Large Stimulation of Recalcitrant Dissolved Organic Carbon Degradation by Increasing Ocean Temperatures

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More than 96% of organic carbon in the ocean is in the dissolved form, most of it with lifetimes of decades to millennia. Yet, we know very little about the temperature sensitivity of dissolved organic carbon (DOC) degradation in a warming ocean. Combining independent estimates from laboratory experiments, oceanographic cruises and a global ocean DOC cycling model, we assess the relationship between DOC decay constants and seawater temperatures. Our results show that the apparent activation energy of DOC decay (E_a) increases by three-fold from the labile (lifetime of days) and semi-labile (lifetime of months) to the semi-refractory (lifetime of decades) DOC pools, with only minor differences between the world's largest ocean basins. This translates into increasing temperature coefficients (Q_{10}) from 1.7–1.8 to 4–8, showing that the generalized assumption of a constant Q_{10} of ~2 for biological rates is not universally applicable for the microbial degradation of DOC in the ocean. Therefore, rising ocean temperatures will preferentially impact the microbial degradation of the more recalcitrant and larger of the three studied pools. Assuming a uniform 1°C warming scenario throughout the ocean, our model predicts a global decrease of the DOC reservoir by 7 ± 1 Pg C. This represents a 15% reduction of the semi-labile + semi-refractory DOC pools.

Keywords: temperature, dissolved organic carbon, mineralization, Arrhenius law, global ocean biogeochemical model

INTRODUCTION

Dissolved organic carbon (DOC) in the ocean represents one of the largest reservoirs of organic matter on the Earth's surface, containing a similar amount of carbon as atmospheric carbon dioxide (CO_2) (Hedges, 2002). The main processes responsible for the removal of DOC from the ocean water column are: (1) photochemistry, where DOC is degraded directly to CO_2, carbon monoxide (CO) or low molecular weight organic compounds readily available for prokaryote uptake (Moran and Zepp, 1997; Mopper et al., 2015); (2) abiotic aggregation into microparticles (Kerner et al., 2003) or sorption to particles (Chin et al., 1998); (3) abiotic degradation via free radical reactions with oxygen (Rontani et al., 2014); and (4) degradation by marine heterotrophic prokaryotes (Lønborg and Álvarez-Salgado, 2012), with the latter representing the major DOC sink in the ocean (Carlson and Hansell, 2015).

Although the DOC pool comprises a myriad of compounds covering a widespread molecular size-reactivity continuum (Amon and Benner, 1996; Benner and Amon, 2015), it is operationally divided into a biologically labile fraction (DOC$_L$) that is degraded over hours to days, a semi-labile fraction (DOC$_{SL}$) with turnover times from weeks to months, a semi-refractory fraction (DOC$_{SR}$) that can be stored for decades, a refractory fraction (DOC$_R$) with lifetimes of thousands of years, and an ultra-refractory fraction (DOC$_{UR}$) resistant to removal for tens of thousands of years (Hansell, 2013). Bioavailability has traditionally been linked to the chemical composition and structure of DOC, but more recently it has been shown to also vary depending on a range of other external factors (Raymond and Spencer, 2015). These factors include nutrient status, redox state, mineral-particle associations, terrestrial inputs, sunlight, biological production of recalcitrant compounds, changing microbial community composition, and the effect of priming or the extreme dilution of individual molecules (e.g., Amon and Benner, 1996; Thingstad et al., 1999; Del-Giorgio and Davies, 2003; Bianchi, 2011; Keil and Mayer, 2014; Arrieta et al., 2015; Letscher et al., 2015). About 4% of the ocean's net primary production escapes degradation in the surface layer to be exported as DOC to the ocean interior at a rate of about 2 Pg C year^{-1} (Hansell et al., 2012), roughly equalling the annual net ocean uptake of CO_2 (Sarmiento and Gruber, 2006). Therefore, climate induced changes in DOC production, degradation, and/or export to deeper waters could potentially impact the atmospheric CO_2 concentration and the Earth climate system. Previous studies have proposed that changes in the degradation of ocean DOC over global scales could have an important role in regulating the long-term climate, with the rate and magnitude of degradation impacting atmospheric CO_2 levels, which in turn influences the cooling and warming of the Earth surface (Peltier et al., 2007; Swanson-Hysell et al., 2010; Sexton et al., 2011).

The temperature sensitivity of natural organic matter degradation has been studied extensively in soils (Davidson et al., 2000; Davidson and Janssens, 2006), demonstrating that increasing ambient temperature preferentially stimulates the microbial degradation of the more recalcitrant organic matter fractions. These studies suggest that the lability of a substrate can be defined by the change in the activation energy (E_a) needed in order for the degradation to take place; the more recalcitrant the compound, the higher its E_a and, following the Arrhenius law, the higher its temperature sensitivity to microbial degradation (Davidson et al., 2000; Davidson and Janssens, 2006; Sierra, 2012). In the marine environment, studies of the microbial activity response to temperature in sediments have shown that the E_a varies as a function of compound class and the organisms degrading the organic matter (Westrich and Berner, 1988; Middelburg et al., 1996). More recently, the Arrhenius law has been used for calculating the E_a of plankton community metabolism, suggesting that marine autotrophs and heterotrophs might react differently to ocean warming (Yvon-Durocher et al., 2012; Chen and Laws, 2017). It has also been shown that the temperature dependence of heterotrophic prokaryote production is fundamentally different between the upper and deeper layers of the ocean (Lønborg et al., 2016). Dissolved oxygen utilization rates in the ocean, computed from dissolved oxygen concentrations and apparent water age estimates, have also revealed a noteworthy temperature sensitivity of microbial respiration (Brewer and Peltzer, 2016, 2017).

Here, we quantify the E_a associated with the microbial degradation of DOC$_L$, DOC$_{SL,}$ and DOC$_{SR}$, which partly controls the ocean prokaryotic production and oxygen consumption. To achieve this goal, we combine data from laboratory microbial cultures and latitudinal DOC concentration and water mass age gradients collected during oceanographic cruises, with the outputs from a global ocean DOC cycling model. This analysis allows us to also assess the impact of future ocean warming on the microbial degradation and size of the DOC fractions and the potential implications for the ocean carbon cycle.

METHODS

Sensitivity of the DOC$_L$ and DOC$_{SL}$ decay constants to temperature, on the order of days to months, can be tested with microbial incubation experiments. However, this approach is not feasible for DOC$_{SR}$, which turns over in years to decades. In this case, calculating rates using latitudinal gradients of DOC concentrations and water ventilation times obtained during oceanographic cruises are more suitable (Carlson et al., 2010). Furthermore, models that combine ocean circulation with DOC biogeochemical cycling provide insights into the global implications of temperature dependence of DOC$_{SL}$ and DOC$_{SR}$ degradation.

Determination of DOC$_L$ and DOC$_{SL}$ Decay Constants from Incubation Studies

Studies of the degradation of DOC$_L$ usually involve the dilution of a natural microbial community to follow the utilization of DOC over days in controlled laboratory conditions; when the incubation time is extended for months, the kinetics of the degradation of DOC$_{SL}$ can also be followed (Lønborg and Álvarez-Salgado, 2012). While numerous studies have determined the DOC$_L$ and DOC$_{SL}$ decay constants (k_C) measuring changes in DOC concentration over time using incubation experiments (see Lønborg and Álvarez-Salgado, 2012; for recent overview) very few were conducted at different temperatures (**Table 1**). In order to overcome methodological differences between the few available studies, we only included data where changes in DOC concentration over time had been measured at different temperatures. These include laboratory incubations using phytoplankton-derived DOC (Seiki et al., 1991), marine humic substances (Bussmann, 1999), and DOC collected in a coastal system (Lønborg et al., 2009). In one case (Bussmann, 1999), only initial DOC was measured but the time course of dissolved oxygen was followed over time. We included this study in the analysis because of the interest on the degradation of natural humic substances. Therefore, it should be kept in mind that in this case the temperature response of DOC respiration rather than utilization (= growth + respiration) has

TABLE 1 | Summary of values obtained applying the Arrhenius law to experimental DOC degradation.

	DOC pool	Q_{10}	E_a (kJ mol^{-1})	Temp. range (°C)	Ref. temp (°C)	k_C (10^{-3} day^{-1})	Turnover time (day)	Ref.
Incubation of phytoplankton-derived DOC	DOC$_L$	1.7 ± 0.1	37 ± 3	[5, 30]	15	110 ± 10	9.2 ± 0.8	29
Incubation of natural marine DOC (spring)	DOC$_L$	1.7 ± 0.3	35 ± 10	[8, 18]	11	61 ± 6	16 ± 2	31
Incubation of natural marine DOC (summer)	DOC$_L$	1.8 ± 0.3	41 ± 11	[8, 18]	14	101 ± 4	9.9 ± 0.3	31
Incubation of natural marine DOC (winter)	DOC$_{SL}$	2.1 ± 0.4	50 ± 11	[8, 18]	8	13 ± 1	76 ± 8	31
Incubation of isolated humic substances	DOC$_{SL}$	2.7 ± 0.4	67 ± 11	[−1, 10]	0	5 ± 1	220 ± 26	30
Bathypelagic N Atlantic DOC gradients/ventilation times	DOC$_{SR}$	3.8 ± 0.5	87 ± 9	[2.5, 7.5]	5	0.20 ± 0.04	$5 \pm 1 \times 10^3$	32
Mesopelagic N Atlantic DOC gradients/ventilation times	DOC$_{SR}$	8 ± 3	146 ± 21	[7.5, 14.5]	11	0.20 ± 0.07	$5 \pm 2 \times 10^3$	32

The temperature coefficient, Q_{10}, apparent activation energy, E_a, temperature ranges used for calculation, and the average DOC decay constants standardized to a reference temperature, k_C. Average values ± standard errors are shown. DOC pool assignments were based on the DOC turnover times; DOC$_L$, days; DOC$_{SL}$, months; DOC$_{SR}$, years.

been followed. DOC samples collected during these experiments were either left unfiltered (Bussmann, 1999) or passed through a 0.45 μm membrane (Seiki et al., 1991) or GF/F filter (Lønborg et al., 2009). All studies but one (Seiki et al., 1991), which used wet oxidation, employed high-temperature combustion to determine the DOC concentration. Note that studies inferring the temperature sensitivity of marine organic matter degradation in long-term microbial incubation experiments using oxygen consumption estimates were not included in our analysis as they either did not distinguish between the particulate and dissolved fraction and/or did not report initial DOC values (e.g., Robinson and Williams, 2005; Hansen and Bendtsen, 2014; Bendtsen et al., 2015).

Estimation of DOC$_{SR}$ Decay Constants from Latitudinal Gradients

Field data used in this work were collected in June–July 2003 along the CLIVAR section A16N in the North Atlantic Ocean (latitudinal range: 6°S to 63°N; longitude range: 20°-29°W) as part of the US CLIVAR Repeat Hydrography program (See Figure 6 in Hansell, 2013). Hydrographic data were obtained at 73 stations spaced by about 50 km using a conductivity, temperature, and depth (CTD) profiler equipped with 36 twelve-liters Niskin bottles. More than two thousand DOC samples were collected during the cruise. Samples taken in the depth range 0–250 m were passed through an in-line polycarbonate filter cartridge holding a combusted GF/F filter attached directly to the Niskin bottle, while samples below this depth were left unfiltered.

The ventilation time of each sample, an estimate of water apparent age, was estimated from measurements of chlorofluorocarbon (CFC) concentrations as described elsewhere (Carlson et al., 2010). In brief, the water mass ventilation year was estimated by comparing the partial pressure of CFC-12 in each water sample with the annual average of CFC-12 in the atmosphere as a function of time (Bullister and Weiss, 1988; Karstensen and Tomczak, 1998). The accuracy of the CFC-12 method is not only impacted by the analytical error but also by under saturation in surface waters at the time of water

masses formation and isopycnal/diapycnal mixing of more recent high-CFC with older zero-CFC water, which adds uncertainty to the ventilation times estimates. The CFC-12 method has an approximate accuracy of 1 year for the water masses with an age range between 3 to 5 years, 0.5 year in the age range 5 to 45 years and 2 years for the waters with an age between 45 and 55 years (Carlson et al., 2010).

Fitting the decline of DOC with water apparent age along isothermal surfaces provides DOC decay constants at different temperatures for the North Atlantic Ocean. Given the apparent age range of the water masses in this hydrographic section, from 3 to 55 years, the DOC$_{SR}$ pool is studied in this case. For the Pacific Ocean two DOC decay estimates for the recalcitrant pools are available but they were measured at approximately equal temperatures (Hansell et al., 2012). As multiple DOC decay estimates over a range of temperatures are needed, we did not include them in our analysis.

DOC Decay Function

Organic matter consists of a wide spectrum of reactivity, each component with its own rate of degradation; therefore, continuum models, rather than those based on the separation of organic matter into distinct reactivity pools, are the most suitable to study the kinetics of organic matter degradation (e.g., Middelburg et al., 1993. However, most DOC degradation studies have been based on the first-order model developed by(Berner (1964). Following this simple model, we used the following 2–pool first-order exponential decay function to fit the DOC decay in the incubation experiments and latitudinal gradients processed in this study:

$$DOC(t) = b_1 \cdot e^{-k_c \cdot t} + b_2 \qquad (1)$$

Where $DOC(t)$ is the concentration of DOC at time t, b_1 is the degraded pool (μmol kg^{-1}), k_C the decay constant (in year^{-1}), t the time (in years) and b_2 the resistant pool (μmol kg^{-1}). For the latitudinal gradients, we fitted DOC and water mass apparent ages (t) to the exponential decay function for different temperature bins (see Table S1).

Arrhenius Law

The temperature sensitivity of k_C is defined by changes in activation energy (E_a):

$$K_c = A \cdot e^{-E_a/R \cdot T} \qquad (2)$$

Where A is the theoretical k_C in the absence of E_a (in year^{-1}); E_a is the energy barrier to be surpassed in order for the reaction to take place (in J mol^{-1}); R is the universal gas constant (8.314 J mol^{-1} K^{-1}); and T is the temperature in Kelvin (K). The factor $e^{-E_a/R \cdot T}$ is proportional to the fraction of DOC molecules with kinetic energies in excess of E_a (Arrhenius, 1889). The Arrhenius equation suggests that more recalcitrant DOC requires a higher amount of energy to be degraded than labile compounds and therefore its degradation is slower. An estimate of the E_a for DOC degradation was derived from the slope of an Arrhenius plot where the ln of DOC decay constants (ln k_C) is plotted against the inverse absolute temperature (1/T) (**Figure 1**). The Arrhenius law assumes that DOC degradation is a well-defined enzymatic reaction with a constant E_a and that temperature is the only factor affecting the rate, while factors such as nutrient limitation are ignored. As all the experimental and *in situ* studies included here had nutrients at non-limiting levels this is a valid assumption (data not shown). Furthermore, as DOC consists of myriad compounds degraded by a variety of microbial populations with different physiologies (Repeta, 2015), the temperature response measured is really the sum of all processes involved and the calculated E_a should be seen as an apparent E_a (Westrich and Berner, 1988; Middelburg et al., 1996). Also as both the estimates from the laboratory experiments and latitudinal gradients were obtained using apparent E_a and apparent Arrhenius pre-exponential factors, the result of this analysis is a likely upper limit to the rate of enzymatic degradation.

T-tests were performed to test the significance of differences and Linear regression analyses were used for the Arrhenius plots applying model II regression (Sokal and Rohlf, 1995). Prior to regressions, normality was checked, and the confidence level was set at 95%.
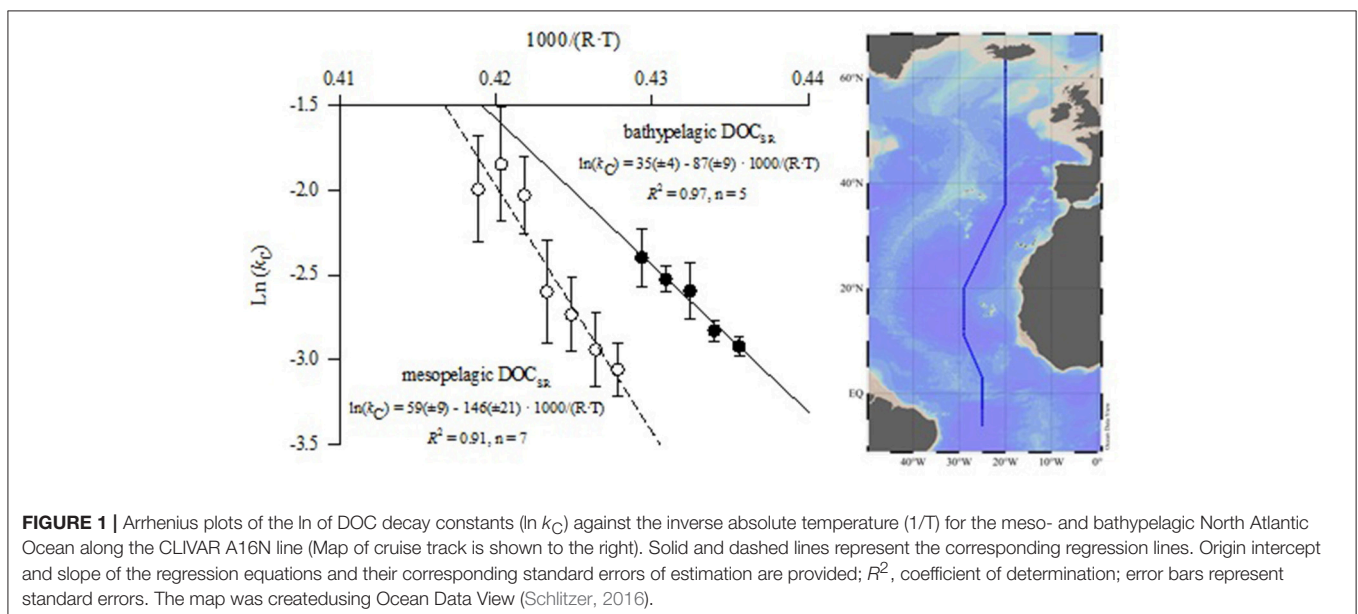
The relationship between temperature and biological rates has been modeled in various ways (Ratkowsky et al., 1983; Ahlgren, 1987), while the factor by which a decay constant increases with a 10°C increase (Q_{10}) is mostly used. Q_{10} values have previously been calculated using multiple functions (Sierra, 2012). In this study we assumed that the relationship between rates and temperature is exponential and we used the following function (Li and Dickie, 1987):

$$Q_{10} = e^{\frac{E_a}{R} \cdot \frac{10}{T_1 \cdot T_2}} \qquad (3)$$

where T_1 and T_2 are the temperatures at which the DOC decay constants were measured.

Describing DOC$_{SL}$ and DOC$_{SR}$ Decay Using a Global Ocean DOC Cycling Model

Following the first-order decay model (Equation 1), a linear DOC cycling model that considers two DOC pools, semi-labile (DOC$_{SL}$) and semi-refractory (DOC$_{SR}$), was coupled with an ocean circulation inverse model (Primeau et al., 2013) constrained by tracer observations of temperature, salinity, sea surface height, heat, and freshwater fluxes, Δ^{14}C-DIC, CFC-11, and phosphate that accurately represents the transport and ideal age of ocean water masses (Devries and Primeau, 2011). The horizontal resolution of the model is $2° \times 2°$ with 24 vertical layers ranging in thickness from $\sim$36 m near the surface to $\sim$663 m at depth. The temperature sensitive DOC decay parameters A and E_a (Equation 2) were estimated using a Bayesian inversion procedure combined with a numerical optimization technique that finds the most probable value

FIGURE 1 | Arrhenius plots of the ln of DOC decay constants (ln k_C) against the inverse absolute temperature (1/T) for the meso- and bathypelagic North Atlantic Ocean along the CLIVAR A16N line (Map of cruise track is shown to the right). Solid and dashed lines represent the corresponding regression lines. Origin intercept and slope of the regression equations and their corresponding standard errors of estimation are provided; R^2, coefficient of determination; error bars represent standard errors. The map was created using Ocean Data View (Schlitzer, 2016).

for each parameter conditioned on the global DOC tracer observations from Letscher and Moore (2015). The tracer conservation equations of the two DOC pools are given by:

$$\frac{\partial \text{DOC}_{SL}}{\partial t} + \mathbf{T}.\text{DOC}_{SL} = f_1.\mathbf{J_P}.r_{CP} - A_1 e^{-E_{a1}/RT}.\text{DOC}_{SL} \quad (4)$$

$$\frac{\partial \text{DOC}_{SR}}{\partial t} + \mathbf{T}.\text{DOC}_{SR} = f_2.\mathbf{J_P}.r_{CP} - A_2 e^{-E_{a2}/RT}.\text{DOC}_{SR} \quad (5)$$

where $\mathbf{T}$ is the 3D advection-diffusion operator of the annually resolved steady-state ocean circulation, $\mathbf{J_P}$ is the biological new production rate of organic matter in the euphotic zone (upper 73 m) which has been optimized using the phosphate tracer distribution and is detailed elsewhere (Primeau et al., 2013), r_{CP} is the ratio of carbon to phosphorus in newly produced organic matter which is assigned a modified Redfield ratio of 117:1, R is the universal gas constant and T, the temperature in degrees Kelvin, is obtained from the ocean circulation inverse model output.

The 6-tuneable parameter set $[f_1 \, f_2 \, A_1 \, A_2 \, E_{a1} \, E_{a2}]$ contains the fraction of biological organic matter production that accumulates as DOC_{SL} (f_1; unit less) and DOC_{SR} (f_2), the theoretical decay constants for DOC_{SL} (A_1; s^{-1}) and DOC_{SR} (A_2; s^{-1}) in the absence of an energy barrier, and the apparent activation energies (E_{a1}; kJ mol^{-1}) and (E_{a2}; kJ mol^{-1}) for DOC_{SL} and DOC_{SR}, respectively. The most probable values of the tuneable parameter set are determined by minimizing an objective function using the Nelder-Mead method (Lagarias et al., 1998), which considers the squared deviations between model-predicted and observed DOC pairs from the global dataset, with additional priors related to the acceptable ranges of each parameter, e.g., $0 \leq f \leq 0.5$; $0 \leq E_a \leq 150$ kJ mol^{-1}, etc. An additional constraint, that the global inventory of $\text{DOC}_{SR} > \text{DOC}_{SL}$ (Hansell, 2013), was needed to accurately simulate the known distributions of each DOC pool.

The linear Equations (4, 5) are solved by direct matrix inversion with the resulting 3D distributions of $\text{DOC}_{SL} + \text{DOC}_{SR}$ added to the concentration of recalcitrant DOC (DOC_R), which was not simulated, and varied with ocean basin. Concentrations of DOC_R were estimated from the mean concentrations observed below 1500 m as 43.3 μmol kg^{-1} (North Atlantic; 65°N-0°), 40.5 μmol kg^{-1} (South Atlantic; 40°S-0°), 38.6 μmol kg^{-1} (Pacific), 41.4 μmol kg^{-1} (Indian), 41.7 μmol kg^{-1} (Arctic; > 65°N), and 40.9 μmol kg^{-1} (Southern; > 40°S).

We tested the sensitivity of the inferred DOC decay temperature parameters to alternate assumptions with respect to marine DOC production and consumption processes (**Table 2**, **Figures 2**, **3**). Model I considers both DOC_{SL} and DOC_{SR} are produced biologically in the euphotic zone as separate fractions with a modified Redfield r_{CP} 117:1, and is represented by Equations (4, 5). Model II is based on the size-reactivity continuum concept of DOC cycling with only DOC_{SL} being produced biologically in the euphotic zone (with $r_{CP} = 117:1$) and DOC_{SR} being produced as a fraction of DOC_{SL} decay by heterotrophic consumption. The Model II tracer conservation equation for DOC_{SR} is:

$$\frac{\partial \text{DOC}_{SR}}{\partial t} + \mathbf{T}.\text{DOC}_{SR} = f_2.(A_1 e^{-E_{a1}/RT}.\text{DOC}_{SL})$$
$$- A_2 e^{-E_{a2}/RT}.\text{DOC}_{SR} \quad (6)$$

With f_2 being the fraction of DOC_{SL} decay that produces DOC_{SR}. The Model II tracer conservation equation for DOC_{SL} is equal to Equation (4). Sensitivity of the model results to variability in the r_{CP} of DOM production was also tested, using the spatially varying r_{CP} of upper ocean organic matter export inferred for twelve ocean biomes in Teng et al. (2014). The twelve ocean biomes are nominally separated by the 0.3 μM [PO_4] iso-concentration at the surface from World Ocean Atlas 2009. The

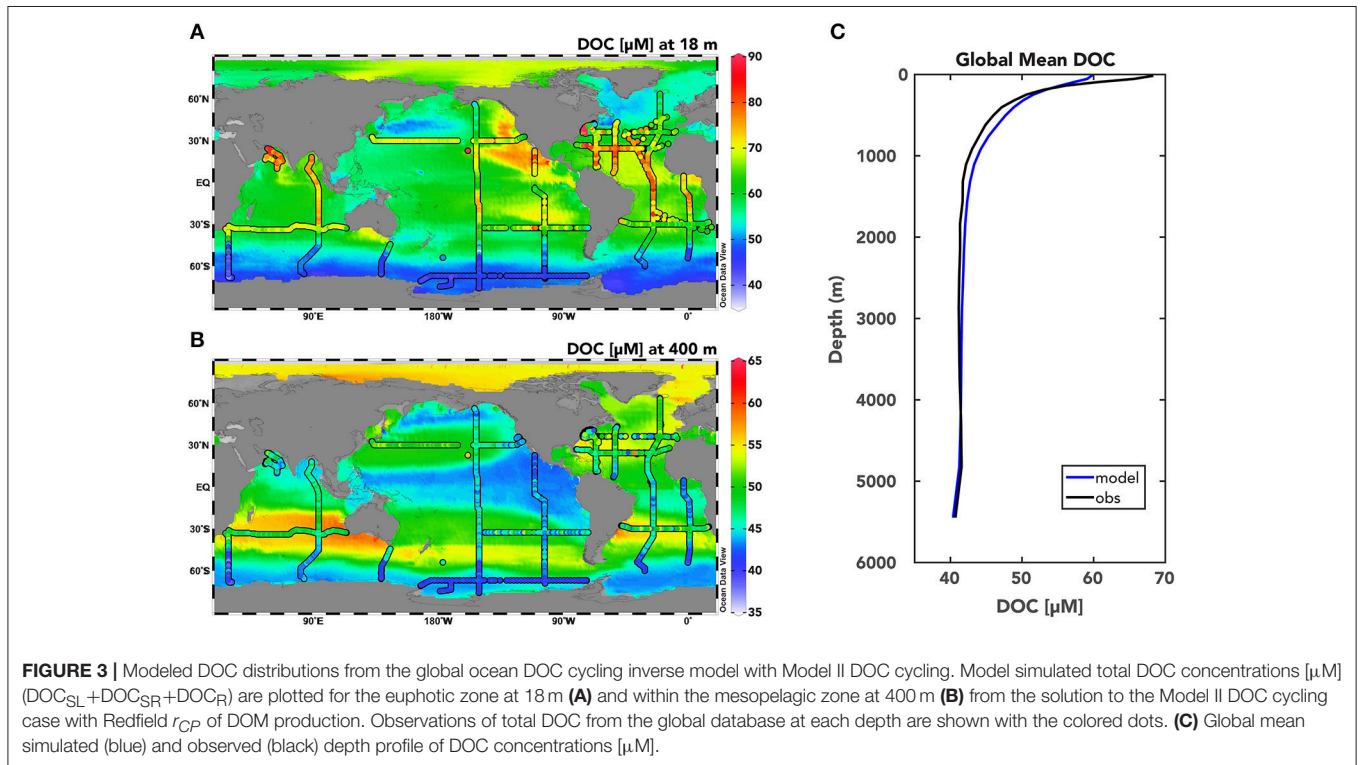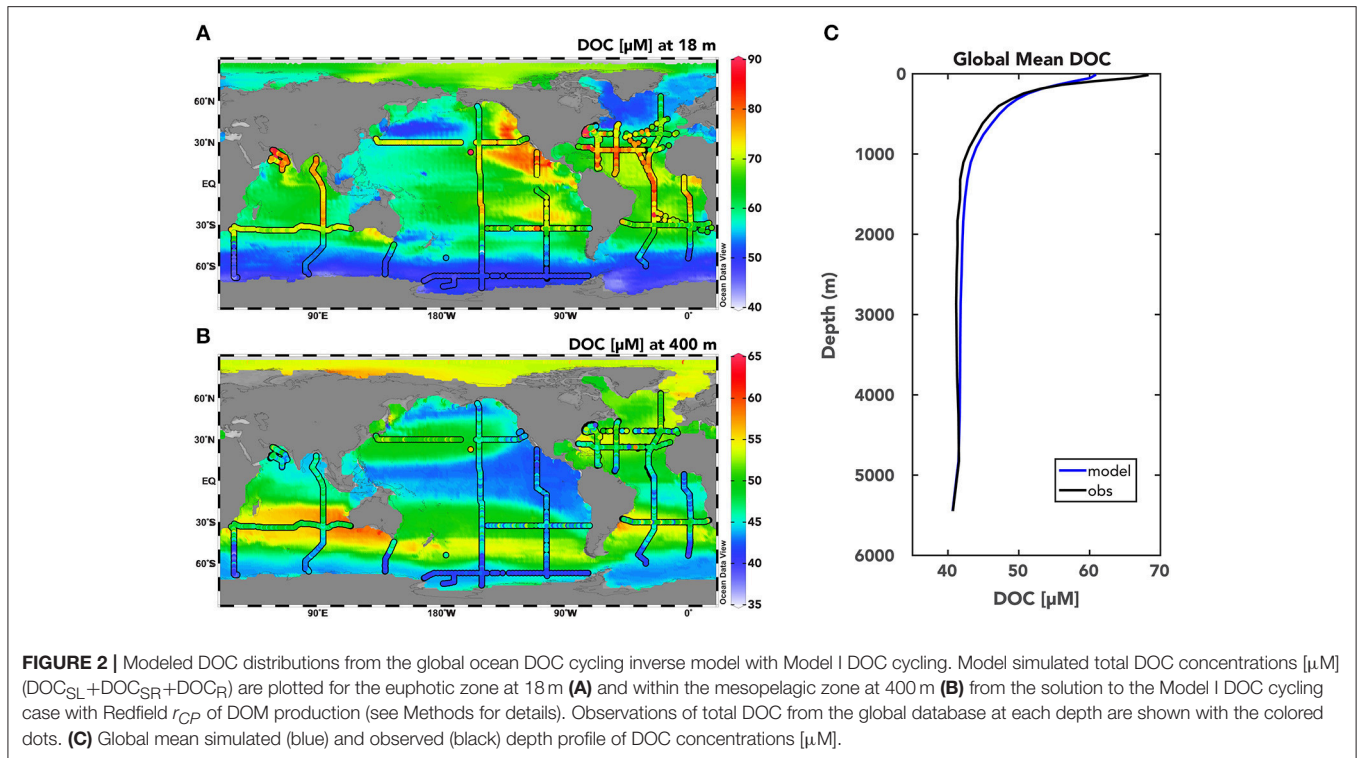**TABLE 2 |** Model-obtained values for the temperature sensitivity of DOC degradation.

	DOC pool	Q_{10}	E_a (kJ mol^{-1})	Ref. temp (°C)	k_C (10^{-3} day^{-1})	Present reservoir (Pg)	Reservoir + 1°C (Pg)	Diff. (%)
REDFIELD C:P								
Model I*	DOC_{SL}	2.2	53.1 ± 1.3	15	10.7 ± 0.5	19.0	17.4	8
	DOC_{SR}	4.4	101.3 ± 31.5	15	0.06 ± 3e-6	38.0	31.1	18
Model II**	DOC_{SL}	2.3	55.8 ± 2.3	15	3.2 ± 0.07	18.7	17.1	9
	DOC_{SR}	4.4	100.3 ± 25.2	15	0.05 ± 1e-6	37.5	30.9	18
VARIABLE C:P								
Model I*	DOC_{SL}	2.3	55.0 ± 2.0	15	3.9 ± 0.1	14.1	12.9	9
	DOC_{SR}	4.5	101.6 ± 33.6	15	0.03 ± 5e-7	28.3	23.3	17
Model II**	DOC_{SL}	2.3	57.3 ± 3.2	15	0.6 ± 0.004	8.7	8.0	8
	DOC_{SR}	3.4	82.8 ± 15.6	15	0.07 ± 8e-6	34.8	29.6	15

The temperature coefficient, Q_{10}, apparent activation energy, E_a, reference temperature used for calculation, and the average DOC decay constants, standardized to a reference temperature, k_C are shown for all tested cases of DOC cycling pathways and production stoichiometry. Present DOC reservoir estimates are shown together with the difference in pool size from an equilibrium 1°C increase in temperature. Average values with ± standard errors are shown.

*Model I: In this case both DOC_{SL} and DOC_{SR} are produced as constant fractions of the new production field. Thus, all DOC_{SR} is produced in the euphotic zone and exported to the deep ocean with the overturning circulation.

**Model II: In this case, the model assumes that DOC_{SR} is produced as some fraction of DOC_{SL} degradation. Thus, DOC_{SR} is produced throughout all depths of the ocean as DOC_{SL} is microbially degraded.

FIGURE 2 | Modeled DOC distributions from the global ocean DOC cycling inverse model with Model I DOC cycling. Model simulated total DOC concentrations [μM] (DOC_{SL} + DOC_{SR} + DOC_R) are plotted for the euphotic zone at 18 m **(A)** and within the mesopelagic zone at 400 m **(B)** from the solution to the Model I DOC cycling case with Redfield r_{CP} of DOM production (see Methods for details). Observations of total DOC from the global database at each depth are shown with the colored dots. **(C)** Global mean simulated (blue) and observed (black) depth profile of DOC concentrations [μM].

FIGURE 3 | Modeled DOC distributions from the global ocean DOC cycling inverse model with Model II DOC cycling. Model simulated total DOC concentrations [μM] (DOC_{SL} + DOC_{SR} + DOC_R) are plotted for the euphotic zone at 18 m **(A)** and within the mesopelagic zone at 400 m **(B)** from the solution to the Model II DOC cycling case with Redfield r_{CP} of DOM production. Observations of total DOC from the global database at each depth are shown with the colored dots. **(C)** Global mean simulated (blue) and observed (black) depth profile of DOC concentrations [μM].

spatially varying r_{CP} values are reported in Table S2. All cases fit the data equally well as, and neither significantly altering the conclusions drawn from, the standard case (Model I, Redfield r_{CP}) presented above, i.e., $A_2 >> A_1$; $E_{a2} > E_{a1}$. The reported model parameter standard error bars were assigned by expansion of the log posterior probability function in a Taylor series about

the most probable values and truncating at second order, i.e., Laplace's approximation.

For all approaches used it should be remembered that we are assuming that geochemical DOC scavenging processes, such as interaction with suspended particles (Druffel et al., 1992), are negligible. As these processes are purely physical/chemical they should have low temperature sensitivity (Q_{10} around 1; Oelkers, 1991) and the importance of these processes will therefore not be as severely impacted by changing ocean temperature as the biological processes. Furthermore, the major pool of DOC_R, which amounts to 630 ± 32 Pg C and has a half-life of thousands of years (Hansell, 2013), has been excluded from our analysis because the nature of its removal, biotic or geochemical, is still unclear.

RESULTS

Apparent E_a values, temperature coefficients (Q_{10}), and average decay constants (k_C) of DOC degradation estimated from microbial incubation experiments conducted with phytoplankton-derived DOC, marine humic substances, and natural DOC from a coastal embayment are summarized in **Table 1**. Applying the Arrhenius law, we estimated apparent E_a, values varying from (average ± standard error) 35 ± 10 kJ mol^{-1} for the DOC_L to 67 ± 11 kJ mol^{-1} for the DOC_{SL} pool, while the Q_{10} increased from 1.7 to 2.7 (**Table 1**). The corresponding average DOC decay constants ranged from 110 ± 0.1 × 10^{-3} day^{-1} (half-life, ln2/k_C, 6.3 ± 0.6 days) for the DOC_L to 5 ± 1×10^{-3} day^{-1} (half-life, 152 ± 18 days) for the DOC_{SL} (**Table 1**).

The Arrhenius plot of the DOC_{SR} decay constants, obtained from the DOC concentrations and CFC apparent water ages collected during the CLIVAR A16N cruise, clearly show two distinct data clusters for the bathy- and mesopelagic North Atlantic Ocean (**Figure 1**) with significantly different (t-test, $p < 0.05$) apparent E_a (average ± standard error) of 87 ± 9 and 146 ± 21 kJ mol^{-1}, which translate into Q_{10} values of 3.8 ± 0.5 and 8 ± 3, respectively (**Table 1**). The most likely reason for this difference is that the bathypelagic North Atlantic is filled with fresher DOC during the massive water mass formation that occurs in the Arctic seas, which constitutes the engine of the meridional overturning circulation. Uncertainties in this analysis of the temperature response of DOC_{SR} primarily stem from the fact that the surface ocean waters ultimately ventilating the meso- and bathypelagic zones do not have identical initial DOC content; while both waters contain DOC_{SR} and DOC_R, they are at different concentrations and likely partially different chemical compositions. Note that for the bathypelagic ocean, b_1 (degraded pool) and b_2 (resistant pool) in Equation (1) remained constant at 5.6 ± 0.4 and 40.6 ± 0.7 µmol kg^{-1} for all temperatures, but for the mesopelagic ocean b_1 decreased and b_2 increased with increasing temperature (Table S1). These changes are most likely explained by an increasing proportion of recalcitrant DOC in subtropical compared with subpolar mode waters, although the influence of decreasing age range with increasing temperature cannot be disregarded (Table S1). In any case, to avoid this effect, we restricted our analysis of the temperature response of the mesopelagic layer to the 8 to 11°C isotherms, where b_1 and b_2 remained constant at 11 ± 2 and 42 ± 2 µmol kg^{-1} for all temperatures. When extrapolating this analysis, it should be remembered that our dataset is restricted to one CLIVAR section (A16N). Other cruises have not been included as they contained too few data points (2–3) and it was therefore not possible to obtain k_C over a wide temperature range, which is a prerequisite for calculating reliable E_a and Q_{10} values.

The E_a values of DOC_{SR} obtained for the North Atlantic could be affected by water mass mixing because the latitudinal gradients of DOC and CFC apparent age were followed along isothermal rather than isopycnal surfaces. Note that although isopycnal surfaces are preferred to minimize the impact of mixing, it is compulsory to use isothermals when studying temperature sensitivities. Therefore, we used a global ocean DOC cycling model that accounts for ocean mixing of DOC to both constrain the validity of our approach (i.e., following gradients along isothermals) and provide estimates of the global impact. The most probable values for the apparent E_a conditioned on the global database of DOC observations were found to be 53.1 ± 1.3 kJ mol^{-1} (average ± standard error) for DOC_{SL} and 101.3 ± 31.5 kJ mol^{-1} for DOC_{SR} (**Table 2**). Corresponding Q_{10} values using a reference temperature of 15°C yield a value of 2.2 ± 0.1 for the DOC_{SL} pool and 4.4 ± 2.1 for DOC_{SR}. These estimates are all within the ranges obtained from the incubation studies and the latitudinal gradients of DOC in the north Atlantic (**Tables 1**, **2**). This good agreement between the model and experimental data, shows that the water mass mixing on the latitudinal DOC gradients did not significantly affect the estimate of DOC_{SR} decay constants, and secondly that our results are generally valid.

The most probable basin-specific apparent E_a values were also tested for the Atlantic and Pacific basin, yielding Atlantic values of 55.2 ± 2.1 kJ mol^{-1} (Q_{10} = 2.3 ± 0.1) and 86.2 ± 13.4 kJ mol^{-1} (Q_{10} = 3.1 ± 0.7) and Pacific values of 54.6 ± 1.8 kJ mol^{-1} (Q_{10} = 2.2 ± 0.1) and 92.7 ± 52.0 kJ mol^{-1} (Q_{10} = 3.9 ± 3.3) for the DOC_{SL} and DOC_{SR} pools, respectively (data not shown). Thus, apparent E_a (Q_{10}) values for the DOC_{SL} pool are statistically the same between the Atlantic and Pacific basins. More data are required to reduce the uncertainties in the inferred basin specific E_a for the DOC_{SR} pool in order to address the possibility of differing temperature sensitivities between ocean basins.

Using our estimates, we calculated the sensitivity of the size of the global ocean DOC reservoir per 1°C of equilibrium ocean warming, by comparing the modern ocean reservoir, computed with the most probable parameter values to the DOC cycling model, with that assessed by uniformly increasing the ocean temperature by 1°C. The modern ocean is found to hold 57.0 Pg C of DOC_{SL} + DOC_{SR} and 630.0 Pg C of DOC_R decreasing to 48.5 Pg C of DOC_{SL} + DOC_{SR} for a 1°C warming (**Table 2**; Model I, Redfield r_{CP} case). Therefore, in terms of size changes of the DOC reservoir for a 1°C warming scenario, our DOC cycling model predicts a decrease by 7 ± 1 Pg C (mean and SD of the four modeled DOC cycling sensitivity tests), i.e., ~15% of the DOC_{SL} + DOC_{SR} reservoirs (**Table 2**). In these calculations, we assume for simplicity a uniform warming throughout the

ocean, which approximates the sensitivity of the ocean DOC reservoir to an equilibrium warming of the global ocean by $1°C$. We ignore regional differences in warming and that most heat is absorbed by the surface and then slowly redistributed throughout the ocean interior that defines the transient response of the ocean to Earth surface warming (Drijfhout et al., 2014). The impact of changing ocean temperatures on DOC degradation will therefore vary, and would for the deep ocean be delayed relative to both the initial warming and the subsequent uptake of CO_2 and heat. Given the current observed rate of deep ocean ($>1,000$ m) warming of $\sim 0.01°C$ per decade (Purkey and Johnson, 2010), the deep ocean would warm by $1°C$ from present in ~ 1 millennium, i.e., the 7 ± 1 Pg C reduction in the global ocean DOC reservoir would occur on a similar timescale as deep ocean ventilation. The temperature coefficients, Q_{10}, at a reference temperature of $15°C$ (see Equation 3 in methods) are 1.7–1.8 for DOC_L, 2–3 for DOC_{SL}, and 4–8 for DOC_{SR}, indicating that DOC compounds with higher activation energies have higher temperature dependence.

DISCUSSION

Considering that most of the 662 ± 32 Pg C of DOC in the oceans has half-life times of decades to thousands of years (Hansell, 2013), knowledge on the impact of rising ocean temperatures on the decay constants of the less bioavailable DOC pools is relevant for predicting how climate change will affect the global carbon cycle.

Our combined modeling and experimental approaches indicate that DOC_{SR} has an apparent E_a of ~ 83–146 kJ mol^{-1}, which is comparable to values found for soil (67–120 kJ mol^{-1}; Leifeld and Von Lützow, 2013) and mesopelagic ocean dissolved oxygen consumption (86.5 mol^{-1}; Brewer and Peltzer, 2016). Comparatively, DOC_L and DOC_{SL} have lower apparent E_a of ~ 35–40 and ~ 50–70 kJ mol^{-1}, respectively, which are comparable to values estimated for the degradation of glucose (30 kJ mol^{-1}), tannin (70 kJ mol^{-1}), labile soil organic matter (~ 44 kJ mol^{-1}), and values recently predicted for marine respiration (~ 56 kJ mol^{-1}) and mesopelagic prokaryote production (~ 72 kJ mol^{-1}) (Knorr et al., 2005; Davidson and Janssens, 2006; Yvon-Durocher et al., 2012; Lønborg et al., 2016). Overall this suggests that the DOC_{SR} pool has higher activation energies and temperature dependence than the DOC_L and DOC_{SL} pools. A recent study demonstrated that in soils the Q_{10} values scales inversely with temperature, with low temperature environments having a higher Q_{10} than warmer ones (Koven et al., 2017). In a similar way we find that DOC_{SR}, mostly present in the deep ocean with lower temperatures, has a higher Q_{10} of ~ 3–4, while DOC_{SL}, with higher concentrations in warmer mesopelagic waters, has a lower Q_{10} of ~ 1.8–2. DOC decay in the future ocean will also vary depending on how factors other than temperature will be impacted by global change. These factors, amongst others, include changes in ocean circulation and the supply of inorganic nutrients, UV light exposure, dissolved oxygen levels, bacterial community composition, DOC chemical structure, and/or an extreme dilution of individual organic substrates (Lønborg et al.,

2009; Kattner et al., 2011; Mopper et al., 2015; Repeta, 2015). Ocean models have predicted that warming may strengthen vertical stratification, thereby suppressing upward mixing of nutrients from the deep ocean and causing longer exposure to UV-light, with possible consequences for the DOC decay. Currently we do not have sufficient data to determine how this would impact our findings of the temperature sensitivity of DOC cycling. Over the last few years it has been demonstrated that global increases in ocean temperatures will reduce the overall O_2 content (i.e., "ocean deoxygenation"; Keeling et al., 2010) both directly (e.g., decreased solubility) and indirectly (e.g., increased respiration and decreased ocean ventilation). Studies in marine sediments have found that the degradation of organic matter under hypoxic and anoxic conditions is slower and less efficient than under oxic conditions (Zehnder and Stumm, 1988; Fenchel and Finlay, 1995), but due to the lack of data on DOC cycling under different O_2 levels we are not able to conclude how this might influence the relationships found in this study. The deep ocean bacterial community composition has been shown to vary over spatial and temporal scales, which could potentially affect DOC decay rates in the deep Ocean (Delong et al., 2006). However, a major influence seems unlikely as previous studies have suggested that DOC decay is generally independent of the bacterial community composition (Sjöstedt et al., 2013). The chemical composition of DOC in the deep ocean varies spatially (e.g., Martínez-Pérez et al., 2017 and our higher diagnosed activation energy for the DOC_{SR} than the DOC_{SL} pool point to a compositional control on the temperature sensitivity, i.e., the molecule types that make up the DOC_{SR} pool require more energy to be consumed than DOC_{SL} molecules. A similar conclusion was reached by Brewer and Peltzer (2017), who showed that the activation energy of ocean oxygen consumption varies widely (60.8 to 1662.9 kJ mol^{-1}) which they suggested was partly explained by some compounds being harder to oxidize than others.

Recent studies have also suggested that the dilute nature of individual compounds that constitute the DOC pool control its persistence in the oceans (Kattner et al., 2011; Arrieta et al., 2015). At very low concentrations, molecular diffusion could limit the utilization of DOC. Since molecular diffusion of organic matter is temperature sensitive, this could influence our findings. However, the E_a for molecular diffusion (~ 15 kJ mol^{-1}; Oelkers, 1991) is low compared with the E_a obtained in this study. The approaches combined here are also biased by different limitations; as an example, the incubation studies do not include the effects of some environmental factors (e.g., sunlight, pressure) and they could also be impacted by so called "bottle effects," which could lead to different conditions compared with those found in the natural environment. On the other hand, both the DOC latitudinal gradients and modeling approach do not explicitly measure the microbial degradation but infer it indirectly from subsurface spatial gradients in DOC and temperature. However, it can be assumed that these approaches assess the temperature effects on microbial consumption of DOC, as long as abiotic particle-DOC scavenging or solubilization processes are minimal (Druffel et al., 1992, 2016).

Ocean warming varies spatially and over time, partly linked with the steady heat accumulation in the deep ocean, resulting in $\sim$30% of the ocean warming occurring below 1,000 m (Whitney et al., 2007; Meehl et al., 2011; Balmaseda et al., 2013). As the ocean will most likely experience temperature increases of a few (1–4°C) degrees Celsius over the next decades (Meehl et al., 2011), we have estimated that the decay rates of the DOC_L, DOC_{SL}, and DOC_{SR} pools will increase by 4–6, 7–12, 15–18% for 1°C of warming. Note that for an increase of 2°C, which is possible for the surface ocean layer by the end of this century, the degradation rate of the DOC_{SR} pool will increase by 32–40% compared with the current situation. According to the microbial carbon pump (MCP) hypothesis, stimulation of microbial respiration will lead to an increase in the production of DOC_R relative to the production of the other DOC pools, with the magnitude and impact of this stimulation depend on the sensitivity of DOC_R degradation to changing temperature (Jiao et al., 2010; Legendre et al., 2015). In terms of size changes of the DOC reservoir for a 1°C warming scenario, our DOC cycling model predicts a decrease by 7 ± 1 Pg C ($\sim$15%) of the DOC_{SL} + DOC_{SR} reservoirs. Assuming a warming rate equal to the current sea surface increase of $0.01°C$ year^{-1} (Rhein et al., 2013), the annual loss of DOC_{SL} + DOC_{SR} would be 0.07 Pg C year^{-1}, which represents about 3.5% of the annual net ocean uptake of CO_2 (Sarmiento and Gruber, 2006). Therefore, the overall loss of bioavailable DOC would significantly, but not massively, counteract the ocean CO_2 sink.

CONCLUSION

Our study found that, (1) the assumption of a constant Q_{10} of $\sim$2 is not universally applicable for the microbial degradation of DOC in the open ocean, (2) the empirically estimated Q_{10} values indicate that increasing ocean temperature will enhance the microbial degradation of the more biologically resistant DOC with a high apparent E_a compared to the more labile DOC fractions with a low apparent E_a, and (3) increasing the

equilibrium ocean temperature by just 1°C will result in a net loss of $\sim$7 Pg C of bioavailable DOC. In this analysis we have not tested the temperature sensitivity for the DOC_R pool, since knowledge on the controls for removal of this pool is lacking, however abiotic processes are thought to contribute significantly (Hansell and Carlson, 2013). Further studies are therefore needed to determine the dominant loss processes for DOC_R before the possible temperature sensitivity can be assessed on this largest contributor to the global ocean carbon reservoir.

AUTHOR CONTRIBUTIONS

CL and XÁ-S conceived the study. CL, XÁ-S, and DH authors contributed equally to the data survey, analysis, and interpretation. RL performed the model simulation, developed new tracer transport diagnostics, and interpreted the model outputs. All authors wrote the paper.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2017.00436/full#supplementary-material

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