of the MCP [Jiao *et al.*, 2010]; however, the rates and biological pathways by which it operates to form RDOC remain unknown. One key problem is that the foundations of refractory DOM formation and the microbial carbon pump hypothesis rely on observations from short-term laboratory experiments [Barber, 1968; Ogawa *et al.*, 2001]; thus, RDOC production on time scales of 50–1000 years is difficult to investigate.

DOC molecular size and composition can have a significant effect on DOC bioavailability [Amon and Benner, 1994]. Commonly described as the “size-reactivity continuum” hypothesis [Benner and Amon, 2015], this idea is consistent with the relatively small number of available observations, which show that high molecular weight (HMW) DOC has higher $\Delta^{14}\text{C}$ values and lower molecular weight (LMW) DOC has lower $\Delta^{14}\text{C}$ values [Guo *et al.*, 1996; Loh *et al.*, 2004; Santschi *et al.*, 1995; Walker *et al.*, 2011]. Initial studies

exploring the age of various HMW DOC fractions (>10 kDa and >3 kDa) provided radiocarbon evidence in support of the size-reactivity continuum concept, with larger particulate organic carbon (POC) and HMW DOC fractions having higher $\Delta^{14}\text{C}$ values and smaller DOC fractions having the lower $\Delta^{14}\text{C}$ values [Guo *et al.*, 1996; Santschi *et al.*, 1995]. Work by Loh *et al.* [2004] also provided evidence that POC, HMW, and LMW DOC $\Delta^{14}\text{C}$ decreases with size. In addition, their compound-class $\Delta^{14}\text{C}$ measurements of these size fractions showed that protein- and carbohydrate-like material had the highest $\Delta^{14}\text{C}$ values and thus are likely the most labile POC and DOC constituents. A study by Walker *et al.* [2011] reports HMW DOC $\Delta^{14}\text{C}$ values from samples with increasing concentration factors (i.e., increasing average HMW DOC molecular size). Here positive concentration factor versus $\Delta^{14}\text{C}$ relationships were observed, which also reconciled all previously published surface and deep HMW DOC $\Delta^{14}\text{C}$ values in the Pacific Ocean. Most recently, quantitative size-age-composition relationships (i.e., C:N ratios and $\Delta^{14}\text{C}$) were reported for large and small POC and DOC fractions from a coastal upwelling system, suggesting a new tool for quantifying C and N flux via the size-reactivity continuum [Walker *et al.*, 2014].

Generally speaking, negative DOC $\Delta^{14}\text{C}$ values would imply material that is less bioavailable and more recalcitrant. However, biological reactivity is not necessarily synonymous with changes in $\Delta^{14}\text{C}$. For example, both “new” and “old” ^{14}C components have been isolated from HMW DOC, possibly contradicting the two-pool model paradigm [Repeta and Aluwihare, 2006]. In addition, hydrothermal and methane seep studies indicate deep ocean inputs of freshly produced DOC with old ^{14}C ages [McCarthy *et al.*, 2011; Pohlman *et al.*, 2011]. Together, these observations may preclude a direct relationship between molecular size and $\Delta^{14}\text{C}$ in the deep ocean. Whereas linkages between DOC biological reactivity and molecular size have been implicated, the degree to which molecular size may be systematically coupled to ^{14}C age of DOC in major ocean basins (i.e., its direct relationship to global DOC cycling) requires further study.

As mentioned above, in an earlier paper we demonstrated a strong relationship between ultrafiltration (UF) concentration factors (CFs) and $\Delta^{14}\text{C}$ values [Walker *et al.*, 2011]. Here we use these $\Delta^{14}\text{C}$ measurements of increasing average molecular size (via CF) from both surface and deep DOC pools to directly test the relationships between DOC molecular size, ^{14}C age, and reactivity in the North Central Pacific Ocean. We further evaluate DOC size versus $\Delta^{14}\text{C}$ relationships through the application of several modeling approaches. Here we focus on these relationships in more detail, with the goal of understanding major mechanisms underlying the MCP, DOC remineralization, and preservation in the ocean.

2. Materials and Methods

2.1. Sample Collection and Isotopic Analysis

Total and ultrafiltered dissolved organic carbon (UDOC) samples of increasing average molecular size (i.e., increasing overall sample molecular size with increasing CF) were collected in December of 2005 from three depths (20 m, 670 m, and 915 m) at the Natural Energy Laboratory of Hawaii Authority (NELHA) site, near Kona, HI. Our UDOC sample collection and preparation for isotopic analysis have been described previously [Walker *et al.*, 2011]. Dissolved inorganic carbon (DIC) isolations were performed by vacuum line extraction at the University of California (UC) Davis Department of Geology–Stable Isotope Lab, and were sealed into precombusted (450°C, 5 h) borosilicate tubes, following established protocols for $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ analyses [McNichol *et al.*, 1994]. Total and UDOC samples were quantitatively oxidized to CO_2 either with a mercury arc lamp photochemical reactor system [S. R. Beaupre *et al.*, 2007] or via closed-tube combustion for ^{14}C analysis at UC Irvine Keck Carbon Cycle Accelerator Mass Spectrometry Facility or Lawrence Livermore National Laboratory (LLNL)/Center for Accelerator Mass Spectrometry, respectively. All isotopic measurements were blank-corrected for graphitization and AMS analysis and also corrected with error propagation for the ultraviolet-extraction procedural blank [S. R. Beaupre *et al.*, 2007].

2.2. Keeling Models

Keeling models used in this study are analogous to those previously described for total and size-fractionated DOC [Mortazavi and Chanton, 2004]. Briefly, Keeling models are two end-member mixing models, used for estimating the isotopic composition of the “excess” carbon component added to a homogenous background carbon pool. They make no assumptions about the magnitudes of DOC concentration or the $\Delta^{14}\text{C}$ value of

the background DOC pool but do assume that both are constant. Specifically, Keeling models are derived from a simple isotopic mixing model:

$$\text{DOC}_z \cdot \Delta^{14}\text{C}_z = \text{DOC}_{xs} \cdot \Delta^{14}\text{C}_{xs} + \text{DOC}_b \cdot \Delta^{14}\text{C}_b, \quad (1)$$

where DOC at depth z (DOC_z) is comprised of a background DOC pool (DOC_b) of unknown concentration and an *excess* DOC (DOC_{xs}) is added to DOC_b via surface productivity. By assuming a two-component mixing model, a linear relationship between $1/\text{DOC}_z$ and $\Delta^{14}\text{C}_z$ is predicted. The y intercept determined from a model II geometric mean regression of $\Delta^{14}\text{C}_z$ versus $1/\text{DOC}_z$ is equal to $\Delta^{14}\text{C}_{xs}$ or the $\Delta^{14}\text{C}$ signature of DOC added to the background DOC pool. Coefficients of determination (R^2) were calculated as the square of model II correlation coefficients (r). See supporting information for more details.

2.3. DOC Molecular Size-Age Distribution Ultrafiltration Model

To further summarize the radiocarbon data in light of the size-reactivity continuum hypothesis, we formulated a simple parametric model that describes the molecular size and $\Delta^{14}\text{C}$ value of DOC as a function of molecular weight (x). We assume that the molecular weight of the excess and background DOC is lognormally distributed with the means (μ_{xs}, μ_b) and variances ($\sigma_{xs}^2, \sigma_b^2$) being parameters to be estimated from the available data. Previous work from this same study demonstrated logarithmic permeation of DOC and $\Delta^{14}\text{C}$ with increasing CF and thus increasing average MW of the retentate solution [Walker *et al.*, 2011]. These seawater DOC solutions were therefore shown to behave ideally with respect to UF theory [Cheryan, 1998; Kilduff and Weber, 1992] and not affected by membrane fouling, changes in permeation flow rates, or system pressures. Accordingly, the logarithmic permeation of DOC and $\Delta^{14}\text{C}$ may also suggest logarithmic DOC size-age distributions. Whereas a logarithmic size distribution of deep $\Delta^{14}\text{C}$ can be prescribed, for modeling purposes the abundance of DOC molecules cannot reach a maximum at $\text{MW} = 0$ Da. Therefore, we prescribe a lognormal distribution of DOC molecules, such that the abundance of DOC molecules approaches zero at $\text{MW} = 0$ Da. Such lognormal DOC distributions are qualitatively supported by mass distributions of hydrophobic DOC as estimated using Fourier transform ion cyclotron resonance mass spectrometry data for the 150–2000 Da size range have presented evidence for lognormal molecular size distributions [D'Andrilli *et al.*, 2010; Hertkorn *et al.*, 2006]. Furthermore, we make the simple assumption that the $\Delta^{14}\text{C}$ value of the DOC is a linear function of $\log(x/x_0)$, where x_0 is a reference molecular weight (e.g., $x_0 = 1$ Da). Specifically, we assume that the $\Delta^{14}\text{C}$ value of the excess DOC is independent of molecular size and equal to the $\Delta^{14}\text{C}$ value of surface DIC, i.e.,

$$\text{DOC}_{xs} \Delta^{14}\text{C} = +57\text{‰}, \quad (2)$$

and that the $\Delta^{14}\text{C}$ value of the background DOC ranges from -100‰ (the $\Delta^{14}\text{C}$ of deep particulate organic matter in the NE Pacific Ocean [Hwang *et al.*, 2010]) at the highest molecular weights ($x \sim 10^6$ Da) to -600‰ (lower than the most negative total DOC $\Delta^{14}\text{C}$ measured [S. R. Beaupre and Druffel, 2009]) at the low molecular weights ($x \sim 10^0$ Da), i.e.,

$$\text{DOC}_b \Delta^{14}\text{C}(x) = \frac{500\text{‰}}{\log(10^6)} \log(x/x_0) - 600\text{‰}. \quad (3)$$

The size distribution and $\Delta^{14}\text{C}$ signature of DOC at each depths are then modeled as a linear mixture of the excess and background distributions

$$\text{DOC}(x) = \text{DOC}_{xs}(x) + \text{DOC}_b(x), \quad (4)$$

$$\text{DOC} \Delta^{14}\text{C}(x) = \text{DOC}_{xs}(x) \Delta^{14}\text{C}_{\text{DOC}_{xs}}(x) + \text{DOC}_b(x) \Delta^{14}\text{C}_{\text{DOC}_b}(x), \quad (5)$$

where $\text{DOC}(x)dx$ represents the number of carbon atoms per unit volume in dissolved organic carbon molecules which have between x and $x + dx$ carbon atoms and similarly for $\Delta^{14}\text{C}(x)$.

For each depth level, the model has six free parameters ($f_{xs}, f_b, \mu_{xs}, \sigma_{xs}^2, \mu_b,$ and σ_b^2), which we estimate from the UDOC, UF, and $\Delta^{14}\text{C}$ data [Walker *et al.*, 2011]. The parameters f_{xs} and f_b are equal to the total number of carbon atoms per unit volume of the excess and background pools, respectively. To compare the model to the data we developed a mathematical model for the ultrafiltration process used to collect the DOC material. To fit the model to the data we used a Bayesian approach. See supporting information

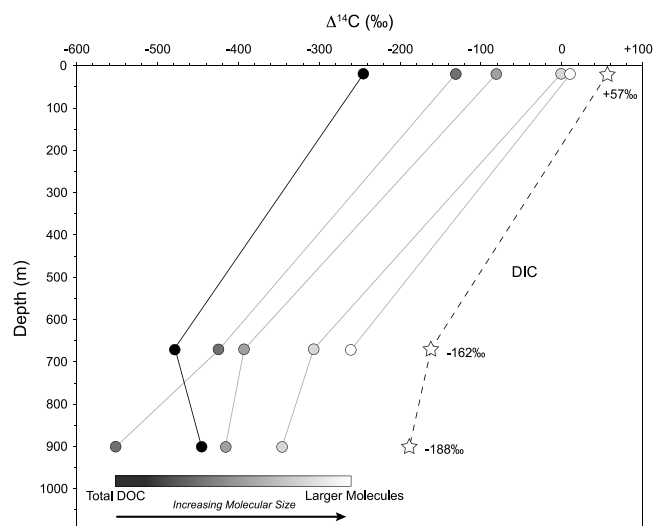


Figure 1. The $\Delta^{14}\text{C}$ depth profiles of average increasing DOC molecular size fractions in the North Central Pacific. Relative DOC molecular size fractions are arranged from left to right in order of increasing relative molecular size as reported Walker *et al.* [2011]. The progression of increasing molecular size versus increasing $\Delta^{14}\text{C}$ indicates tight coupling between DOC relative molecular size and $\Delta^{14}\text{C}$ within oceanic DOC at three depths. Dissolved inorganic carbon (DIC; open stars) and total DOC (black circles) $\Delta^{14}\text{C}$ values bracket the DOC size fractions (shaded to light circles). The white circles represent the data from Repeta and Aluwihare [2006].

–162‰ and –188‰ at 670 m and 915 m. Total DOC $\Delta^{14}\text{C}$ decreases from –246‰ at the surface to –479‰ and –446‰ at 670 m and 915 m. The DIC and total DOC profiles also show increasingly negative $\Delta^{14}\text{C}$ values with depth, also consistent with previously published values from the NCP [Druffel *et al.*, 1992]. Finally, all DOC molecular size fractions (with the exception of one 915 m sample) also have $\Delta^{14}\text{C}$ depth profiles similar to both total DOC and DIC.

These observations indicate a regular progression in DOC $\Delta^{14}\text{C}$ values with increasing size throughout the ocean water column. They further indicate that linked size versus $\Delta^{14}\text{C}$ distributions are present in *both* the surface and mesopelagic ocean, spanning a significant range in $\Delta^{14}\text{C}$ values. These observations are significant because DOC in deep North Central Pacific waters also comprise some of the lowest $\Delta^{14}\text{C}$ values of subsurface DOC anywhere in the world ocean [S. R. Beaufre and Druffel, 2009; Druffel and Griffin, 2015]. The presence of size versus $\Delta^{14}\text{C}$ relationships in the North Central Pacific suggests that this is likely a global ocean phenomenon. As noted above, the size fractions we isolated cannot be assigned known molecular size ranges, based on VCF-UF partitioning. Instead, each fraction represents a molecular size mixture containing progressively less LMW molecules (and therefore increasing HMW molecules) with continued filtration (i.e., increasing CF). It is important to note that this lack of specific molecular size range information is not problematic since our main interpretations are based on the clear *relative* progression of UDOC $\Delta^{14}\text{C}$ values versus size (via VCF-UF) at all depths.

3.2. Keeling Models and Two-Component Mixing of DOC Molecular Size Fractions

In order to more directly examine DOC molecular size versus $\Delta^{14}\text{C}$ relationships in the surface and deep ocean, we applied Keeling models to each relative molecular size fraction [Mortazavi and Chanton, 2004]. As noted in section 2, Keeling models are two end-member mixing models used to estimate the isotopic composition of a new surface carbon (such as freshly produced autotrophic DOC) added to a homogenous background pool. As such, Keeling models are consistent with previous two-component models addressing the persistence of ocean DOC [Williams and Druffel, 1987]. Keeling models can also be applied to size-fractionated DOC by assuming a two-pool model where recently produced excess HMW DOC ($\text{DOC}_{\text{HMWxs}}$) in the surface ocean is added to an existing background pool of HMW DOC

for details on the mathematical model for the size distribution, for the ultrafiltration process, and for the Bayesian probability model used for parameter estimation.

3. Results and Discussion

3.1. Linked Changes in DOC Molecular Size and $\Delta^{14}\text{C}$ Values

A prior study by Walker *et al.* [2011] showed that variable CF UF (VCF-UF) represents an effective new tool for separating relative DOC molecular size fractions for evaluating DOC cycling. Using this framework, DOC $\Delta^{14}\text{C}$ depth profiles of progressively larger DOC size fractions (isolated via VCF-UF) can be evaluated. When DOC $\Delta^{14}\text{C}$ values for these increasing molecular size fractions [Repeta and Aluwihare, 2006; Walker *et al.*, 2011] are placed in the context of in situ DIC $\Delta^{14}\text{C}$ values, a clear progression of increasing $\Delta^{14}\text{C}$ values versus increasing average molecular size is observed (Figure 1). DIC $\Delta^{14}\text{C}$ values decrease from +57‰ in the surface to

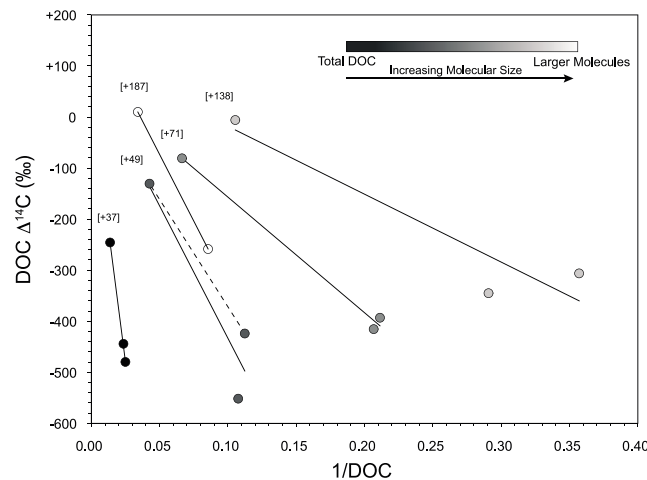


Figure 2. Keeling model regressions for increasing DOC molecular size fractions in the North Central Pacific. Progressive offsets of Keeling model II regressions (solid lines) show that the DOC higher molecular sizes have higher $\Delta^{14}\text{C}$ signatures in both the surface and mesopelagic ocean. Keeling intercept values in square brackets indicate the surface DOC $\Delta^{14}\text{C}_{\text{XS}}$ sources for samples of increasing molecular size (see Table S1). The dashed line indicates the regression with the 915 m depth value excluded. All symbols are the same as in Figure 1.

Due to intensive VCF-UF sample experimental requirements (i.e., extremely long filtration times and large volumes), we only have three depths for each Keeling regression. The limited sample population results in large slope errors. However, we note that Keeling plots are essentially two end-member mixing lines driven by surface DOC and $\Delta^{14}\text{C}$ signatures (i.e., < 1000 m depth) [S. R. Beapre and Aluwihare, 2010]. In this way we believe that it is appropriate to *qualitatively* interpret these broad regression trends and $\Delta^{14}\text{C}_{\text{HMWXS}}$ intercept values. In particular, by performing these regressions on each progressive size fraction depth profile, we can evaluate the relative results of multiple independent relationships.

Applying Keeling regressions to each DOC relative molecular size fraction (Figure 2) reveals uniformly strong R^2 correlations for all DOC MW fraction depth profiles ($R^2 > 0.87$; Table S1 in the supporting information). However, as discussed above, because there are only three data points for each regression the statistical significance of these R^2 values cannot be determined unambiguously. *Qualitatively speaking*, these correlation coefficients and increases in y intercept $\Delta^{14}\text{C}_{\text{HMWXS}}$ values are consistent with two-component mixing within each progressive DOC size fraction. Thus, UDOC molecular size fractions likely comprise both $\text{DOC}_{\text{HMWXS}}$ and DOC_{HMWb} components, each with a unique $\Delta^{14}\text{C}$ signature that becomes more positive with increasing CF and average retentate molecular size.

Another key aspect of the Keeling models is that their y intercepts can be used to evaluate the $\Delta^{14}\text{C}$ content of “newly produced” DOC in the surface ocean [S. R. Beapre and Aluwihare, 2010; McNichol and Aluwihare, 2007; Mortazavi and Chanton, 2004]. Our Keeling y intercepts result in $\Delta^{14}\text{C}_{\text{HMWXS}}$ values (Figure 2 and Table S1) that also increase progressively with molecular size, from values approximating in situ DIC for the lowest MW fraction (total DOC = +37‰) to much higher $\Delta^{14}\text{C}_{\text{HMWXS}}$ values containing maximum “bomb” $\Delta^{14}\text{C}$ signatures (largest DOC molecules = +187‰). Whereas this latter value seems quite high, we note that it is similar to independent mass balance estimates of newly produced surface DOC in the Pacific Ocean ($\Delta^{14}\text{C} = +147‰$) during the 1970s [Bauer, 2002]. The interpretation of the exact intercept value for any individual line is again limited by a lack of data points for each size fraction. However, our main observation of a progression in $\Delta^{14}\text{C}_{\text{HMWXS}}$ is clear. The high $\Delta^{14}\text{C}_{\text{HMWXS}}$ values predicted for the highest MW fractions are also consistent with past work in suggesting that the largest DOC molecules (i.e., “semilabile” DOC) persist in the surface ocean for several decades before being remineralized and/or advected to the deep sea. For example, one recent estimate indicated an ~60 to 90 year weighted mean turnover time of surface ocean DOC [Loh et al., 2004], based on the relative abundance and ^{14}C age of HMW and LMW DOC compound classes. In addition, the turnover times implied by our Keeling intercepts are comparable to estimates of HMW DOC persistence derived from compound-specific $\Delta^{14}\text{C}$ analysis of carbohydrates from the North

(DOC_{HMWb}) [McNichol and Aluwihare, 2007; Mortazavi and Chanton, 2004] as represented by the following equation:

$$\begin{aligned} \text{DOC}_{\text{HMWz}} \Delta^{14}\text{C}_{\text{HMWz}} &= \text{DOC}_{\text{HMWb}} \Delta^{14}\text{C}_{\text{HMWb}} \\ &+ \text{DOC}_{\text{HMWXS}} \Delta^{14}\text{C}_{\text{HMWXS}} \quad (6) \end{aligned}$$

In this case, the y intercept, determined by a linear regression of $1/\text{DOC}_{\text{HMWz}}$ and $\Delta^{14}\text{C}_{\text{HMWz}}$, will be equal to $\Delta^{14}\text{C}_{\text{HMWXS}}$ or the $\Delta^{14}\text{C}$ signature of the HMW DOC “source” in the surface ocean [McNichol and Aluwihare, 2007; Mortazavi and Chanton, 2004].

In this study, we used an identical approach to evaluate source $\Delta^{14}\text{C}$ signatures for samples of varying molecular size distributions (via VCF-UF [Walker et al., 2011]) from the NCP. Due to intensive VCF-UF sample experimental requirements (i.e., extremely long filtra-

Pacific [Repeta and Aluwihare, 2006]. Together, the consistency of these independent estimates further supports our overall interpretation of $\Delta^{14}\text{C}_{\text{HMWxs}}$ values from each molecular size fraction.

Most broadly, the observed progression of both Keeling model slopes and intercepts indicate that two-component mixing can also explain DOC cycling (via $\Delta^{14}\text{C}$) within distinct molecular size fractions. We hypothesize that DOC size-age distributions are therefore also linked throughout the water column. These observations may also suggest that “preformed” surface DOC molecular size distributions are strongly linked to subsequent DOC reactivity at depth—however, more work is needed to test this hypothesis.

3.3. DOC Cycling Using Molecular Size-Age Distributions: A Modeling Exercise

If average molecular size is important for determining DOC $\Delta^{14}\text{C}$ values, then it should be possible to predict measured total DOC $\Delta^{14}\text{C}$ values, based on assumed DOC molecular size-age distributions. We tested this idea by using our previously published UF parameters, DOC recoveries, and $\Delta^{14}\text{C}$ values [Walker et al., 2011], together with measured in situ DIC $\Delta^{14}\text{C}$, to parameterize a molecular size-age distribution ultrafiltration model for seawater DOC.

Using simulated total DOC molecular size and $\Delta^{14}\text{C}$ seawater at 20 m, 670 m, and 915 m (Figures 3a and 3b), our model accurately predicted surface and deep DOC concentrations (within 2σ of measured values) at three CFs tested in the Walker et al.'s [2011] study (Figures 3c and 3d). This result suggests that our modeled DOC size distributions are generally representative of actual seawater DOC molecular size distributions. The model also predicts recent production of both large (>500 Da) and small (<200 Da) DOC molecules in the surface ocean (i.e., that DOC_{xs} $\Delta^{14}\text{C}$ is equal to that of DIC $\Delta^{14}\text{C} = +57\%$; Figure 3b) and only a small range of molecules containing low $\Delta^{14}\text{C}$ values. This model result is broadly consistent with an overall size age trend but also suggests that the oldest, most abundant DOC in the surface ocean may not be the material with the smallest molecular weight but rather LMW material between ~ 200 and 500 Da. Whereas this modeling exercise can only suggest this as a hypothesis, such a negative $\Delta^{14}\text{C}$ size offset is consistent with recent work proposing an “island of stability” for DOC molecules of sizes ~ 330 – 550 Da, which can be produced by bacterial degradation in days but persist for millenia [Lechtenfeld et al., 2014].

The model also accurately reproduces surface UDOC and $\Delta^{14}\text{C}$ values at all CFs (Figure 3e). This is a key result, since surface UDOC $\Delta^{14}\text{C}$ values are derived from subtraction of integrated DOC_{deep} and DOC_{xs} size-age ($\Delta^{14}\text{C}$) populations at a given CF and not assumed. Modeled deep UDOC $\Delta^{14}\text{C}$ values at high CFs were very similar to measured 670 m and 915 m values. However, in contrast with close correspondence in the surface, the predicted deep $\Delta^{14}\text{C}$ values at lower CFs were consistently more positive and did not closely approximate our measured deep UDOC $\Delta^{14}\text{C}$ values (Figure 3f). The fact that modeled UDOC concentrations were reproduced at depth, but UDOC $\Delta^{14}\text{C}$ values were not, may suggest a different deep $\Delta^{14}\text{C}$ size distribution or perhaps multiple deep DOC $\Delta^{14}\text{C}$ sources. Given our relatively small sample data set, and the potential for multiple DOC sources, it is possible that our model underestimates the true uncertainty of deep UDOC $\Delta^{14}\text{C}$.

There may be multiple explanations for the deep DOC $\Delta^{14}\text{C}$ model results. Perhaps the most direct is the hypothesis that deep DOC $\Delta^{14}\text{C}$ distributions cannot be adequately explained with only two components. Multiple alternate deep DOC sources have been proposed, which might alter DOC $\Delta^{14}\text{C}$ values at depth, including hydrothermal DOC, chemosynthesis, and particle solubilization [Hansman et al., 2009; McCarthy et al., 2011; Smith et al., 1992]. If any of these processes were in fact significant, this would result in source heterogeneity consistent with the mismatch between our model results in surface versus deep ocean.

4. Implications

Together, our UF model results demonstrate that DOC molecular size-age distributions can predict surface and deep UDOC concentrations and surface $\Delta^{14}\text{C}$ values at all CFs. This represents a significant advance from previous observations of a $\Delta^{14}\text{C}$ versus CF relationship in determining the $\Delta^{14}\text{C}$ signature of HMW DOC [Walker et al., 2011]. These results suggest that in the surface ocean, molecular size serves as a proxy for both biological reactivity and chemical composition—largely explaining DOC $\Delta^{14}\text{C}$ values and its biogeochemical cycling. Qualitatively speaking, the two-component Keeling model results for increasing relative molecular size fractions are also consistent with a two-component framework, which can be applied across a progression of DOC molecular sizes at all depths. Whereas HMW DOC is *on average* predictably younger than LMW

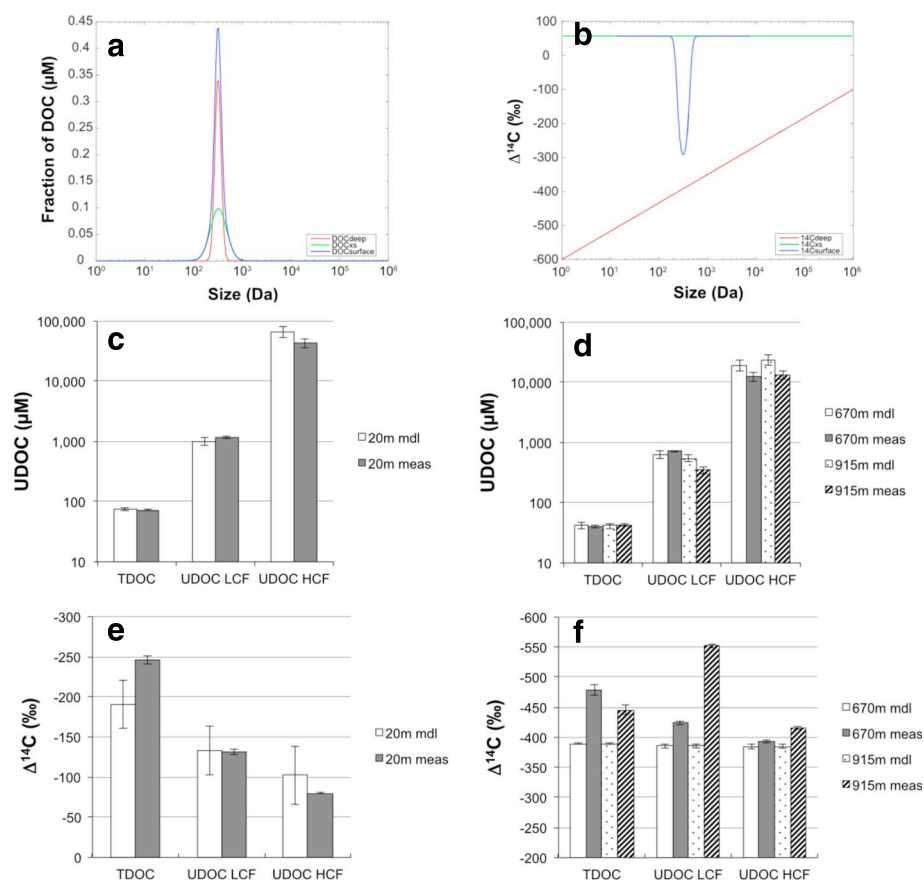


Figure 3. Size-age distribution ultrafiltration model results for the NCP. (a and b) Lognormal DOC molecular size (Da) and radiocarbon ($\Delta^{14}\text{C}$) distributions of modeled deep (red) excess (green) and surface (blue) DOC solutions that were then run through the ultrafiltration model. Surface DOC and $\Delta^{14}\text{C}$ size distributions were determined via addition of weighted DOC_{xs} and DOC_{deep} concentrations and $\Delta^{14}\text{C}$ values. (c–f) Comparison of measured versus model-predicted total DOC (TDOC) and UDOC retentate concentrations and $\Delta^{14}\text{C}$ at each concentration factor (CF) in the Walker *et al.*'s [2011] study. These CFs are the following: total DOC (TDOC; CF = 1), UDOC low CF (LCF; CF = 28 to 46), and UDOC high CF (HCF; CF = 2495 to 3018). The error bars represent the propagated uncertainty (1σ). For more detail on this model, please see the provided supporting information.

DOC, our UF model also suggests that within each nominal molecular size class there likely also exists a range of ^{14}C ages. If newly produced surface HMW material is added to background HMW at depth, then to arrive at the newly produced HMW $\Delta^{14}\text{C}$ signature, the influence of deep HMW DOC must be subtracted. Observations of both old and new surface HMW DOC components have been interpreted as precluding a size-reactivity framework for DOC cycling [Repeta and Aluwihare, 2006]. However, our results suggest that size reactivity and two-component mixing can be complementary.

Overall, our core observation of progressively increasing UDOC $\Delta^{14}\text{C}$ values with increasing CF suggests that molecular size and composition are key parameters in determining DOC cycling and persistence in the ocean. These data represent the most detailed evidence for a size-age continuum within the marine DOC pool, significantly expanding upon previous observations of DOC size-bioavailability relationships [Benner and Amon, 2015], and also potential linkages between organic matter size, composition, and $\Delta^{14}\text{C}$ [Walker and McCarthy, 2012; Walker *et al.*, 2014]. Our model results show that molecular size can largely predict DOC cycling, suggesting that the size distribution of DOC molecules likely have a pronounced effect on DOC residence times.

These results may also have implications for a more mechanistic understanding of RDOC formation and the operation of MCP processes. Specifically, our results support the view that decreasing DOC molecular size is coupled to progressive degradation of organic matter quality, a conclusion previously inferred from decreasing recoveries of identifiable biochemicals [Benner and Amon, 2015]. Our $\Delta^{14}\text{C}$ size data support the idea that

degradation imparts biological resistance to further DOC microbial utilization and therefore a longer oceanic residence time. This recognized paradigm [Benner and Amon, 2015] opposes earlier ideas of “geomolecule” formation—where small DOC subunits condense to larger, recalcitrant polymers [Hedges et al., 2000]. These size-age trends are also inconsistent with recent hypotheses, suggesting that dilution of DOC ultimately governs its biogeochemical cycling [Arrieta et al., 2015]. Instead, a direct linkage between molecular size, composition, and $\Delta^{14}\text{C}$ is indicative of intrinsic biological reactivity differences and ^{14}C age of the DOC pool.

Most broadly, these results suggest that DOC molecular size connects seemingly disparate prior observations on DOC composition and cycling. Previous work on HMW DOC has clearly shown that DOC is comprised of many labile biomolecules, in particular complex carbohydrates and amino acids [Biddanda and Benner, 1997; Biersmith and Benner, 1998; Kaiser and Benner, 2009]. In contrast, recent results on LMW material isolated by hydrophobic resins has indicated complex and heterogeneous chemical composition, far more similar to that observed in fulvic acids in terrestrial systems [Dittmar and Kattner, 2003; Hertkorn et al., 2006; Hertkorn et al., 2007]. A size versus $\Delta^{14}\text{C}$ continuum links these very different molecular level results into a unified view based on a progressive gradient in ocean DOC composition and age.

We suggest that better understanding the nature of size versus composition relationships may provide useful research directions for understanding the balance between DOC lability and recalcitrance. New methods of DOC size fractionation focused on isolating the more recalcitrant (and ^{14}C -depleted) DOC fractions, coupled with molecular-level studies, may reveal the underlying structural changes leading to RDOC formation. Ultimately, the central importance of molecular size, composition, and biological reactivity provide a path by which MCP processes may be tested.

Acknowledgments

We acknowledge the Natural Energy Laboratory of Hawaii Authority (NELHA) and staff for providing facilities capable of large-volume seawater DOC isolations; Leslie Germain and Jennifer Walker (UC Santa Cruz) for the help with sample collection and laboratory assistance; and Paula Zermeño (LLNL), Sheila Griffin, and John Southon (UCI) for the aid in ^{14}C sample preparation and analysis. We also thank Ed Peltzer (MBARI) for the MATLAB scripts of model II geometric mean regression analysis used in Keeling models. This work was funded by a UCOP Campus Laboratory Collaboration (to M.D.M. and T.P.G.), NSF Chemical Oceanography program (OCE 0961980 and OCE 1458941 to E.R.M.D. and OCE 1436922 to F.W.P.), NSF Graduate Research Fellowship (to S.R.B.), and a Keck Carbon Cycle AMS Laboratory Postdoctoral Fellowship (to B.D.W.). A portion of this work was performed under the auspices of the U.S. Department of Energy (contracts W-7405-Eng-48 and DE-AC52-07NA27344). Data are included as tables in the supporting information file; any additional data may be obtained from B.D.W. upon request (e-mail: brett.walker@uci.edu).

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