

Net removal of major marine dissolved organic carbon fractions in the subsurface ocean

Dennis A. Hansell,¹ Craig A. Carlson,² and Reiner Schlitzer³

Received 14 March 2011; revised 9 November 2011; accepted 29 November 2011; published 4 February 2012.

[1] Marine dissolved organic matter is a massive reservoir of carbon holding >200x the ocean biomass inventory. Primarily produced at the ocean surface and then exported to depth with overturn of the water column, this carbon can be sequestered in the ocean interior for centuries. Understanding the loss of dissolved organic carbon (DOC) upon export has been data limited, but recent global ocean surveys are overcoming that problem. Here we characterize three fractions of exported carbon by apparent continuity in removal rates: semi-labile and semi-refractory, summing to 20 PgC, and the balance as refractory DOC. Distinct lifetimes coupled with ocean circulation control where the fractions are exported to depth, and thus the carbon sequestration time scales. Maximum remineralization rates of exported DOC occur in the convergent subtropical gyres, where a range of ~ 500 to <1500 mmol C m⁻² yr⁻¹ can exceed remineralization of sinking biogenic particles. Regions of high particle export production and highly stratified systems exhibit minimal exported DOC remineralization.

Citation: Hansell, D. A., C. A. Carlson, and R. Schlitzer (2012), Net removal of major marine dissolved organic carbon fractions in the subsurface ocean, *Global Biogeochem. Cycles*, 26, GB1016, doi:10.1029/2011GB004069.

1. Introduction

[2] At a global inventory of 662 ± 32 Pg C, dissolved organic carbon (DOC) exists in the open ocean at low concentrations (~ 34 to >70 $\mu\text{mol C kg}^{-1}$) [Hansell *et al.*, 2009]. Its production largely occurs in the euphotic zone as a product of photosynthesis (at ~ 30 – 50% of net primary production) and subsequent food web interactions [Carlson, 2002]. A small fraction of that produced escapes rapid remineralization, accumulating in the surface layer for eventual export to the ocean interior by vertical mixing at ~ 1.9 Pg C yr⁻¹ [Hansell *et al.*, 2009]. This export is distributed over a large ocean surface, resulting in small concentration gradients at depth that had proven difficult to assess given historically poor analytical skill. Refinements to the high temperature combustion method for DOC analysis began to resolve the relatively small vertical gradients in the pool [Sharp *et al.*, 2002], while institution of a reference material program for DOC analysis has furthered the analytical skill [Hansell, 2005].

[3] The distributions and radiocarbon ages of DOC [Bauer *et al.*, 1992] led to its conceptual partitioning into broad pools of reactivity. Originally, a multicompartamental model divided the bulk DOC into qualitatively described labile,

semi-labile and refractory fractions [Kirchman *et al.*, 1993; Carlson and Ducklow, 1995]. Refractory DOC was directly observed below 1000 m where DOC vertical profiles showed little gradient and mean ¹⁴C-DOC ages were 4000–6000 years. Upper ocean DOC concentrations in excess of deep DOC were assumed to be the sum of two fractions: semi-labile DOC (assumed turnover of months to years) and labile DOC, which meets short-term microbial carbon demand (turnover of minutes to days). The absence of rigorous quantitative descriptions of the fractions precluded confirmation of their existence, and the lack of DOC concentration/water mass age tracer data pairs precluded reliable decay rate determinations of the exported DOC.

[4] Here we seek to improve previous characterizations of the DOC fractions by examining bulk DOC concentration data collected in the major ocean basins. In 2003, the U.S. Climate Variability and Predictability (CLIVAR) Repeat Hydrography program sought to provide the first high-resolution global view of DOC distribution and variability in the context of a global ocean hydrographic survey. Using these observational data in combination with water mass age tracers and a coupled ocean circulation, biogeochemical model we discern 3 major photosynthetic DOC fractions susceptible to export, each with unique timescales of decay: semi-labile, semi-refractory, refractory. Here we focus on the 2 DOC fractions that are intermediate in reactivity (i.e., the semi-labile and semi-refractory fractions), together constituting 20 ± 3 PgC in the global ocean and representing the most quantitatively important DOC fractions contributing to the biological pump. These analyses provide quantitative constraints on the magnitudes and locations of DOC sinks in the mesopelagic (~ 150 – 1000 m) and bathy/abyssopelagic

¹Division of Marine and Atmospheric Chemistry, Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida, USA.

²Department of Ecology, Evolution and Marine Biology, University of California, Santa Barbara, California, USA.

³Alfred Wegener Institute, Bremerhaven, Germany.

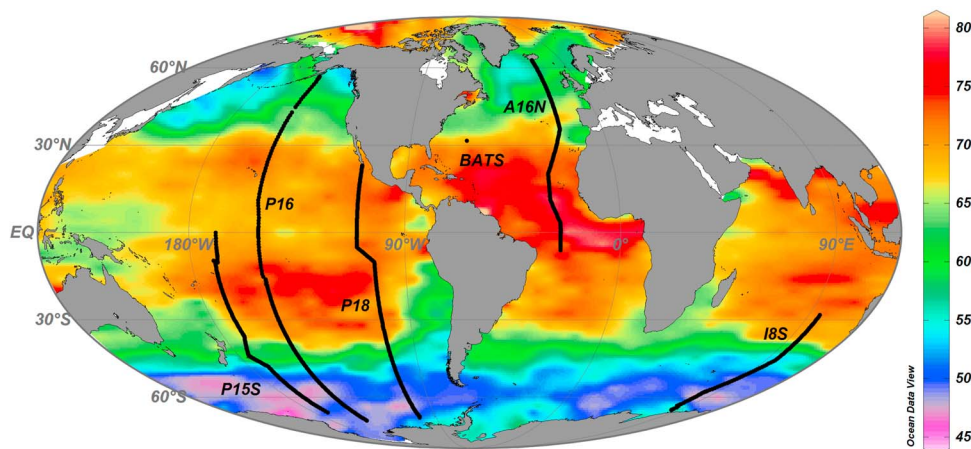


Figure 1. Locations of the BATS site and hydrographic sections A16N (North Atlantic), P16 (central Pacific), P18 (eastern Pacific), I8S (Indian Ocean) and P15S (western South Pacific) over a modeled field of DOC ($\mu\text{mol C kg}^{-1}$) at 30 m throughout the global ocean [from *Hansell et al.*, 2009]. A16N was occupied in June and July, 2003; P16 in January and February, 2005 (southern hemisphere) and February and March, 2006 (northern hemisphere); P18 in December 2007 and January 2008; I8S in February 2007; P15S in January and February 1996.

(>1000 m) zones of the deep ocean. We place less focus on the deep ocean dynamics of the refractory pool because it remains under-constrained by observations.

2. Methods

2.1. Observational Data

[5] Data employed include: U.S. CLIVAR hydrographic sections A16N (North Atlantic), P16 (central Pacific), P18 (eastern Pacific) and I8S (Indian Ocean); World Ocean Circulation Experiment transect P15S (western South Pacific). The locations of these lines are plotted over a modeled DOC field across the upper global ocean (Figure 1). All observational data employed in this analysis, along with meta-data providing cruise details and analytical methods (including DOC, CFC, $^{14}\text{C-CO}_2$, and hydrographic variables), were taken from the Web site of the Carbon Dioxide Information Analysis Center (<http://cdiac.ornl.gov/oceans/>).

2.2. DOC Modeling

[6] The DOC model is based on a coupled physical/biogeochemical model [*Schlitzer, 2007; Hansell et al., 2009*] in which flow velocities as well as water mass formation and ventilation rates are determined by an automatic optimization procedure. The procedure requires that flows remain close to geostrophic estimates and that simulated distributions of a large suite of tracers (temperature, salinity, oxygen, nutrients, carbon, $^{14}\text{C-CO}_2$, and chlorofluorocarbons CFC-11 and CFC-12) be in good agreement with observations. The resulting modeled and observed global $^{14}\text{C-CO}_2$, CFC-11 and CFC-12 distributions are well simulated [*Schlitzer, 2007*]. CFCs, like DOC, enter the deep ocean from the surface layer, and the ability to correctly reproduce interior CFC distributions makes this model particularly well suited for DOC simulations. In addition, because of the excellent fit to $^{14}\text{C-CO}_2$, the model has realistic global ocean

overturning rates, thus allowing estimates of deep ocean DOC degradation rates.

[7] Based on the observations described below, DOC in the model is decomposed into 3 fractions (semi-labile, semi-refractory, and refractory DOC) with lifetimes of 1.5, 20, and 16 k years, respectively. The lifetimes of the semi-labile and semi-refractory pools were determined on the basis of empirical correlations of DOC with water mass age from chlorofluorocarbon data, with agreement between simulated and observed water column DOC values [*Hansell et al., 2009*] identifying the most appropriate lifetimes.

[8] Model DOC is produced in the euphotic zone at rates proportional to the square root of primary production as estimated from satellite data [*Antoine et al., 1996*]. After production, the DOC is transported laterally and vertically by the model's three-dimensional flow field and removed at rates inversely proportional to the respective lifetime. Absolute DOC production rates in the euphotic zone (q_{DOC}) were adjusted to achieve an optimal fit with observed surface DOC. Different empirical parameterizations of DOC production with satellite-derived primary production (PP) rates were tried, but it was found that a square-root dependence

$$q_{\text{DOC}} = \propto (\text{PP})^{1/2} \quad (1)$$

had better agreement with observed surface ocean DOC as compared to, for instance, a linear PP dependency, which produced unrealistically large DOC gradients between equatorial and coastal productive regions and the centers of the oligotrophic subtropical gyres.

[9] Equation (1) was applied for the production of the three DOC fractions in the model; individual α factors were manually adjusted until agreement between modeled and observed DOC concentrations was deemed satisfactory. World-ocean integrated, euphotic zone production rates of the three DOC fractions in the model amount to 3.4, 0.34 and 0.043 Pg C yr^{-1} , respectively. Once the production parameters are fixed in the model, redistribution of DOC in

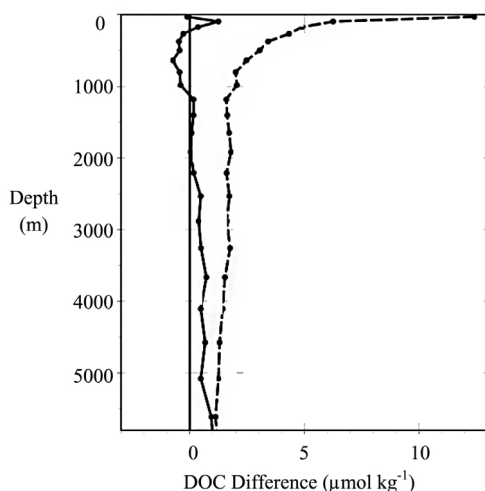


Figure 2. Total DOC in the model (obtained as the sum of the three DOC pools) compared with observations (given as DOC difference; $\mu\text{mol C kg}^{-1}$), with layer averaged mean differences (solid line) and root-mean square differences (dashed line) shown.

the surface ocean as well as its downward flux and subsurface removal rates depend on the 3D model flow field and the assumed lifetimes of the DOC fractions.

[10] The separation of DOC in the present ocean model into distinct pools with widely different lifetimes and removal rates is similar to the treatment of soil organic carbon in a number of model studies [Parton *et al.*, 1987; Jenkinson, 1990; Smith *et al.*, 1997]. Like this ocean model, many of the soil models include three fractions and allow for exponential removal using lifetimes ranging from a few years to decades and millennia. An ocean model considering DOC dynamics by Yamanaka and Tajika [1997] applied spatially varying lifetimes to just two DOC pools (semi-labile and refractory). Bendtsen *et al.* [2002] employed a mechanistic model where production and decay of DOC are dependent on specific processes, such as a microbial loop with assumed temperature dependencies of bacterial activity and abundance. Their approach illuminates processes responsible for producing or consuming DOC, but the predicted DOC distributions of both Bendtsen *et al.* [2002] and Yamanaka and Tajika [1997] differ markedly from observations. The approach taken here is to estimate DOC removal (and production) rates that are consistent with DOC distributions. The actual production and removal processes are not considered.

[11] Modeled semi-labile DOC (fractions are characterized below) is mostly confined to the upper 500 m of the water column, with average concentrations ranging between $\sim 12 \mu\text{mol kg}^{-1}$ near the surface and $1 \mu\text{mol kg}^{-1}$ at 500 m depth. Semi-refractory DOC reaches deeper into the water column, with average concentrations of $\sim 10 \mu\text{mol kg}^{-1}$ near the surface and $1 \mu\text{mol kg}^{-1}$ at 1000 m depth. Refractory DOC ranges from $\sim 45 \mu\text{mol kg}^{-1}$ in the North Atlantic to $\sim 37 \mu\text{mol kg}^{-1}$ in the North Pacific.

[12] Total DOC concentrations in the model (obtained as the sum of the three DOC fractions) have been compared with available observations, with layer averaged mean differences as well as root-mean square differences shown in

Figure 2. The model reproduces the marine DOC concentrations within mean differences of $<0.5 \mu\text{mol kg}^{-1}$ for most depths. The model correctly reproduces the large-scale features in the DOC distributions as indicated by the small root-mean square (rms) differences between ~ 1 and $3 \mu\text{mol kg}^{-1}$ for depths >500 m. Near the surface the RMS difference is larger ($\sim 10 \mu\text{mol kg}^{-1}$) and mainly caused by model/data differences in regions of sharp DOC fronts.

[13] DOC removal rates in the model are calculated for each fraction separately and then added together for removal of the entire exported DOC pool. The model assumes exponential DOC degradation for the semi-labile and semi-refractory DOC pools. Concentrations decrease to $1/e$ of their initial values during the lifetime of the pools; degradation rates are proportional to the DOC concentration and inversely proportional to the lifetime of the respective DOC pool.

[14] In the upper water column the removal rate of semi-labile DOC dominates because of the short lifetime of this pool; in the recently ventilated deep ocean it is the removal of semi-refractory DOC that dominates the rates (since the semi-labile material has been mostly removed at greater depths). The removal rate of refractory DOC is small and quite uniform throughout the interior ocean. The magnitude of the refractory DOC removal rate in the model is dictated by the requirement to match the observed inter-basin DOC gradients, resulting in an average removal of $0.0027 \mu\text{mol C kg}^{-1} \text{ yr}^{-1}$. This value is consistent with a previous estimate of $0.003 \mu\text{mol C kg}^{-1} \text{ yr}^{-1}$ based on observations [Hansell *et al.*, 2009]. Since this work focuses on the dynamics of exported DOC and its removal within the ocean's interior, the model does not consider photo-oxidative removal of refractory DOC in the euphotic zone.

3. Results and Discussion

3.1. Exported DOC Fractions Characterized by Relative Rates of Removal

3.1.1. Observations of DOC Fractions

[15] Here we establish the existence of DOC fractions in the ocean as defined by reactivity. Reactivity is considered in the context of ventilation timescales of three ocean depth zones: shallow overturning circulation as observed in subtropical gyres, overturning ventilation of deep and intermediate waters, and overturning circulation into the abyssopelagic. Observed removal rates are net values since an unknown (but presumably small) amount of DOC is added to the water column with solubilization of sinking particles, chemoautotrophy, and efflux from the sediments and hydrothermal vents.

[16] A well studied system for DOC removal in the upper subsurface ocean following export by winter overturn of the water column is the western Sargasso Sea at the site of the Bermuda Atlantic Time-series Study (BATS) site [Hansell and Carlson, 2001]. DOC in the euphotic zone increases by 5 to $10 \mu\text{mol C kg}^{-1}$ during the spring-summer transition. Upon winter-time delivery of this accumulated DOC to the upper mesopelagic zone by convective overturn, the material is rapidly mineralized as it is exposed to subsurface nutrients and microbes with the required enzymatic capabilities [Carlson *et al.*, 2002, 2004]. Two consecutive years (1995 and 1996) with strong overturn and associated DOC export

Table 1. Mean DOC Concentrations and Removal Rates in Specific Water Masses

DOC Fraction	Water Mass	Ocean Basin	Sigma Theta or Depth Range	Mean DOC (Standard Deviation) ($\mu\text{mol kg}^{-1}$)	DOC Removal Rate (Standard Error) ($\mu\text{mol C kg}^{-1} \text{ yr}^{-1}$)	n	r	p
Semi-labile	Winter Mixed Layer ^a	North Atlantic	100–250 m	58.4 (3.3)	6.3 (1.4)	na ^b	na	na
Semi-labile	Levantine Intermediate Water ^c	Mediterranean Sea	na	45–67 ^d	2.2 (na)	na	na	na
Semi-labile	Adriatic Deep Water ^c	Adriatic Sea	na	51–57 ^d	6–14.4 ^e	na	na	na
Semi-refractory	Upper Thermocline ^f	North Atlantic	25–26.4 kg m ⁻³	55.4 (4.7)	0.9 (0.06)	167	-0.57	<0.0001
Semi-refractory	Subtropical Mode Water ^f	North Atlantic	26.4–26.6 kg m ⁻³	50.2 (3)	0.3 (0.03)	105	-0.52	<0.0001
Semi-refractory	Lower Thermocline ^f	North Atlantic	26.6–27.0 kg m ⁻³	48.2 (1.8)	0.3 (0.01)	311	-0.62	<0.0001
Semi-refractory	Labrador Seawater ^f	North Atlantic	27.80–27.975 kg m ⁻³	43.3 (2.1)	0.2 (0.01)	436	-0.83	<0.0001
Semi-refractory	Iceland-Scotland Overflow Water ^f	North Atlantic	27.975–28.05 kg m ⁻³	42.4 (1.6)	0.2 (0.01)	141	-0.76	<0.0001
Semi-refractory	Denmark Strait Overflow Water ^f	North Atlantic	28.05–28.14 kg m ⁻³	41.6 (1.3)	0.2 (0.01)	278	-0.73	<0.0001
Semi-refractory	Subantarctic Mode Water ^g	South Pacific	26.8–27.06 kg m ⁻³	43.1 (2.3)	0.3 (0.03)	148	-0.58	<0.0001
Semi-refractory	Antarctic Intermediate Water ^g	South Pacific	27.06–27.4 kg m ⁻³	41.1 (1.9)	0.2 (0.01)	118	-0.7	<0.0001
Semi-refractory	Subantarctic Mode Water ^g	SE Indian	26.7–26.9 kg m ⁻³	43.9 (1.5)	0.3 (0.02)	111	-0.63	<0.0001
Refractory	Lower Circumpolar Deep Water ^g	Pacific	>2000 m	37.7 (1.3)	0.0042 (0.0002)	271	-0.63	<0.0001

^aData from *Hansell and Carlson* [2001].

^bNot available.

^cData from *Santinelli et al.* [2010].

^dObserved concentration range.

^eObserved removal of DOC in Adriatic Deep Water over 5 months was $\sim 6 \mu\text{mol C kg}^{-1}$; it is uncertain if this rate of loss would continue for a full year (i.e., $\sim 14 \mu\text{mol C kg}^{-1} \text{ yr}^{-1}$); given the uncertainty as to the true amount of DOC removed in one year, a range is given.

^fData from *Carlson et al.* [2010].

^gData from this analysis. DOC removal rates from *Carlson et al.* [2010] and this analysis calculated as the slope of Model II reduced major axis regression using orthogonal regression function in JMP 8.0 statistical package assuming single end-member mixing.

are taken as representative for this analysis. During winter, depth-normalized DOC concentration reductions of 7.3 and 5.3 $\mu\text{mol C kg}^{-1}$ at 100–250 m occurred within 2 months of the two export events, respectively; a mean of $6.3 \pm 1.4 \mu\text{mol C kg}^{-1}$ of exported DOC was mineralized annually at this site (Table 1). These rates are similar to those previously reported from the surface 300 m of the North Pacific (σ_θ range of 24.4 to 26.1), ranging from 2 to 9 $\mu\text{mol C kg}^{-1} \text{ yr}^{-1}$ [*Abell et al.*, 2000]. We term this fraction of exported DOC, resistant to decay while at the surface but removed over the time frame of months upon export, as semi-labile. A plot of DOC against water mass age in the western South Pacific (Figure 3a; location given in Figure 1) demonstrates relatively rapid removal of this DOC fraction.

[17] Deeper water masses are ventilated with overturning circulation at higher latitudes, with DOC being exported deeper into the water column. The correlation between DOC concentrations and water ages at >100 m in the North Atlantic is shown in Figure 3b. In the first ~ 40 years of water mass aging, $\sim 10 \mu\text{mol C kg}^{-1}$ was removed. We term this fraction, removed over a few decades, *semi-refractory* DOC. In waters >40 years since ventilation, DOC is at the lowest concentrations observed on this section and is relatively invariant (at 40–45 $\mu\text{mol C kg}^{-1}$). DOC removal over more than a few decades is better observed in Lower Circumpolar Deep Water, which invades the Pacific as a net northward current in near-bottom waters, demonstrating a decrease in DOC concentration [*Hansell et al.*, 2009]. DOC concentrations plotted against radiocarbon ages of inorganic carbon along P16 (Figure 1) demonstrate two fractions of DOC (Figure 3c). The most quickly removed fraction is largely semi-refractory DOC; its rate cannot be resolved on

the radiocarbon time scale since these young waters are contaminated with bomb radiocarbon (note negative radiocarbon ages). However, DOC removal rates using the pCFC12 age tracer in these young waters indicate removal that is consistent with the semi-refractory removal rates observed in the North Atlantic (see rates for South Pacific intermediate and mode waters in Table 1). A second, longer-lived fraction of DOC is observable in the waters of the deep and bottom Pacific (>2000 m), with concentrations decreasing by $\sim 5 \mu\text{mol C kg}^{-1}$ over ~ 1500 years. This slowly removed fraction is here termed *refractory* DOC.

3.1.2. Removal Rates and DOC Fractions

[18] These examples illuminate three exported DOC fractions distinguished by removal rates. A broader survey of water masses establishes ranges in rates for the semi-labile and semi-refractory fractions (Table 1). Rates from the western Sargasso Sea and the Adriatic and Levantine Seas ranging from 2.2 to 14.4 $\mu\text{mol C kg}^{-1} \text{ yr}^{-1}$ are taken as representative of the semi-labile fraction. Removal of the semi-refractory DOC occurs over a narrow range (0.2–0.9 $\mu\text{mol C kg}^{-1} \text{ yr}^{-1}$), with a mean $0.3 \pm 0.2 \mu\text{mol C kg}^{-1} \text{ yr}^{-1}$. Data on the semi-refractory fraction were taken from an analysis of the major North Atlantic water masses [*Carlson et al.*, 2010], as well as analyses conducted here for Subantarctic Mode Water (Indian and Pacific Ocean sectors) and Antarctic Intermediate Water (Pacific) using pCFC12 ages from meridional CLIVAR sections P18 in the South Pacific and I8S in the eastern Indian Ocean (Figure 1), respectively. Only the Pacific Ocean has water masses old enough to observe refractory DOC loss, where the rate of $0.0042 \pm 0.0002 \mu\text{mol C kg}^{-1} \text{ yr}^{-1}$ is $\sim 1\%$ of the mean semi-refractory and $\sim 0.05\%$ of the semi-labile DOC

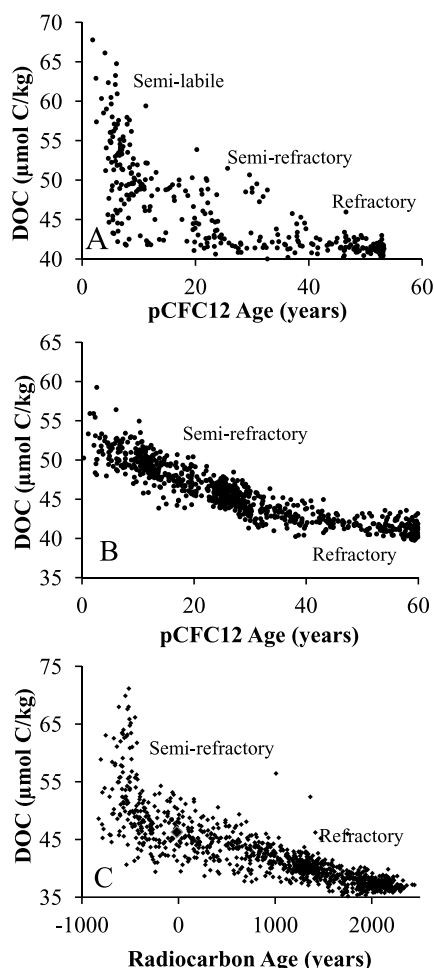


Figure 3. (a) DOC versus pCFC12 age from Pacific P15S (>130 m). (b) DOC versus pCFC12 age from Atlantic A16N at >20°N (>100 m). (c) DOC versus radiocarbon age of dissolved inorganic carbon from Pacific P16 (>100 m). DOC fractions are identified by relative rates of removal.

removal rates. This removal rate of refractory DOC is somewhat higher than that reported previously ($0.003 \mu\text{mol C kg}^{-1} \text{yr}^{-1}$) [Hansell *et al.*, 2009] due to small differences in the bounds of data employed for regression.

[19] These wide ranging removal rates, spanning 3 orders of magnitude, are plotted against associated mean DOC concentrations in Figure 4. These data primarily reflect conditions in the North Atlantic, as most points in Figure 4 were determined in that basin. The semi-labile fraction is depleted at mean DOC concentrations $\sim 53\text{--}55 \mu\text{mol C kg}^{-1}$, while semi-refractory DOC is largely exhausted at DOC concentrations $\sim 42\text{--}43 \mu\text{mol C kg}^{-1}$. These concentration thresholds are not exact as the inflections exist in data clouds that likely reflect imprecision in measurement skill and in nature (Figure 3), and they are not fixed globally as the foundational concentrations of the refractory fraction vary between ocean basins (highest in the North Atlantic and lowest in the North Pacific). In contrast to the more labile fractions, refractory DOC is present at all depths throughout the ocean [Bauer *et al.*, 1992]. Removal of refractory DOC

was observable in the Pacific only, where inputs and removal of other fractions of exported DOC were modest.

[20] Our partitioning of exported DOC as fractions is somewhat subjective due to the limited size of the data set and by the limited time scales of observation offered by the ocean water masses evaluated. There may exist additional high reactivity fractions that were not observable in the data employed here. Alternatively, removal rates may fit a simple linear organic matter decomposition model, such as described by Middelburg [1989] for marine sediments. There, sediment organic matter reactivity decreases linearly with time (log reactivity versus log time). If this result held with the exported DOC data, it would imply that there exists a continuum of reactivity rather than the continua we have employed for DOC fractions. There are, however, characteristics of DOC reactivity that challenge the linear model. First, a single continuity of reactivity is incompatible if water column removal of DOC transitions from biotic-dominated processes at high concentrations to abiotic-domination at low concentrations; different processes with different controls should be at work. Second, DOC that accumulates in the surface layer is resistant to biological decay by resident microbial communities; it is only made bioavailable upon export to subsurface microbe populations. In this situation the bulk DOC is least available while at its highest (surface) concentrations, a situation that does not fit the linear decay model. Third, our implementation of DOC fractions in the biogeochemical model described above (and employed below) results in realistic simulations of the deep DOC distributions (Figure 2) [Hansell *et al.*, 2009], lending credence to the description of fractions as uniquely varying in reactivity. Continued

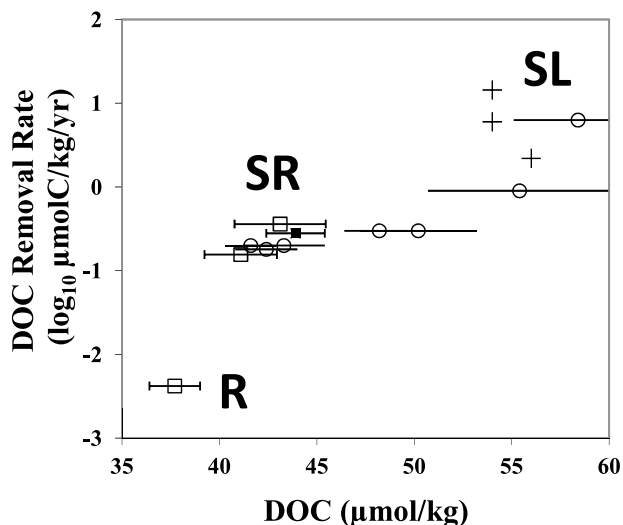


Figure 4. DOC removal rates in specific water masses of the Atlantic (open circles), Pacific (open squares), Indian (solid squares), and Mediterranean/Adriatic (crosses) (data from Table 1). The rates are plotted against the mean of the DOC concentrations employed in determining the rates, with the standard deviation shown as error bars; for Mediterranean waters the median observed DOC concentrations are used. The semi-labile (SL), semi-refractory (SR), and refractory (R) pools are distinguished by relative rates of removal.

Table 2. Characterization of Exported DOC Fractions

Fraction	Removal Rate ^a ($\mu\text{mol C kg}^{-1} \text{ yr}^{-1}$)	Global Inventory ^b (Pg C)	Lifetime (model years)
Semi-labile	~2–9	6 ± 2	1.5
Semi-refractory	~0.2–0.9	14 ± 2	20
Refractory	~0.0026 (0.004)	642 ± 32	16,000

^aObserved and modeled removal rate ranges for the semi-labile and semi-refractory fractions overlap, while the observed removal rate of refractory DOC (in parentheses) was higher than the rate required by the model to reproduce observed distributions.

^bObtained by integrating the model simulated concentrations of semi-labile, semi-refractory, and refractory DOC over the global ocean. Uncertainties reflect model results with small variations in DOC production parameters and lifetimes.

investigation of the most accurate description of exported DOC reactivity is warranted.

3.1.3. Unobserved DOC Removal: Ultra-Refractory DOC Fractions

[21] Our ability to differentiate DOC fractions by removal rates is limited by the circulation time of the deep ocean. Removal of the semi-labile, semi-refractory, and refractory pools is observable within the time frame of circulation (Figure 3), but removal of longer lived fractions (referred to here as ultra-refractory DOC) cannot be observed directly. The existence of ultra-refractory DOC is suggested by molecular and radiocarbon compositions of marine organic carbon. Potential components of ultra-refractory DOC include polycyclic aromatic compounds [Dittmar and Paeng, 2009] such as black carbon, the latter shown in ocean sediments [Masiello and Druffel, 1998] and the water column [Ziolkowski and Druffel, 2010] to have radiocarbon ages much greater than the ambient dissolved organic matter pools. Some very old carbon present in deep waters may also originate from hydrothermal vents [McCarthy et al., 2011], though this is not a fraction of DOC exported from the surface ocean.

3.2. Removal of DOC Fractions in the Global Ocean

[22] The global distribution of DOC removal is modeled based on our knowledge of turnover in the fractions (Table 2). Net removal of the semi-labile and semi-refractory pools occurs upon export, with semi-labile DOC consumption being relatively rapid and thus largely occurring in the upper mesopelagic (~ 100 – 400 m), and semi-refractory DOC removal over a greater depth range. Refractory DOC is presumably removed slowly throughout the water column, though higher rates of removal occur in the surface layer due to photolysis [Mopper and Kieber, 2002; Mopper et al., 1991; Benner and Biddanda, 1998].

[23] In the coupled model employed here, inventories are 6 ± 2 , 14 ± 2 and 642 ± 32 Pg C for the semi-labile, semi-refractory and refractory DOC fractions, respectively (Table 2). The vertically integrated, water column removal rates of exported DOC are shown in Figure 5. The highest rates approach $1500 \text{ mmol C m}^{-2} \text{ yr}^{-1}$, while the lowest are an order of magnitude slower (Figure 5a). Low integrated rates of removal exist in: regions impacted by upwelled waters (such as the west coast of the Americas, northwest and southwest Africa, and the equatorial Pacific); regions renewed by DOC-impoverished deep waters (the Southern Ocean); and strongly stratified low-latitude zones, where vertical mixing into the mesopelagic zone, and therefore DOC export, is restricted. Highest rates are associated with the convergence zones of the subtropical gyres, where the highly reactive semi-labile DOC (Figure 5b) contributes ~ 60 – 70% to total water column DOC removal. Loss of the semi-refractory fraction (Figure 5c) is greatest in the regions of gyre convergence as well as within higher northern latitude thermohaline (overturning) circulation, where surface waters enriched in this fraction are delivered to the deep interior for long-term sequestration (e.g., northern North Atlantic). The distribution of refractory DOC removal reflects the water column depths in the basins; the

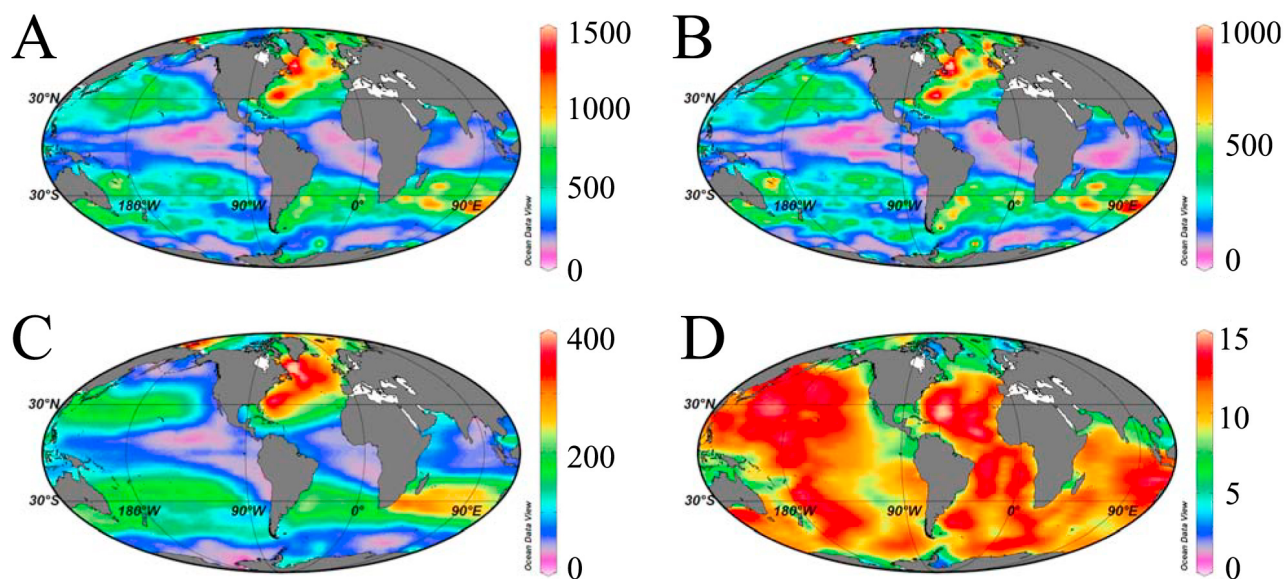


Figure 5. Water column integrated rates of DOC removal ($\text{mmol C m}^{-2} \text{ yr}^{-1}$ at >130 m). (a) Total DOC (sum of semi-labile, semi-refractory, and refractory fractions). (b) Semi-labile DOC. (c) Semi-refractory DOC. (d) Refractory DOC.

volumetric rate varies little in the model, so water column depth largely controls the integrated rate (Figure 5d).

[24] Exported DOC removal is complemented by carbon delivered to depth as sinking biogenic particles generated by the biological pump in the surface ocean, but the locations where these two processes dominate are strongly contrasting. Carbon exported as sinking particles (~80% of global export production) [Hansell, 2002] is ultimately controlled by introduction of new nutrients to a system. Upwelling of nutrients in equatorial and coastal environments drives the majority of global export production by particles, but DOC removal is relatively weak in those locations (Figure 5a). Instead, DOC removal is strongest in convergence zones, where the supply of new nutrients to surface waters is comparatively small, as is the corresponding export of biogenic particles. This situation illustrates the physical separation of biogenic particles versus exported DOC as the dominant source for carbon mineralization at depth. For example, at the BATS site in the western Sargasso Sea (Figure 1), the modeled DOC removal rate (estimated from Figure 5a at ~1000–1200 mmol C m⁻² yr⁻¹) is larger than a 9-year annual mean particulate organic carbon (POC) flux at 150 m of 800 mmol C m⁻² yr⁻¹ [Steinberg *et al.*, 2001]. In contrast, POC export fluxes will far exceed water column integrated rates of DOC removal in equatorial and coastal upwelling areas. DOC removal in the equatorial Pacific (Figure 5a) is an order of magnitude lower than the >3 mol C m⁻² yr⁻¹ net community production in that system [Quay *et al.*, 2009].

3.3. Uncertainties in Rate Estimates and Responsible Processes

[25] At steady state, DOC removed in the ocean interior each year is renewed as the deep water is returned to the surface layer. While surface accumulation of DOC is observed [Álvarez-Salgado *et al.*, 2001; Hansell and Carlson, 2001], the mechanisms responsible for formation of the various fractions have not been established. A recently proposed “microbial carbon pump” addresses the generation of biologically recalcitrant DOC and associated carbon storage [Jiao *et al.*, 2010], whereby marine microbes and their food web interactions effectively transform reactive carbon to recalcitrant carbon, thus building a large marine DOC reservoir (i.e., the refractory DOC pool) for carbon storage.

[26] Both biotic and abiotic processes may be responsible for the removal of exported DOC in the ocean [Hansell *et al.*, 2009], but the role of each likely varies with the fraction of DOC considered. Semi-labile DOC is likely consumed by heterotrophic microbes. Time-series studies at BATS have revealed that distinct bacterioplankton communities within the mesopelagic zone respond to the delivery of exported DOM [Morris *et al.*, 2005; Carlson *et al.*, 2009], and that response coincides with diagenetic alteration of DOC within the mesopelagic [Goldberg *et al.*, 2009]. Distinguishing biotic and abiotic contributions to removal of the semi-refractory pool is challenging. The low rate of removal (<1 μmol C kg⁻¹ yr⁻¹) precludes attribution through the use of incubation experiments. Typically, interior ocean DOC concentrations are regressed against oxygen utilization and the result taken to indicate the fraction of oxygen con-

sumption due to DOC mineralization [Ogura, 1970; Carlson *et al.*, 2010; Aristegui *et al.*, 2002; Doval and Hansell, 2000; Hung *et al.*, 2007]. It is possible, though, that the losses of semi-refractory and refractory DOC include abiotic mechanisms such as scavenging onto suspended or sinking particles, leaving observed correlations with oxygen loss as coincidental.

[27] The removal rates reported here are net since presumably small amounts of DOC are added to the water column through processes such as the solubilization of sinking particles, metabolic processing of sinking particles (e.g., leading to the production of fluorescent dissolved organic matter), deep ocean chemoautotrophy, and efflux from sediments and/or geothermal systems. DOC released by particle solubilization is largely consumed by resident microbes [Nagata *et al.*, 2010], with an unknown fraction left to accumulate. The systematic DOC underestimation between 200 and 1000 m in the present model (Figure 2) may be evidence that this additional production and accumulation mechanism is occurring. But deep distributions of ¹⁴C-DOC suggest that advective (horizontal) processes dominate the DOC input terms for the deep ocean [Beaupré and Aluwihare, 2010], contrary to an important fraction of modern DOC accumulating due to solubilization. Fluorescent organic matter is added at <2% the global rate of DOC export, mostly at the mesopelagic depths of maximum particle mineralization [Yamashita and Tanoue, 2008]. It is in regions with high particle export and remineralization that its impacts would be most important. Radiocarbon-aged DOC can be added to the water column from below, by release from the sediments or, perhaps by geothermal cycling [McCarthy *et al.*, 2011]. Fossil methane-derived carbon has been identified as an input to deep ocean DOC [Pohlman *et al.*, 2011], but its global significance and reactivity is unknown. Lang *et al.* [2006] reported DOC concentrations in hydrothermal fluids collected from high-temperature vents and diffuse low-temperature vents. The high temperature systems were reported to remove DOC while a diffuse system added it. The authors speculated that geothermal DOC removal exceeds addition, with global removal reaching 0.002 PgC yr⁻¹, or 4% of the global rate of removal of exported refractory DOC estimated by Hansell *et al.* [2009].

4. Concluding Comments

[28] Based on the relationship between DOC concentrations and removal rates (Figure 4), we hypothesize that removal of each DOC fraction can be described as a continuum following first-order kinetics. One model (Figure 6) has each DOC fraction completely formed in the surface layer, with the more slowly removed fractions only observable as they emerge with exhaustion of the more labile fractions. An alternative model has one exported fraction (such as semi-labile DOC) being modified through microbial actions toward formation of the more refractory fractions as the water ages. In this case, the more refractory fractions would be fully renewed subsequent to export, rather than in the surface layer. The suggested reactivity continua require further elucidation and understanding, particularly for mechanisms such as those implied by Figure 6. Testing

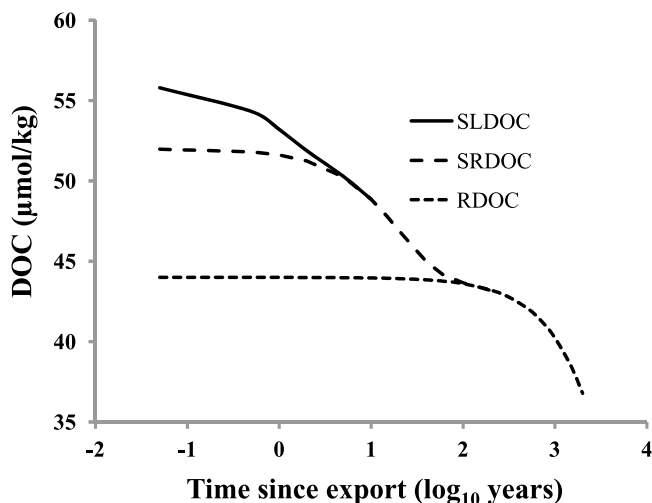


Figure 6. Schematic model for the existence of 3 major exported DOC fractions upon ventilation of the ocean interior, with net removal of each at distinctive rates. The decrease in bulk DOC concentration with time represents the sum of the removal rates. Exhaustion of more labile fractions allows observation of removal of the more refractory fractions. This model has the fractions fully formed at the time of export. The concentrations of each fraction at the time of export vary with the location in the global ocean; the model depicts approximate concentrations of the semi-labile and semi-refractory fractions in the North Atlantic. SLDOC, SRDOC, and RDOC are semi-labile, semi-refractory and refractory fractions, respectively.

proposed mechanisms of DOC formation and removal, and the sensitivity of these to a changing climate, is an important challenge. An increasingly stratified ocean has uncertain future DOC scenarios (e.g., changes in concentrations at the surface and at depth; changes in retention time of the mineralized fractions at depth), each dependent on how exportable DOC is actually formed and removed.

[29] **Acknowledgments.** We thank James H. Swift for his leadership of the U.S. CLIVAR Repeat Hydrography program, without which we could not have done these analyses. DAH and CAC were supported by U.S. NSF OCE-0752972, NSF OCE-0801991.

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C. A. Carlson, Department of Ecology, Evolution and Marine Biology, University of California, Santa Barbara, CA 93103-9610, USA. (carlson@lifesci.ucsb.edu)

D. A. Hansell, Division of Marine and Atmospheric Chemistry, Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Cswy., Miami, FL 33149, USA. (dhansell@rsmas.miami.edu)

R. Schlitzer, Alfred Wegener Institute, Columbusstrasse, Bremerhaven D-27568, Germany. (reiner.schlitzer@awi.de)