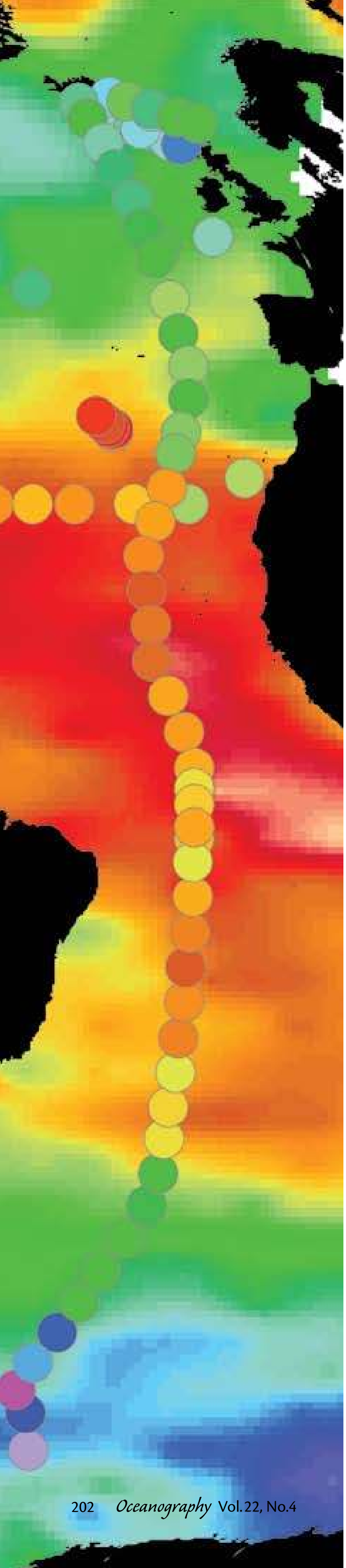

REGULAR ISSUE FEATURE

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DISSOLVED ORGANIC MATTER IN THE OCEAN

A CONTROVERSY STIMULATES NEW INSIGHTS

ABSTRACT. Containing as much carbon as the atmosphere, marine dissolved organic matter is one of Earth's major carbon reservoirs. With invigoration of scientific inquiries into the global carbon cycle, our ignorance of its role in ocean biogeochemistry became untenable. Rapid mobilization of relevant research two decades ago required the community to overcome early false leads, but subsequent progress in examining the global dynamics of this material has been steady. Continuous improvements in analytical skill coupled with global ocean hydrographic survey opportunities resulted in the generation of thousands of measurements throughout the major ocean basins. Here, observations and model results provide new insights into the large-scale variability of dissolved organic carbon, its contribution to the biological pump, and its deep ocean sinks.

BACKGROUND

Two decades ago, in the inaugural volume of *Oceanography*, the ocean science community learned of a brewing controversy on the role of marine dissolved organic matter (DOM) in the biogeochemical cycling of the major elements (Williams and Druffel, 1988). Historically, DOM had been considered a spatially invariant, biologically refractory pool of carbon (and associated elements) uniformly distributed throughout the deep sea. In 1988, Sugimura and Suzuki shook the marine biogeochemical world by reporting dissolved organic carbon (DOC) and nitrogen (DON) concentrations that exceeded by several fold previously thought-to-be-reliable values. Their results challenged well-established paradigms on how the biological pump functioned in the ocean. Instead of sinking particles being the primary agent of biogenic carbon export to the deep abyss, the "new" values made DOM dominant in the biological pump (Toggweiler, 1989).

As then assessed by Williams and Druffel (1988), "these elevated concentrations, as yet unconfirmed, have been accepted as gospel by some, as heresy by others." The key phrase there is "as yet unconfirmed." Shouldering the challenge, the marine science community proceeded to expend great resources in testing the new gospel. Community-wide method intercomparison exercises identified the analytical problems to overcome, while individual and small-group efforts contributed to their solution (Hedges and Lee, 1993). With improvement of the high-temperature combustion method, the magnitude of DOC concentrations was found to be consistent with the "old, low" concentrations (see discussions in Hansell and Carlson, 2002). With support from the US National Science Foundation, the widespread use of analytical reference materials for DOC determinations was instituted (Hansell and Carlson, 2001; Sharp et al., 2002; Hansell, 2005) to ensure intercomparability of data from vast reaches of the ocean, and continues today.

Although the outcome of the "DOM controversy" was seemingly anticlimactic, our curiosity about the role of DOM in ocean biogeochemistry had been piqued. Great community efforts resulted in improved DOC and DON analytical skill that yielded data of higher precision and accuracy, but these slowly emerging data were as yet inadequate to describe the biogeochemical role of DOM. The international Joint Global Ocean Flux Study, World Ocean Circulation Experiment, and Climate Variability and Predictability (CLIVAR) Repeat Hydrography project provided the opportunities required to obtain global observations of DOM variability, its contribution to the biological pump, and its subsequent fate within the ocean interior in unprecedented detail. Below we outline findings on DOC in the global ocean as revealed by the most recent, spatially extensive data sets.

DISSOLVED ORGANIC CARBON IN THE BIOLOGICAL PUMP

At 662 Pg C (Table 1), marine DOM is the largest ocean reservoir of reduced carbon, holding greater than 200 times the carbon inventory of marine biomass. Oceanic DOM is mostly produced autochthonously by photosynthetic plankton in the surface ocean, and it serves as substrate to vast heterotrophic microbial populations and as a source of nitrogen and phosphorus to nutrient-starved autotrophs. DOC export through overturn of the ocean water column can be an important contributor to the biological pump whereby biogenic carbon is sequestered in the deep ocean, away from the atmosphere.

Despite its large global inventory, DOC exists in the open ocean at extremely low concentrations (34 – ~ 80 µmol kg^{-1}). Due to limitations in analytical skill, we were until recently unable to resolve concentration gradients in the deep sea, so little had been known about the fate of DOC once it was removed to the deep ocean interior. A few high-precision measurements made to assess the distribution of DOC in the deep ocean indicated an ~ 29% decrease in concentration along the path of the deep global thermohaline circulation (from the deep North Atlantic to the deep North Pacific; Hansell and Carlson, 1998a), but the data were too sparse to develop further insights.

In 2003, the US CLIVAR Repeat Hydrography project sought to provide the first high-precision, high-resolution global view of DOC distribution and variability in the context of a global ocean hydrographic survey. Since then, more than 20,000 individual DOC values have been determined for the Atlantic, Indian, Pacific, and Southern oceans. Using these observational data in combination with a coupled circulation-biogeochemical model, we add new details on and insights into the role of DOC in the biological pump.

The biological pump is the sum of processes that transport biogenic carbon from the surface euphotic zone to the ocean's interior where the material is mineralized, thus maintaining the strong vertical gradients of oceanic inorganic carbon. Passively sinking particulate carbon, active vertical

Table 1. Global inventories of DOC differentiated by water column depth zone. Values result from modeled inventories of DOC.

Depth Zone	Inventory (Pg C)
0–200 m	47
0–1000 m	185
> 1000 m	477
0–bottom	662

migration by zooplankton, and DOC mixed downward from the surface comprise the main components of the pump (Ducklow et al., 2001). Strong contributions by DOC to the biological pump initially require strong vertical gradients in DOC and then an active overturning circulation of the water column, thus moving DOC-enriched surface waters to the ocean interior for ultimate mineralization.

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Open ocean surface waters exhibit a DOC concentration range of ~ 40 µmol kg^{-1} (Figure 1A). High values of 70–80 µmol C kg^{-1} are present in the tropical and subtropical systems (40°N to 40°S), where vertical stratification of the upper water column favors the slow accumulation of organic matter resistant to biological degradation. Lower concentrations (~ 40–50 µmol C kg^{-1}) are observed at the surface in subpolar seas and in the circumpolar Southern Ocean (> 50°S), where low-DOC, deep ocean waters are more readily mixed to the surface. The highly stratified surface Arctic Ocean is enriched in DOC by the input of terrigenous organic matter via high fluvial fluxes to the system (Dittmar and Kattner, 2003).

Autotrophic production in the euphotic zone is the chief source of DOC to the open ocean, while microbial mineralization is the dominant sink. In marine systems, the amount of DOC that is routed through rapid bacterial production may be as much as 50% of primary production (i.e., equivalent to a DOC flux of ~ 30 Pg C yr^{-1}; Williams, 2000).

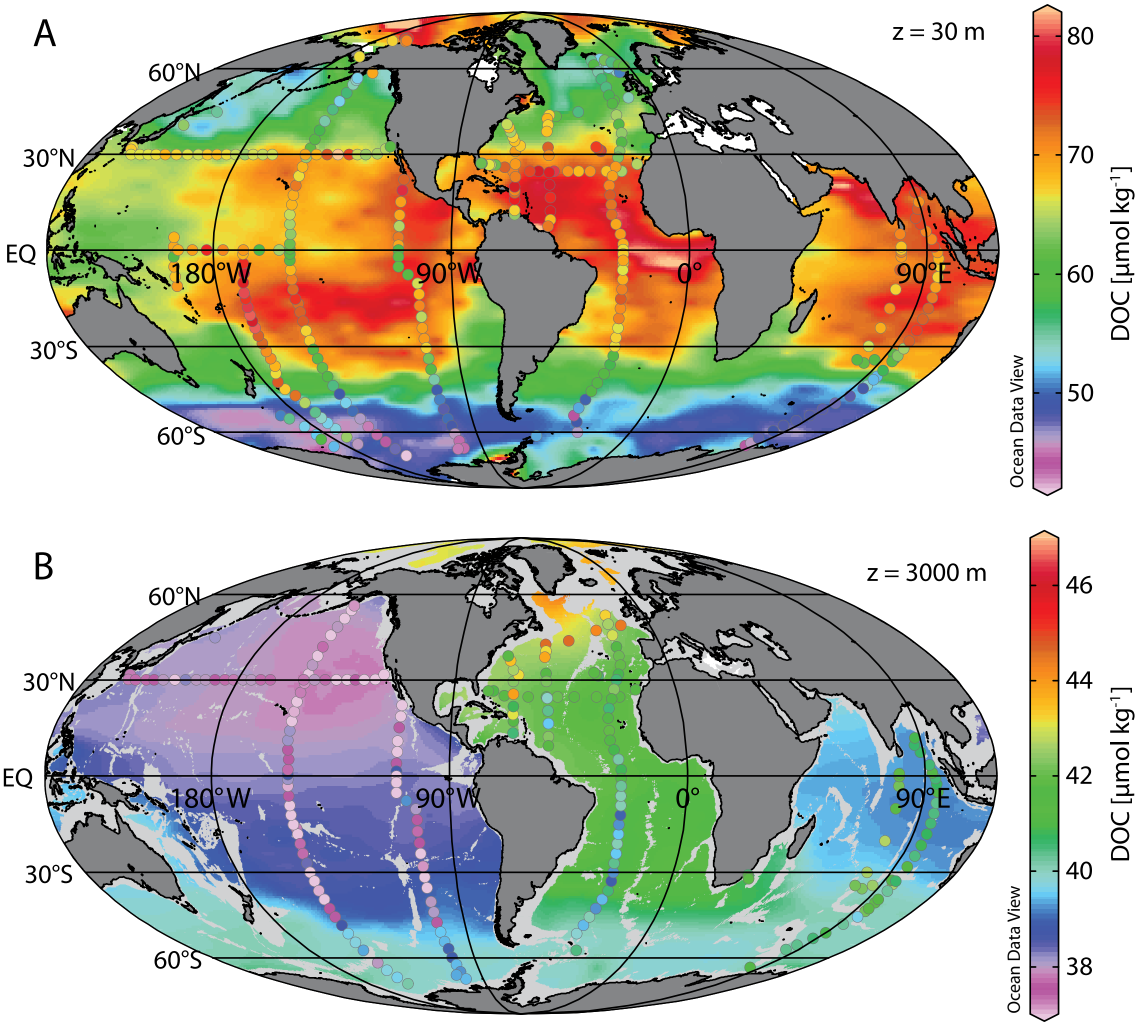

Figure 1. Distributions of dissolved organic carbon (DOC; µmol kg^{-1}) at 30 m (A) and 3000 m (B). Meridional and zonal lines of data are observed values, while the background field is modeled (see Box 1 for model description). Central elements of the global meridional overturning circulation include net northward upper layer and southward deep layer flows in the Atlantic, and northward flow near bottom in the western Pacific.

This biologically labile fraction represents a large flux of carbon in the ocean, but with rapid turnover it constitutes a very small fraction (< 1%) of the ocean DOC inventory. A more biologically resistant fraction, produced in the euphotic zone at 15–20% of net community productivity (~ 2 Pg C yr^{-1}; Hansell and Carlson, 1998b), is not immediately mineralized and instead accumulates in the surface ocean as biologically semi-labile DOC (Carlson, 2002; Hansell, 2002).

Semi-labile DOC is now recognized to be a family of carbohydrates that have remarkably conservative spectroscopic and chemical properties throughout the global ocean (Aluwihare et al., 1997). The elemental ratios of carbon, nitrogen, and phosphorus, the major sugars released by chemical hydrolysis, and the partitioning of carbon between functional groups all fall within a narrow range for the semi-labile fraction. These properties can be used to trace semi-labile DOC into the deep sea, and to illuminate changes in DOC composition that may be related to biolability. Small changes in the amount and ratio of component sugars, which may parallel structural changes acting to decrease DOC lability, occur as semi-labile DOC accumulates to high concentrations in mid-ocean gyres (Skoog and Benner, 1998; Goldberg et al., 2009). Isotopic measurements of carbohydrates in the upper ocean semi-labile DOC pool show significant amounts of bomb (post 1955) radiocarbon, at levels equal to dissolved inorganic carbon. Such high levels of bomb radiocarbon imply turnover of only a few years or less for much of this surface-accumulated material (Repeta and Aluwihare, 2006).

Semi-labile DOC that accumulates in the subtropical gyres can be exported in all ocean basins by Ekman convergence of surface waters, downwelling the DOC-enriched waters to depths of a few hundred meters (note deepening of DOC-enriched surface waters in gyre centers; Figure 2). Most organic carbon exported and mineralized along this path is returned for exchange with the atmosphere within months to years.

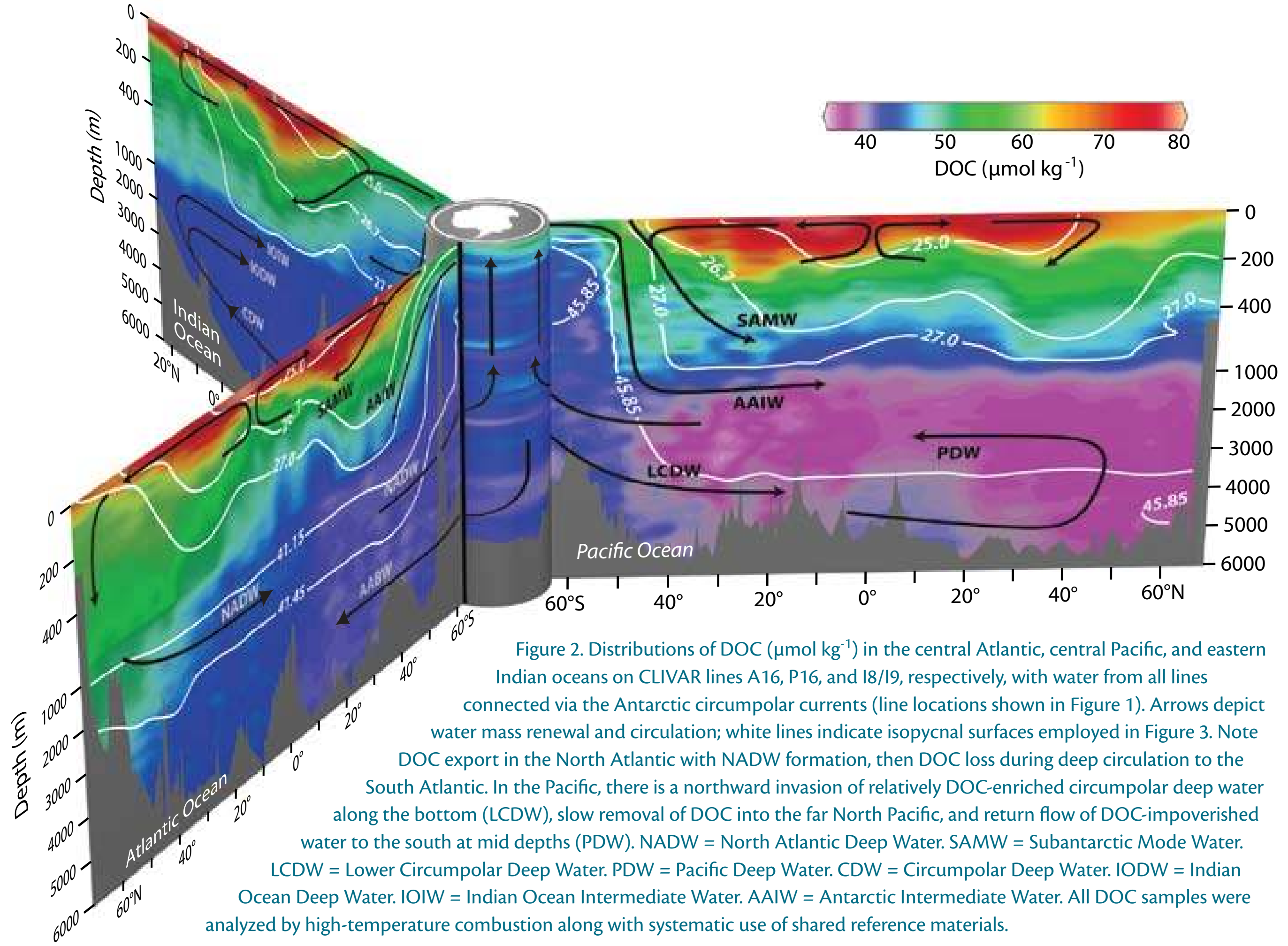

Figure 2. Distributions of DOC (µmol kg^{-1}) in the central Atlantic, central Pacific, and eastern Indian oceans on CLIVAR lines A16, P16, and I8/I9, respectively, with water from all lines connected via the Antarctic circumpolar currents (line locations shown in Figure 1). Arrows depict water mass renewal and circulation; white lines indicate isopycnal surfaces employed in Figure 3. Note DOC export in the North Atlantic with NADW formation, then DOC loss during deep circulation to the South Atlantic. In the Pacific, there is a northward invasion of relatively DOC-enriched circumpolar deep water along the bottom (LCDW), slow removal of DOC into the far North Pacific, and return flow of DOC-impoverished water to the south at mid depths (PDW). NADW = North Atlantic Deep Water. SAMW = Subantarctic Mode Water. LCDW = Lower Circumpolar Deep Water. PDW = Pacific Deep Water. CDW = Circumpolar Deep Water. IODW = Indian Ocean Deep Water. IOIW = Indian Ocean Intermediate Water. AAIW = Antarctic Intermediate Water. All DOC samples were analyzed by high-temperature combustion along with systematic use of shared reference materials.

In contrast, DOC transported with the wind-driven surface currents from low to high latitudes is exported to greater depth via meridional overturning circulation and ventilation of the ocean interior, resulting in a longer-term sequestration of the biogenic carbon (Figure 2; Copin-Montégut and Avril, 1993; Carlson et al., 1994; Hansell and Carlson, 2001; Hansell et al., 2002; Hopkinson and Vallino, 2005). Waters ventilating the intermediate and deepest portions of the ocean can effectively sequester carbon exported as DOC for years to centuries. This process is particularly evident in the Atlantic Ocean, where DOC-enriched subtropical water is transported to the regions of deep-water formation in the far north (Carlson et al., in press; Figure 2).

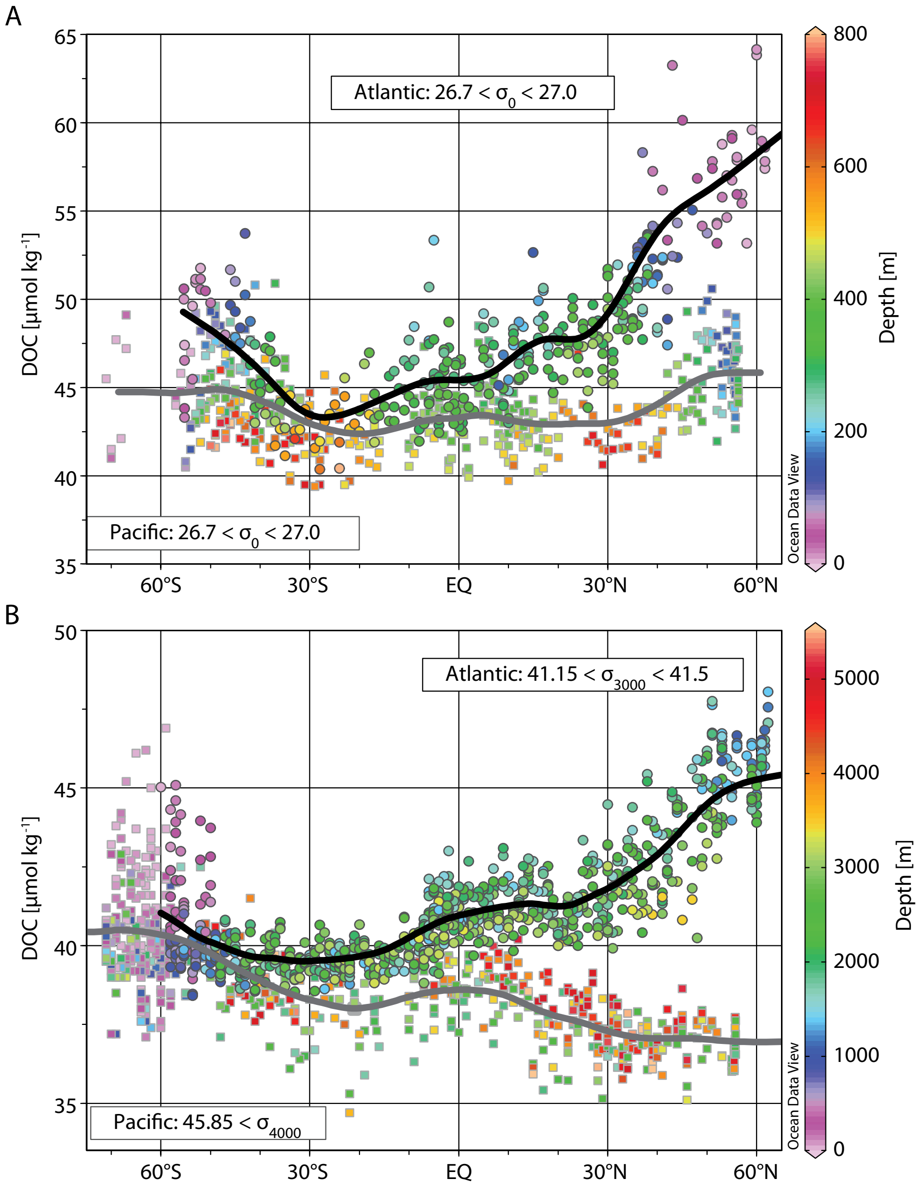

Figure 3. Concentrations of DOC (μmol kg^{-1}) on density surfaces (A) 26.7 to 27.0 (reference pressure is surface ocean), ventilating the upper ocean, and (B) 41.15 to 41.5 in the Atlantic (black lines; reference pressure 3000 m) and > 45.85 in the Pacific (gray lines; reference pressure 4000 m). The lighter-density plot (A) approximates the density range for upper intermediate waters ventilated at subpolar latitudes. The higher-density plot (B) follows North Atlantic Deep Water at mid depth in the Atlantic and Lower Circumpolar Deep Water near bottom in the Pacific, both of which are ventilated at higher latitudes.

The largest deep ocean DOC gradients along intermediate and deep ventilation pathways (~ 12 μmol C kg^{-1}) are observed in the North Atlantic basin (Figure 3A and 3B, respectively). Vertical input with North Atlantic Deep Water (NADW) formation results in bathypelagic DOC concentrations > 50 μmol kg^{-1} C north of 50°N. Along the intermediate and deep ventilation pathways, DOC then decreases to 40–45 μmol kg^{-1} C by the equator (Figures 1B and 3). DOC concentrations in the deep South Atlantic are further depleted to ~ 39 μmol kg^{-1} at 25°–50°S (Figure 3B). Biotic remineralization of the exported DOC as well as dilution with northward flowing, DOC-impoverished water masses at intermediate (Antarctic Intermediate Water; AAIW) and bottom (Antarctic Bottom Water; AABW) depths (Figure 2) create this deep Atlantic meridional gradient. The deep Atlantic, including export by intermediate, deep, and bottom water formation in both the north and the south (totaling 31 Sv, where $1 \text{ Sv} = 1 \times 10^6 \text{ m}^3 \text{ s}^{-1}$), represents a DOC sink of ~ 86 Tg C yr^{-1} (calculated as water mass formation rates times DOC concentration gradients from Figure 3).

The isopycnal concentration gradients between ~ 60°S and 30°S (Figure 3) in both the Atlantic and the Pacific suggest net input and subsequent removal of DOC with waters formed in the Southern Ocean (unless there is a bias imparted by the limited locations of sampling).

Box 1. Model Description

The DOC model is based on a coupled physical/biogeochemical model (Schlitzer, 2002, 2007), which is fitted to the global ocean distributions of temperature, salinity, oxygen, nutrients, carbon, radiocarbon ^{14}C-CO_2, and chlorofluorocarbons CFC-11 and CFC-12 by means of an automatic optimization procedure. The model explains the global ^{14}C-CO_2, CFC-11, and CFC-12 distributions extremely well, and thus supposedly has realistic global ocean overturning rates as well as realistic ventilation rates and material transports from the surface to deeper layers. Ventilation and vertical mixing are essential processes for the transport of DOC from the near-surface production layers into the intermediate and deep layers of the ocean.

DOC in the model is decomposed into three pools: two pools of semi-labile DOC with lifetimes of about three and 10 years, and a pool representing refractory DOC with a lifetime of about 15,000 years. The lifetimes of the fast-turnover, semi-labile pools were determined on the basis of empirical correlations of DOC with water mass age from chlorofluorocarbon data. The lifetime of the refractory DOC was adjusted to obtain an optimal fit with deep ocean DOC data. DOC is produced in the euphotic zone at rates proportional to the square root of primary production, as estimated from satellite data. Absolute production rates were adjusted to achieve an optimal fit with surface DOC data.

Downward DOC fluxes (Figure 4) are global integrals of local fluxes based on model vertical velocities, mixing coefficients, and DOC concentrations at the considered depths. Model downward POC fluxes (Figure 4) are determined by the automatic optimization procedure using the constraint to reproduce measured dissolved nutrient and oxygen distributions realistically.

DOC is exported with deep ventilation there, then transported north as near-bottom water flow in both the Atlantic (as AABW) and the Pacific (as Lower Circumpolar Deep Water; LCDW). Bottom waters of the Pacific Ocean gradually lose carbon as they move northward; DOC is ~ 42 µmol kg^{-1} in the circumpolar waters of the South Pacific, decreasing to ~ 36 µmol kg^{-1} (Figure 3B) as the water slowly invades the deep North Pacific (Figure 1B). Unlike the North Atlantic, water masses at great depth in the North Pacific are not locally formed and so are greatly aged. As the near-bottom water mass enters the North Pacific from the south, it gains buoyancy via vertical mixing, rising to the mid water column where it returns south as Pacific Deep Water (PDW; Figure 2). During southward transit of PDW, DOC continues to decline, reaching a global low concentration of ~ 34 µmol kg^{-1} at mid depth in the South Pacific. Including both intermediate and bottom water ventilation of the Pacific Ocean (~ 25 Sv), the basin is a sink for ~ 43 Tg C yr^{-1} as DOC.

On a global ocean basis, model results indicate that semi-labile DOC undergoes net export to depths > 100 m at 1.8 Pg C yr^{-1}, or ~ 20% of global export production (Figure 4). Because DOC concentrations in the surface layer are highest at low latitudes (Figure 1), it is the relatively shallow water masses ventilated with those surface waters

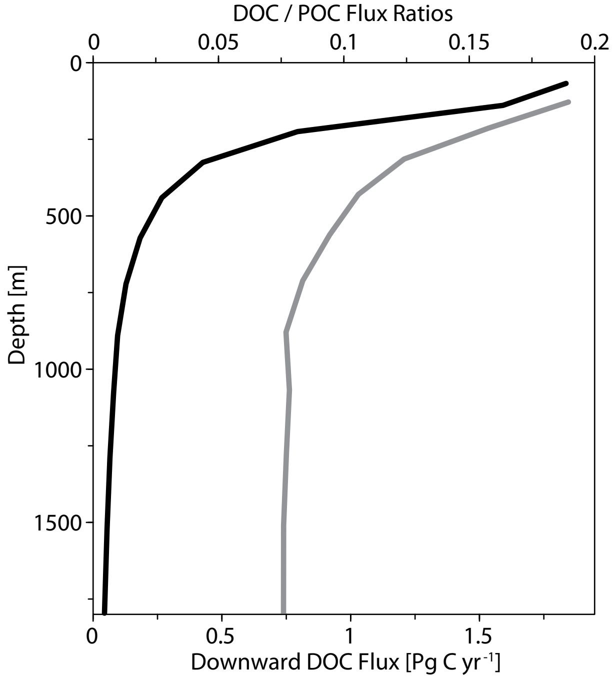

Figure 4. Modeled downward flux of DOC (Pg C yr^{-1}; black line) and the DOC/POC export flux ratio (gray line) as a function of depth for the global ocean.

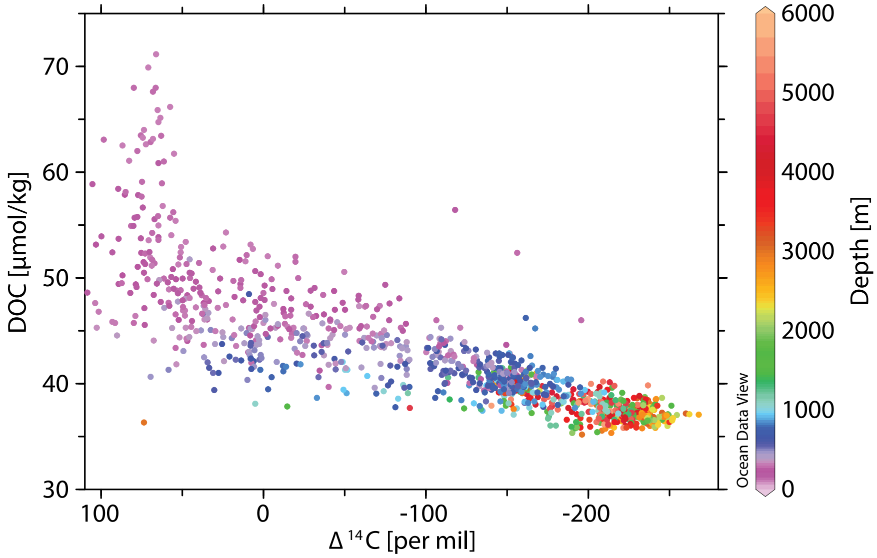

Figure 5. Concentrations of DOC plotted against Δ^{14}C-TCO$_2$ and depth along line P16 in the Pacific Ocean. Semi-labile DOC is removed relatively rapidly (note initial drop in DOC concentration with decreasing radiocarbon content), primarily by biotic processes. Refractory DOC is lost more slowly, perhaps due to abiotic transformation of the DOC to particles. Note nonlinearity of depth (color) scale.

that receive most of the exported DOC. Only ~ 0.2 Pg C yr^{-1} of the exported DOC survives to depths > 500 m, so the contribution of DOC export decreases relative to particulate organic carbon (POC) export with increasing depths (Figure 4). As such, DOC mineralization makes its greatest contribution to oxygen consumption in the upper ocean (up to 70% of oxygen consumption at < 400 m; Doval and Hansell, 2000; Abell et al., 2000) and its least at greater depths (< 10–20% in deep waters; Arístegui et al., 2002; Carlson et al., in press).

DEEP OCEAN SINKS FOR EXPORTED DOC

At a global export rate of 1.8 Pg C yr^{-1}, the calculated residence time for the full ocean DOC inventory of 662 Pg C is 370 years. Most of the oceanic DOC, however, is highly depleted in radiocarbon and is therefore reactive only on a multi-millennial time scale (referred to here as refractory DOC, which survives several cycles of interior ocean circulation). It is the semi-labile fraction that is most reactive during cycling through the deep ocean. Spectroscopic and chemical analyses indicate the presence of semi-labile carbohydrates even in the oldest waters of the deep North Pacific basin. Isotopic Δ^{14}C values (per mil deviation from that in nineteenth century CO$_2$) of semi-labile DOC in the deep North Pacific are equal to Δ^{14}C-TCO$_2$ values, but up to 300 per mil enriched relative to total DOC. These findings confirm that deep sea DOC is a mixture of chemically distinct forms of carbon of different radiocarbon ages (the semi-labile and refractory fractions). DOC concentrations plotted against Δ^{14}C-TCO$_2$ in the Pacific Ocean distinguishes these two fractions by time scale of removal (Figure 5). The semi-labile pool (with annual to multi-decadal time scale of removal) is largely present in the upper ocean (< 500 m) and exhausted at greater depths (Figure 2). A portion of the *refractory* fraction (or perhaps a longer-lived semi-labile fraction) is removed during several hundred years of deep ocean circulation.

DOC concentrations in the deep ocean range from 34 to ~ 50 µmol C kg^{-1}, with the gradient established over a single circulation of the abyss (Figures 2 and 5). The mechanisms of loss are not understood, but both biotic and abiotic processes are likely involved. Large increases in apparent oxygen utilization (AOU) with aging of water masses reveal that heterotrophic processes dominate the deep ocean carbon cycle. The observed relationship between DOC and AOU in deep waters indicates that DOC flux supports < 10%–20% of bathypelagic respiration (Arístegui et al., 2002; Carlson et al., in press). Overall O$_2$ consumption rates are low in the bathypelagic relative to the surface waters, but total respiration in the dark ocean is a major component of the carbon flux in the biosphere (Arístegui et al., 2003). Specific prokaryotic respiration rates at depth can be greater than observed in the surface ocean, indicating that individual meso- and bathypelagic prokaryotes can be highly active (Reinthaler et al., 2006). Short-term radioisotope and O$_2$ utilization bioassays provide estimates of prokaryotic DOC metabolism in the bathypelagic, ranging from 0.003–0.15 µmol C kg^{-1} yr^{-1} (Williams and Carlucci, 1975; Turley and Mackie, 1994; Nagata et al., 2000; Ingalls et al., 2006) to as high as 22–82 µmol C kg^{-1} yr^{-1} (Reinthaler et al., 2006). The highest rates of prokaryotic carbon metabolism reported must be supported with supply of new organic matter such as dissolution of sinking POC (Cherrier et al., 1999; Hansman et al., 2009) or by production of organic matter via archaeal chemoautotrophy (Ingalls et al., 2006; Hansman et al., 2009), though these rates may have been overestimated due to limitations in methodologies as discussed in Reinthaler et al. (2006) and Burd et al. (in press). Further measures of the $\Delta^{14}C$ content of deep-sea bacterioplankton DNA are needed to provide insight on the sources of organic matter supporting deep heterotrophic microbial production.

Refractory DOC removal has also been ascribed to two abiotic processes: photolysis by ultraviolet (UV) irradiation at the ocean surface (Mopper et al., 1991) and transformation to and/or interaction with suspended particles (Druffel et al., 1992). Once exposed to surface UV irradiation, refractory DOC is altered via photo-oxidation and made susceptible to microbial remineralization (Kieber et al., 1989; Mopper et al., 1991; Benner and Biddanda, 1998; Anderson and Williams, 1999). The depleted $\Delta^{14}C$ values of surface bacterioplankton DNA indicate the uptake and incorporation of this old DOC, presumably made bioavailable through photolysis (Cherrier et al., 1999). However, photolysis is restricted to the surface ocean and thus cannot account for the DOC gradients observed in the deep ocean (Figures 2 and 5). Organic gel formation by deep ocean DOC (leading to particle formation), or adsorption of these organic gels onto suspended and sinking particles, are abiotic particle interaction processes that may contribute to a reduction in DOC concentrations. Biopolymers present in seawater, such as DOC, gels, and transparent exopolymers (Wells, 1998; Carlson, 2002; Passow and Alldredge, 2004), can move organic molecules up the particle size spectrum to sizes capable of sinking through the water column (Verdugo et al., 2004; Engel et al., 2004). Evidence for stripping ^{14}C-depleted, refractory DOC by one or both of these processes is the lower than expected $\Delta^{14}C$ value of suspended POC in deep water, with a mean 93‰ reduction in $\Delta^{14}C$ value in deep sea POC compared to suspended POC located in the surface ocean (Druffel and Williams, 1990; Druffel et al., 1996, 1998). If such removal processes are at work, then 14% of C on suspended POC in the deep central North Pacific could be due to adsorption (or addition via gel formation) of old DOC (Druffel and Williams, 1990). With deep-ocean-suspended POC concentrations of ~ 0.1 μmol kg^{-1} and residence times of 5–10 years (Bacon and Anderson, 1982), the removal rate of DOC by this process ranges from 1.4–2.8 nmol C kg^{-1} yr^{-1}.

This DOC removal rate, calculated from the $\Delta^{14}C$ content of suspended particles in the deep ocean, can be tested using the data presented here. Figures 2 and 3b depict the concentrations of DOC in the deep Pacific Ocean, demonstrating the input of relatively DOC-enriched waters from the circumpolar deep layer of the Southern Ocean, the transport of that deep water to the north, its slow removal in transit, and the southward return of DOC-impoverished water as PDW (emanating from the North Pacific) at mid depth. The transit time from the Southern Ocean to the mid depths of the North Pacific Ocean is 500–1000 years (Stuiver et al., 1983; Van Aken, 2007). The correlation between DOC concentrations and radiocarbon content of inorganic carbon indicates a net DOC removal rate of 3 nmol kg^{-1} yr^{-1} in the deep Pacific (calculated from linear regression of DOC against radiocarbon age in the South Pacific [$r^2 = 0.49$], using data from Figure 5 at DOC < 50 μmol kg^{-1}). The DOC removal rate assessed from water mass age and DOC concentration gradients is consistent with the Druffel and Williams (1990) removal rate of 1.4–2.8 nmol C kg^{-1} yr^{-1} based on the isotopic composition of the suspended particles. Agreement in rates suggests that a large fraction of the DOC removed in the deep Pacific may be via abiotic interactions with particles.

Refractory DOC removal by abiotic interaction with particles is estimated to be ~ 0.05 Pg C yr^{-1} if the process occurs at 3 nmol kg^{-1} yr^{-1} throughout the volume of the ocean (both refractory DOC and suspended POC are ubiquitous, so the process should be as well). This loss rate means a residence time for refractory DOC of 12,500 years (assuming a global mean refractory DOC concentration of 40 μmol kg^{-1}, given a global inventory of 624 Pg C, or 94% of the global inventory of total DOC). The radiocarbon age of DOC measured in the deep central North Pacific is 6000 years (Williams and Druffel, 1987; Bauer et al., 2002), so photolysis at the ocean surface likely makes up the balance of refractory DOC removal by abiotic processes.

DOC removal via abiotic interaction with particles equals ~ 15% of the 0.3–0.4 Pg C yr^{-1} of sinking particulate organic carbon reaching the deep seafloor, but it is four times the rate of organic carbon sequestration in deep ocean sediments (Lochte et al., 2003; Dunne et al., 2007). This imbalance between refractory DOC removal and sediment sequestration rates indicates that most of the DOC-derived, abiotically formed particles are mineralized while still suspended in the water column or after falling to the ocean bottom. If so, the conversion of refractory DOC to particles is an important mechanism for transforming recalcitrant organic matter to a more biologically available form. If the extent of refractory DOC removal is a first-order function of time (Figure 5), then the minimum DOC concentrations occurring in the deep ocean should vary with its residence time. A more slowly ventilated deep ocean should result in lowered minimum DOC concentrations while a more rapidly ventilated system will result in elevated minima.

CONCLUDING STATEMENTS

Turning our attention so intently to DOM two decades ago highlighted how little we knew about its role in biogeochemical cycles. Although the elevated concentrations of DOM failed to hold up under the scrutiny of the scientific method, vindicating those shouting "heresy," the renewed focus on DOM resulted in vast new insights that continue to grow. Traditional paradigms of the ocean carbon cycle have been revised as we now recognize DOC as an important export term in the biological pump. Great challenges remain to unlock the secret messages held in the molecular composition of DOM (Hedges, 2002), and to develop tracers for the nonadvective additions of DOM to the deep interior ocean (e.g., by particle dissolution and chemoautotrophy). Advances in these techniques will pull back the next thin sheet of the knowledge onion, exposing the community to new and unanticipated opportunities.

The new highly spatially resolving DOM data contradict the previously held view of an invariant pool of refractory carbon, revealing portions of the DOM pool that are quite dynamic even in the deepest ocean interior and operating on time scales that are greater than can be assessed with traditional biological (incubation) assays. These new DOM data, available to anyone who wishes to work with them (http://cdiac.ornl.gov/oceans/RepeatSections/repeat_map.html), allow the community to pose second-order questions and form testable hypotheses (e.g., regarding the fate of exported DOM and mechanisms of removal). The still-evolving DOM story is a testament to the marine biogeochemistry community's (and its funding agencies') dogged pursuit of new knowledge.

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