Chapter 15

DOC in the Global Ocean Carbon Cycle

Dennis A. Hansell[1]
Bermuda Biological Station for Research, Inc.,
St. Georges
Bermuda

I. INTRODUCTION

Dissolved organic carbon (DOC) makes up the second largest of the bioreactive pools of carbon in the ocean (680–700 Pg C; Williams and Druffel, 1987; Hansell and Carlson, 1998a), second to the very large pool of dissolved inorganic carbon (38,000 Pg C). The size of the reservoir, as well as its positions as a sink for autotrophically fixed carbon and as a source of substrate to microbial heterotrophs,

[1] Present address: University of Miami, Rosenstiel School of Marine and Atmospheric Science, 4600 Rickenbacker Causeway, Miami, FL 33149.

Biogeochemistry of Marine Dissolved Organic Matter

indicates that DOC plays a central role in the ocean carbon cycle. But what is this role, how is it realized, and what are its mechanisms and controls. The fundamentals of these questions have remained unchanged over the past 40 years (Duursma, 1962) and continue to challenge the ocean carbon research community today. A considerable amount of financial and intellectual capital has been expended and significant progress has been made over the past decade.

DOC concentrations in the ocean range from a deep-ocean low of 34 μM to surface-ocean highs of >90 μM (Section II). Biological processes set up this vertical gradient (net production at the surface and net consumption at depth), while certain physical conditions (high vertical stability) are required to maintain the gradient (Section II.A). The bulk DOC in the ocean can be resolved into at least three fractions, each qualitatively characterized by its biological lability (see Carlson, Chapter 4). All ocean depths contain (1) the very old, biologically recalcitrant DOC (see Bauer, Chapter 8). Its distribution is thought to be fairly uniform in the ocean, largely comprising the DOC of the deep ocean. Built upon the recalcitrant DOC at intermediate and upper layer depths is (2) material of intermediate (or semi-) lability (months to years). It is this material that is produced in the surface ocean and then mixed into the main thermocline, thereby reducing the vertical concentration gradient and contributing to carbon export (Section IV). Concentrations of this fraction can be 10–30 μM in the upper ocean, and near zero in the deep ocean. The surface ocean alone contains (3) the highly biologically labile fraction of DOC, with lifetimes of days to months and concentrations of just a few to tens of micromolar of C. This latter material is most important for supporting the microbial heterotrophic processes in the ocean (see Carlson, Chapter 4) and shows high variability seasonally.

In this chapter, the role of DOC in the ocean carbon cycle is considered in its broadest temporal and spatial scales. The chapter begins with an evaluation of the spatial distribution of DOC at the regional and basin scales, in both the surface and deep ocean. In this context, the distribution of DOC relative to the distribution and timing of marine productivity is evaluated. The older data sets reporting DOC distributions are appraised here as well. The next Section evaluates temporal variability, with consideration of how DOC varies seasonally from high to low latitudes. Following the assessment of variability, the net community production of DOC is examined. The focus is on DOC that accumulates for durations with biogeochemical relevance. This Section is followed by an evaluation of the contribution of DOC to the biological pump. We examine the mechanisms and locations of DOC export, and thus develop an understanding of the controls on export. The chapter concludes with priorities for present and future research, as well as a brief synthesis of the findings reported.

Note that organic carbon in the ocean is distributed between the dissolved and particulate (POC) fractions. Summed, these fractions are referred to as total organic carbon (TOC). It is common to measure TOC directly in the water column

(analysis of unfiltered water), even when DOC is the pool of interest, when the POC concentrations are very low relative to the DOC concentrations. This situation is common at ocean depths well below the surface layer (at depths >200 m), as well as in some surface ocean regions where POC concentrations are normally a few micromolar. The latter conditions are found in the oligotrophic ocean and in high-latitude systems during winter. In these situations (deep water and low-POC surface water), TOC serves as a very close approximation to the DOC concentrations. A primary reason for measuring TOC in these waters, rather than measuring DOC directly, is to avoid contamination by handling (filtering, transfers, etc.) the sample. The term DOC is used in this chapter both for true DOC analyses, and when TOC was measured in deep or POC-impoverished surface waters. The term TOC is reserved for use when DOC and POC, measured separately, are summed.

II. DISTRIBUTION OF DOC

A. Spatial Variability at the Basin Scale

During the decades leading up to the 1990s, DOC data were relatively sparse because relatively few laboratories made the measurements. An early body of work that stands as providing some of the greatest spatial coverage of an ocean region is that by Duursma (1962). He conducted extensive DOC surveys in the northern reaches of the Gulf Stream and its offshoots south of Greenland, finding the spatial variability associated with hydrographic features that we would likely find today. Since his early work, the few additional ocean sections occupied in the decades leading to the 1990s produced data of uncertain quality (see discussion by Wangersky, 1978, and below). Consequently, our sense for the distribution of DOC in the ocean has been highly uncertain. In this discussion, findings from recently occupied sections in various ocean basins will be discussed (locations identified in Fig. 1) and some of the older sections evaluated.

1. Upper Ocean Distributions

Meridional sections from the eastern and western South Pacific and the central Indian Ocean show that the highest upper ocean DOC concentrations are typically found in the low to mid latitudes (Fig. 2 [see color plate]). Concentrations decrease into colder water, whether as a horizontal gradient along the surface from low to high latitudes or vertically with increasing depth. Vertical stability provided by the main thermocline of the open ocean supports the accumulation of DOC in the surface waters. Where vertical stability is strong, DOC concentrations are relatively high; where stability is weak, DOC concentrations can remain at low levels (Fig. 2c). The cold, deep waters have the lowest concentrations, and where

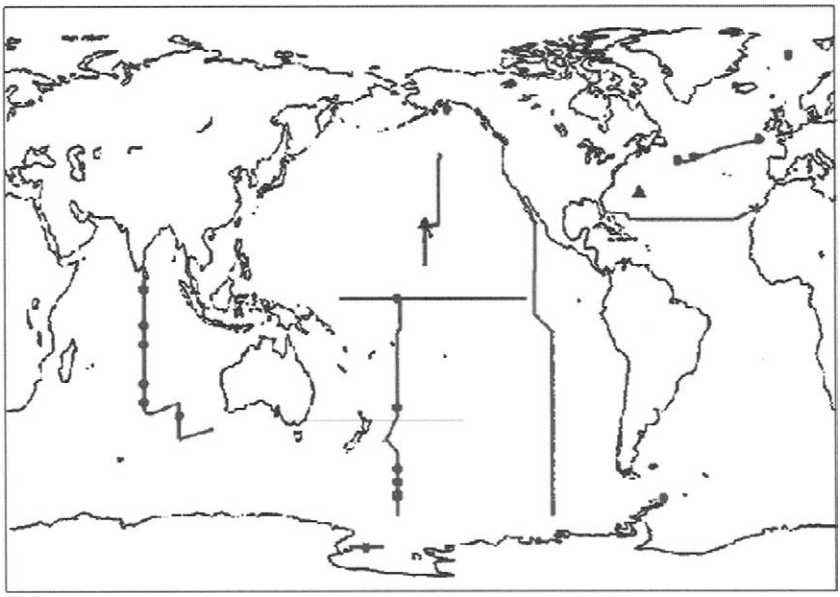

Figure 1 Map depicting locations in the global ocean from which data are shown in this chapter. The solid lines (gray) represent ocean sections; the triangles are the sites of the time-series stations near Bermuda and Hawaii; the filled circles and the triangles are the sites of the deep-water DOC analyses in addition to the time series sites.

these waters ventilate at high latitudes, similarly low DOC values are present (Figs. 2b and 2c).

Where low-DOC, subsurface water mixes to the surface its impact is felt in the surface DOC concentrations. Upwelling sites, both in coastal regions and along the equator, normally have relatively low DOC values at the surface where upwelling is strongest. In the central Equatorial Pacific, DOC is depressed at the surface because of upwelling (note the upward doming of the subsurface DOC contours at the equator; Figs. 2b and 2c). In the central Indian Ocean, where equatorial upwelling is weak, DOC is rather uniform from the subtropical gyre to across the equator (Fig. 2a). DOC along the equator in the Pacific shows the controls by hydrography and biology (Fig. 3 [see color plate]). The Equatorial Undercurrent, near 200 m west of the dateline, has a DOC concentration of $\sim$55 μM (Hansell *et al.*, 1997b). This water is transported to the east, shoaling to near surface in the central and eastern Equatorial Pacific, bringing with it low-DOC water. The return flow of surface water to the west undergoes an increase in DOC (to $\sim$65 μM) due to biological activity. The highest DOC concentrations in Fig. 3 (>70 μM C; largely west of 165° W in the surface 100–120 m) are associated with the Western

Pacific Warm Pool (Hansell *et al.,* 1997b; Hansell and Feely, 2000). The front separating the DOC-enriched Warm Pool to the west and the recently upwelled water to the east varies with the ENSO state, being found further to the west during La Niña conditions (Dunne *et al.,* 2000).

The impact of upwelling on equatorial DOC concentrations exists at coastal upwelling sites as well. Along the coast of Oman in the Arabian Sea, strong upwelling occurs during the Southwest Monsoon. Low surface DOC concentrations are present in coastal water during such periods although productivity can be quite high (Hansell and Peltzer, 1998). Upwelling along the northwest margin of the African continent similarly forces a shoaling of the DOC isolines (Postma and Rommets, 1979). Similarly, Doval *et al.* (1997) reported a decrease in subsurface DOC in northwest Spain due to upwelling.

Ocean margins influenced more by riverine inputs than by upwelling tend to show increases in DOC concentrations. Rivers introduce water with high DOC concentrations (see Cauwet, Chapter 12), thus raising concentrations along the coast. One example is in the Chesapeake Bay outfall, where DOC concentrations increase from 70 μM in the surface Sargasso Sea to >200 μM in the Chesapeake Bay mouth (Bates and Hansell, 1999). Guo *et al.* (1994) reported onshore DOC concentrations of 131 μM off Galveston, Texas, and moderate concentrations of 83 μM offshore in the Gulf of Mexico. Property/property plots of DOC and salinity show the conservative nature of riverine DOC as it mixes with oceanic water. In general, the strength and direction of concentration gradients between the surface open ocean and the coastal ocean depend on the degree of upwelling of low-DOC water from below or invasion of DOC-enriched freshwater from the continent.

Comparing two zonal sections in the North Atlantic provides further evidence for the control physical properties of the water column play on DOC distributions (Fig. 4 [see color plate]). A Section at 24°N shows strongly enhanced DOC concentrations in the upper 200 m (up to 80 μM C), reflecting the strong stratification present in the subtropical gyre. In a more northerly Section, surface DOC is lower (>60 μM C) and the concentration contours are pushed deeper into the water column. Note, for example, the 55 μM DOC contour at 200–300 m along 24°N, but at 200–600 m on the northern Section. This change in contour depths reflects the weaker stratification at higher latitudes, and subsequent downward mixing of the surface produced DOC.

2. Deep-Ocean Distributions

Reports on the distribution and variability of DOC in the deep ocean have been conflicting. Measurements from the 1960s (discussed below) suggested strong, horizontal gradients in DOC. More recently, Druffel *et al.* (1992) reported a modest 5 μM concentration difference between the deep waters near Bermuda and Hawaii. Martin and Fitzwater (1992), in contrast, reported the complete absence of DOC

gradients in the deep ocean. Hansell and Carlson (1998a), in an effort to narrow the uncertainty, surveyed representative sites in the deep ocean (Fig. 1). They found a 29% decrease in DOC concentration from the northern North Atlantic (48 μM in the Greenland Sea) to the northern North Pacific (34 μM in the Gulf of Alaska) (Fig. 5, top). The gradient reflects the export of DOC-enriched (formerly subtropical) water during North Atlantic deep water (NADW) formation (Fig. 5, bottom) and the decrease in DOC (by mineralization and mixing) along the path of deep ocean circulation away from the North Atlantic. The formation of Antarctic bottom water (AABW) does not introduce additional DOC to the deep ocean (see Section IV), so the concentrations remain low near those sites. The small increase in DOC concentrations from the Southern Ocean into the deep South Pacific and Indian oceans is enigmatic and the source unidentified (Hansell and Carlson, 1998a). Possible causes include inputs from marginal seas (Red Sea, Arabian Sea, and Bay of Bengal for the Indian Ocean), inputs due to dissolution of sinking biogenic particles, non-steady-state conditions in the deep-ocean concentration gradients of DOC, and, of course, unidentified processes. The highest deep-water DOC concentrations may be those in the deep Eurasian Basin of the Arctic Ocean (see Anderson, Chapter 14), where concentrations >50 μM C have been reported (Anderson *et al.*, 1994). The sources of this material must be terrestrial runoff and Arctic continental shelf produced DOC (Opsahl *et al.*, 1999; Wheeler *et al.*, 1997).

It is interesting to speculate as to the mechanisms responsible for DOC concentration decreases in the deep ocean. Certainly microbial mineralization and mixing contribute, but, based on our present knowledge, these mechanisms appear to be inadequate. The DOC concentration decreases by 14 μM over the length of the deep limb of the "global conveyor belt," but would the marine microbes we are most familiar with today be satisified with such meager rations over the half millennium required for transport over that distance? The apparent rate of oxidation ($\sim$30 nM year^{-1} over $\sim$500 years), and the amount of energy derived over these several centuries, is miniscule. Perhaps the poorly understood *Archaea,* now known to inhabit the deep ocean, are designed to catabolize recalcitrant DOC at such low rates. Perhaps microbes play only a secondary role, and DOC is removed primarily by coagulation and formation of sinking particles, or it is stripped from the water column by particles passing through the water column. The true mechanisms for DOC loss need to be resolved.

3. Relation to Productivity

Given the surface DOC distributions described here (Fig. 5), of low DOC near sites of upwelling or deep mixing and high values in stratified water, a general observation can be made: upper ocean DOC concentrations are relatively high in oligotrophic waters where regenerated production dominates, and low in systems

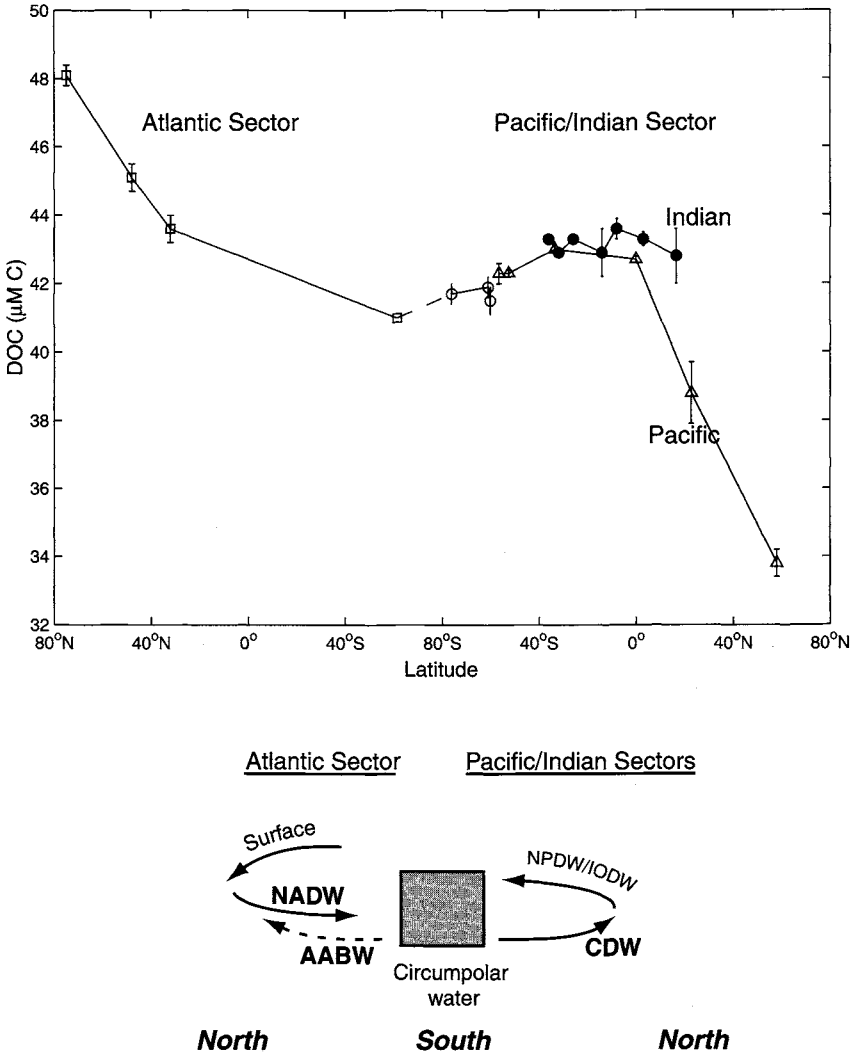

Figure 5 (Top) Distribution of DOC in the deep-ocean. The *x*-axis is viewed in the context of the deep-ocean circulation, with formation in the North Atlantic, circulation around the Southern Ocean, and flow northward into the Indian and Pacific oceans. Station locations in Fig. 1. (Bottom) The general patterns of ocean circulation driving the deep ocean DOC signal. DOC-enriched surface water is introduced to the deep ocean in the North Atlantic. This water moves south as North Atlantic deep water (NADW), to the circumpolar waters of the Southern Hemisphere. DOC-impoverished Circumpolar deep water (CDW) flows north into the Pacific and Indian oceans. Deep return flow to the North Atlantic is via Antarctic bottom water (AABW) and to Antarctica via North Pacific (NPDW) and Indian Ocean deep waters (IODW).

where new nutrients are introduced to the surface. Such a meridional gradient has been reported for the Equatorial Pacific (Tanoue, 1993), the South Pacific (Hansell and Waterhouse, 1997; Doval and Hansell, 2000) and the North Atlantic (Duursma, 1962; Kähler and Koeve, 2001) and is evident in Fig. 2. The regenerated vs new production nature of these systems is a reflection of the community compositions within them. The mechanisms by which community composition controls DOC concentrations are not understood (see Carlson, Chapter 4). DOC concentrations are also controlled by the vertical stability of the water column. The highest DOC concentrations in the open ocean are normally found where stratification of the water column is highest (Hansell and Waterhouse, 1997; Hansell and Feely, 2000). This finding suggests that stability facilitates the retention of DOC in the upper ocean. The lowest DOC concentrations, to the contrary, exist where DOC-depleted subsurface water is introduced to the surface, either by vertical mixing or upwelling. These high nutrient sites can experience large but brief seasonal increases in DOC concentrations, however (see below).

Because of the role of ocean stratification in controlling DOC concentrations, a positive correlation between DOC concentrations and primary productivity (an oft predicted relationship) is absent in much of the oligotrophic, open ocean. Menzel and Ryther (1970) reported the absence of this correlation early and evidence for the generality will be given using data from the Sargasso Sea later in the chapter (Section II.B.2). In fact, in the highly stratified portions of the open ocean, DOC broadly correlates positively with temperature (Hansell and Waterhouse, 1997; Doval and Hansell, 2000), another sign of the importance of physical control on concentrations. At higher latitudes, however, where DOC concentrations are depressed during the winter, elevated DOC values indeed follow springtime elevation of primary productivity (Börsheim and Myklestad, 1997; Chen *et al.*, 1996; Carlson *et al.*, 2000). This positive relationship between primary production and DOC was reported early by Duursma (1963) and has been discussed elsewhere (Williams, 1995). In high-latitude systems, increased water column stability favors both phytoplankton growth and DOC accumulation in the upper ocean. The data indicate that low-latitude, highly stratified environments behave very differently than high-latitude environments in terms of the coupling between DOC dynamics and primary production. So, while their observations are in apparent conflict, both Menzel and Ryther (1970) and Duursma (1963) were correct about the relationship between DOC and productivity; but they were correct specifically for the hydrographic systems they were evaluating.

4. Historical Data

With the onset of discussions surrounding the use of the high-temperature combustion (HTC) systems for DOC analysis (Sugimura and Suzuki, 1988), much attention has been paid to whether or not the earlier data are accurate and, therefore,

of value (Sharp, 1997). A comparison of what we find in the ocean today with that reported in earlier decades shows some older data and findings to have serious flaws. A comparison of historical and recent data from the surface ocean cannot be easily made because of the wide natural variability in those waters (see below). The most useful comparisons between historical and recent data are made in the intermediate and deep ocean, where significant changes in concentration over a few decades (the sampling interval) are unlikely.

Menzel (1964) reported DOC concentrations in the intermediate depths (400–800 m) of the Arabian Sea and western Indian Ocean to range from 0.4 to 1.6 mg/L (30 to 130 μM DOC). This wide range is not reproducible anywhere in the intermediate or deep ocean using modern techniques, nor was it evident during the US Joint Global Ocean Flux (US JGOFS) program in the Arabian Sea during 1995 (Hansell and Peltzer, 1998). Menzel and Ryther (1970) also reported a very unlikely DOC concentration doubling at all depths >1000 m between the waters northeast and southeast of South America. Romankevich and Ljutsarev (1990), reviewing investigations conducted by the Soviet Union, reported DOC off Peru at 500–1000 m to be an unlikely 1 mg/L (~83 μM). Soviet measurements in the deep Bay of Bengal exceeded 1 mg/L as well. These latter DOC concentrations are probably high by a factor of two. Williams *et al.* (1980) reported DOC concentrations in the central North Pacific a few meters off bottom (5650 m) that were elevated by twofold relative to the values at 2000–5000 m. Such a strong DOC gradient, indicative of sedimentary input of DOC to the bottom layer, has not been confirmed using modern techniques and extensive near-bottom surveys. Recent data, using modern HTC techniques, should be viewed with caution as well. Dileep Kumar *et al.* (1990) reported a strong DOC concentration gradient from the central Arabian Sea to the western Indian Ocean, increasing from 100 to 300 μM at 2500 m. The high DOC concentrations and wide range reported are unlikely to be accurate representations of that system.

B. Temporal Variability

The temporal variability of DOC concentrations in the surface ocean has been noted since the earliest days of the measurement. Duursma (1963) reported a twofold increase in DOC concentrations in the North Sea, from winter lows of 0.8 mg/L (~66 μM) to spring and early summer highs of 1.8 mg/L (~150 μM). The increase in DOC concentrations started some weeks after the spring phytoplankton bloom. Holmes *et al.* (1967) reported large spikes in DOC concentrations, from a baseline of 1 mg/L up to 4–5 mg/L (330–415 μM), during several red water dinoflagellate blooms off La Jolla Bay, California. Here, too, the DOC peaks followed the decline of the blooms. Williams (1995) evaluated the seasonal accumulation of DOC using data from Parsons *et al.* (1970), Banoub and Williams (1973),

and Duursma (1963), suggesting that the accumulation of C-rich dissolved organic matter resulted from nitrogen limitation. The possible role of nutrient depletion in the generation of DOC is discussed below. (See Carlson, Chapter 4, for a more complete listing of publications reporting temporal variability of DOC.)

1. High Latitudes

Strong seasonal increases in DOC concentrations associated with phytoplankton blooms appear to be characteristic of systems that receive high input of new nutrients over the winter periods. The waters of the Ross Sea polynya, for example, undergo deep mixing over the winter such that nitrate concentrations exceed 30 μM prior to the spring bloom (Bates *et al.,* 1998). DOC concentrations increase in the surface layer from winter lows of 42 μM to summer highs of 65–70 μM (Carlson *et al.,* 1998). High southern latitude systems can experience large increases in DOC concentrations (tens of micromolar C), with the wintertime baseline concentration as low as the much deeper waters (Carlson *et al.,* 2000; Wiebinga and de Baar, 1998; Kähler *et al.,* 1997). The Ross Sea undergoes DOC concentration increases of 15–30 μM where the *Phaeocystis* and diatom blooms are particularly strong (Carlson *et al.,* 2000). Where the blooms are small because of various controls on plant growth (deep mixing, iron limitation, etc.), the DOC concentrations remain low (e.g., over the Ross Sea shelf break, with a gain of <5 μM relative to winter) (Sweeney *et al.,* 2000). The North Sea (Duursma, 1963), as well as other high-latitude/strong-bloom regions (e.g., the Norwegian Sea, Börsheim and Myklestad, 1997), likely behaves similarly to the Ross Sea. In Trondheimsfjord, Börsheim *et al.* (1999) reported a $>2\times$ increase in DOC concentrations during the summer. It is apparent, though, that the winter lows of DOC concentrations in the high northern latitudes are not as low as the local deep-water values (in contrast to the conditions found in the Southern Ocean). This finding holds true along 20°E in the North Atlantic, where Körtzinger *et al.* (2001) reported the winter low DOC to be 53 μM C, well above the deep-ocean values in the region. The more physically stratified nature of the northern systems prevents full water column overturn and homogenization of the DOC each winter.

2. Mid-latitudes

The more oligotrophic, mid-latitude zones of the ocean do not show the same seasonality (in either strength or direction) as the high latitudes or other nutrient-rich areas. In the Sargasso Sea, where convective overturn during the winter introduces small amounts of new nutrients to the euphotic zone and phytoplankton blooms follow (Michaels and Knap, 1996), the seasonality of DOC in the surface ocean contrasts that found at high latitudes (Carlson *et al.,* 1998; Hansell and Carlson, 2001a). Overturn of the water column coincides with the spring bloom

there because adequate light is present at these mid latitudes. The effect is to mix low DOC subsurface water upward, thereby reducing the DOC concentrations during the periods of highest primary productivity. Once stratification reasserts itself with warming of the surface ocean, and the bloom terminates, DOC concentrations rebuild to normal summer levels (Fig. 6 [see color plate]). The concentration change from the annual low to the annual high is only 3–6 μM, a very small range compared to high-latitude systems. The lowest winter concentrations remain well above the deep-water values. While the DOC concentrations in the Sargasso Sea are lowest during the winter overturn/spring bloom period, the same cannot be said for the integrated DOC stocks. Relatively deep convective overturn maintains the low surface DOC concentrations but the bloom still supports the net production of as much as 1–1.5 mol m^{-2} of DOC over the upper 250 m (Fig. 7; Carlson *et al.*, 1994; Hansell and Carlson, 2001a [see color plate]). This increase in DOC stock is as large as that seen in the much more productive Ross Sea (Carlson *et al.*, 2000).

DOC and bloom dynamics in the Arabian Sea during the NE Monsoon are similar to that in the Sargasso Sea. Convective overturn in the Arabian Sea, forced by cool dry winds off the Tibetan plateau, mixes moderate amounts of nutrient into the euphotic zone. There, too, DOC concentration changes are not large during the bloom, but the increase in DOC stock can be 1.5–2 mol C m^{-2} (Hansell and Peltzer, 1998).

It is interesting that while the seasonal range for DOC in the western Sargasso Sea (at ~31°N) is only 3–6 μM, the seasonal range at the same latitude in the eastern North Atlantic can reach 10–20 μM (Körtzinger *et al.*, 2001). The western North Atlantic is generally warmer and more stratified than in the east, suggesting differing community composition and productivity between the sites. This follows from the gyre circulation patterns: the northward flow of water in the west, from the warm equatorial region to higher latitudes, lends itself to high vertical stability and highly oligotrophic conditions; the southern flow in the east, carrying cooler water from the north, would lend itself to less stability and less oligotrophic conditions. It may be that the more stable system in the west experiences less primary productivity and net DOC production than the system in the east. Physical characteristics of the systems and the biological regimes they support are centrally important in controlling DOC dynamics.

3. Low Latitudes

Low-latitude systems that do not undergo winter freshening of the surface layer do not show seasonality in DOC concentrations. The waters at Station ALOHA, north of Hawaii at 23°N, represent such a system. There, variability in DOC occurs at interannual time scales, but there is no recurring trend with seasons (Fig. 6). Church *et al.* (2001) reported a net accumulation from 1993 to 1999 of a DOM

pool that was enriched in C and N, relative to P. These long-term changes may be a manifestation of the broad, ecosystem-wide shift from N to P limitation described by Karl (1999). No such shifts have been noted in the Sargasso Sea, hence the near constancy in summer time DOC highs from year to year. Note that the surface DOC concentrations at ALOHA are much higher than the highs at BATS (Fig. 6) and higher than any values found along 24°N in the North Atlantic (Fig. 4). Why this difference exists between these similarly low latitude zones of the North Atlantic and North Pacific is unknown. Community composition may be key, but an evaluation has not been conducted.

4. Deep Ocean

Whether or not there is measurable temporal variability of DOC in the deep ocean remains debatable. Hansell and Carlson (2001a) did not resolve DOC variability in the deep Sargasso Sea over 6 years of time series measurements. Similarly, Hansell and Peltzer (1998) found no variability in the deep Arabian Sea over a single year, even through periods of very high sinking particle flux. Bauer *et al.* (1998), in contrast, reported significant (8 μM) long-term (2-year) changes in DOC in the deep eastern North Pacific. They tied these variations to natural variability ("patchiness") and exchanges with sinking POC. Why there may be variability at this site and not at the others studied needs to be resolved.

5. Short-Term Biological Events

Further variability in DOC concentrations can be expected to occur with biological "events." Examples are blooms of red tide organisms described by Holmes *et al.* (1967) and of diazotrophs. Onset of enhanced nitrogen fixation rates in open-ocean systems can increase DOM stocks considerably. Karl *et al.* (1997) reported organic nitrogen concentration increases of several micromolar which should coincide with several tens of micromolar increase in DOC. A case in point is the western tropical South Pacific, where relatively high DOC is present under the zone of the atmospheric South Pacific Convergence Zone. Hansell and Feely (2000) suggested that the excess precipitation in this system increased vertical stability, thereby favoring nitrogen fixers and in turn increasing concentrations of DON and DOC.

Near the continental margins, DOC concentrations will vary with the strength of DOC-enriched riverine inputs or coastal upwelling, both of which vary seasonally (Cauwet, Chapter 12; Hansell and Peltzer, 1998). High riverine input may result in high-DOC concentrations; strong upwelling reduces the DOC concentrations. Zones of equatorial upwelling similarly exhibit the lowest DOC concentrations during strong upwelling (e.g., La Niña), and the highest values during reduced upwelling (e.g., El Niño; Peltzer and Hayward, 1996). In this way, physical stability plays a major role in controlling DOC concentrations both along the margins, in

the open ocean and in equatorial upwelling systems (Carlson and Ducklow, 1995; Hansell and Waterhouse, 1997; Tanoue, 1993).

6. Summary

Our present understanding of seasonal variability in DOC can be summarized here: At high latitudes, where spring blooms are intense, we expect to see large DOC concentration changes. Because the winter DOC concentrations are low in these high-latitude systems, the highest concentrations during summer may be no higher than the summer highs in the low-latitude gyre systems, but the concentration change between seasons may be large. However, the large increases in concentration do not necessarily translate into large accumulations of DOC stock (vertically integrated loads of DOC) because of the normally shallow euphotic zones in these highly productive systems (high concentrations but over little depth). In mid-latitude open-ocean regions, such as the Sargasso and Arabian Seas, where convective overturn introduces moderate nutrient loads, DOC concentration ranges between seasons can be relatively small, though the change in integrated stocks can be a relatively large signal (comparable to the change in DOC stock in the Ross Sea). The overturning water column mixes the DOC too deeply for a strong surface accumulation to occur, as found in blooms occurring in more stratified systems but the small concentration change over large depths results in significant increase in stock. At mid-latitude coastal sites with significant winter recharge of surface nutrients, DOC seasonality will be strong. Upwelling reduces the DOC concentrations while high riverine inputs increase them. At low-latitude sites where spring blooms are absent, no seasonality is evident; but, as with all ocean regions, interannual variability exists.

The DOC that accumulates each year at mid-latitudes has a lifetime exceeding the season in which it was produced, so it can be transported elsewhere with surface currents, or be available for export during the subsequent winter overturn events. At higher latitudes, the seasonally produced DOC is seen to have a lifetime shorter than that of the season of production; thus it undergoes net consumption by microbes once primary production is reduced with the onset of Fall conditions. This material is not as available for export (see Section IV.A).

III. NET COMMUNITY PRODUCTION OF DOC

DOC is produced on a daily basis as part of the primary and secondary production systems in the surface ocean. Most of the DOC released is mineralized on the time scale of hours to days. For DOC to play a role in the ocean carbon cycle beyond serving as substrate for surface ocean microbes, it must act as a reservoir for carbon on the time scales of ocean circulation. This it does, given that the

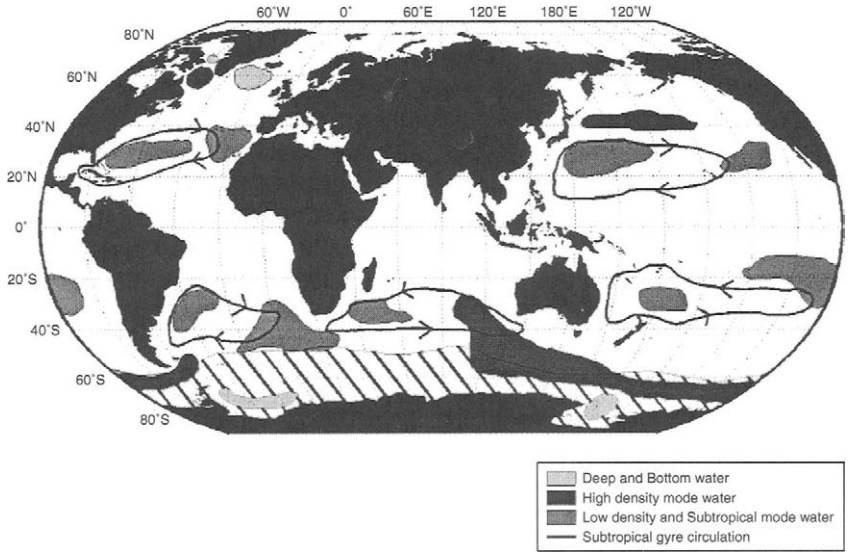

Figure 8 Distribution of sites of water column overturn (from Talley, 1999), general patterns of surface circulation in the subtropical gyres, and proposed distribution of *exportable* DOC. Overlap in the distribution of *exportable* DOC (background field of white) and sites of ocean ventilation (sites colored by gray scale) favors DOC export; a lack of overlap precludes export. The waters of the Southern Ocean (slanted stripes) are without *exportable* DOC present, so where these waters overlap sites of ventilation, little export is expected.

production and accumulation of DOC in the surface ocean has been demonstrated (Figs. 2–8). The rates of, and controls on, the net production of DOC, topics not well understood at this time, are the focus of this section.

Because so few DOC data exist, particularly from ocean systems for which accumulation has been evaluated, it is useful to normalize estimates of DOC accumulation to a more broadly available and easily measured variable. DOC accumulation as a function of net community production (NCP) has proven useful in this way (Hansell and Carlson, 1998b; Körtzinger *et al.*, 2001). NCP occurs when autotrophic production exceeds heterotrophic consumption, such as during a spring bloom. It is a process that largely results in the export of carbon and new nitrogen from the euphotic zone as sinking biogenic particles and in this way is analogous to new production (Dugdale and Goering, 1967). If DOC accumulates, then DOC too is a sink for NCP.

NCP is estimated most directly by measuring the biological drawdown of the reactants (dissolved inorganic carbon and/or nitrate) or as the flux of the products (i.e., accumulation of DOC, suspended POC, export of sinking biogenic particles,

and contributions by migrating zooplankton). The Section above on temporal variability of DOC sheds light on the net production of DOC. As a rule, oceanic regions showing seasonality of DOC concentrations are experiencing some transfer of NCP into the DOC pool.

A. Evidence for Net Production of DOC

Seasonal increases of DOC stocks in the Ross Sea indicate that 8–20% of NCP in the polynya system accumulates each growing season as DOC (Bates *et al.,* 1998; Carlson *et al.,* 2000; Hansell and Carlson, 1998b; Sweeney *et al.,* 2000). The balance of NCP is lost to the deep ocean as sinking biogenic particles, mostly *Phaeocystis* and diatoms. Annual rates of NCP in the Ross Sea polynya are 6–14 mol C m^{-2}, so net DOC production of 1.2–2 mol C m^{-2} occurs over the growing season (Bates *et al.,* 1998; Carlson *et al.,* 2000; Sweeney *et al.,* 2000). The net production of DOC in the Ross Sea is about that in the Sargasso Sea (1–2 mol C m^{-2}; see above), but the Sargasso Sea has a much lower annual rate of net community production.

The rate of DOC production in the Ross Sea, normalized to NCP, is similar to that found in the Equatorial Pacific. Estimates of net DOC production as a percentage of NCP in the central Equatorial Pacific range from 6 to 40%, with most estimates near the 20% level (Archer *et al.,* 1997; Hansell *et al.,* 1997a,b; Zhang and Quay, 1997). These values from the Equatorial Pacific are similar to the Equatorial Atlantic (20%; Thomas *et al.,* 1995), but significantly lower than prior estimates in the Equatorial Pacific by Murray *et al.* (1994), Feely *et al.* (1995), and Peltzer and Hayward (1996). Those latter authors estimated net DOC production closer to 75% of NCP, but those findings have been challenged (Hansell *et al.,* 1997b; Zhang and Quay, 1997). Noji *et al.* (1999) suggested that more than half of NCP in the Greenland Sea accumulated as DOC, high compared to findings from other nutrient-rich sites. Alvarez-Salgado *et al.* (2001) reported that 20% of net ecosystem production accumulated as DOC in a coastal upwelling environment along the Iberian margin in the North Atlantic. This rate is very similar to that reported for the Equatorial Pacific and the Ross Sea.

Net DOC production in the Ross Sea, the Equatorial Pacific and the Iberian margin takes place when the conditions are right for net autotrophy. In the Ross Sea, this occurs when vertical stability and light are available, while in the Equatorial Pacific and the coast of Spain light becomes available following upwelling. At these three sites, vertical stability is relatively strong during the periods of net production. The Sargasso Sea contrasts those systems. Light is generally available year round but nutrients are not, so a *reduction* in vertical stability (convective overturn of the water column and entrainment of nutrients) is required for net autotrophy. A representative year (July 1994 to July 1995) for DOC in the Sargasso

Sea is useful for demonstrating net DOC production (Fig. 7). Winter overturn and mixing of the water column was both the cause of concentration reductions and the trigger for net DOC production each year following nutrient entrainment and subsequent new production (Carlson *et al.,* 1994; Hansell and Carlson, 2001a). The net production of DOC at the BATS site varies interannually as a function of the maximum in the winter mixed layer depth. The greater the vertical mixing (and nutrient entrainment) in the Sargasso Sea, the greater the net production of DOC (Hansell and Carlson, 2001a). In winter 1995 (Fig. 7), the DOC stock increased by 1.4 mol C m^{-2}in response to maximum mixing depths of 260 m (note the net production of DOC in the upper 250 m of the water column; Fig. 7b). In subsequent years experiencing shallower maxima in mixed layer depth (<220 m), DOC stocks increased <0.7 mol C m^{-2} during the overturn event (Hansell and Carlson, 2001a).

For the 1995 spring bloom, net DOC production was estimated to be 59–70% of the NCP (Hansell and Carlson, 1998b). This high rate does not hold for the entire year though. Much of the DOC produced during overturn and then mixed into the subsurface layers is remineralized upon restratification (note the rise and fall in integrated stocks of DOC at 100–250 m; Fig. 7b). Indeed, NCP continues throughout the summer and fall periods (Steinberg *et al.,* 2001), while DOC concentrations remain relatively static (no net production of DOC). As such, net DOC production reduces to ~8% of NCP on an annual basis. Left unanswered is why so much of the NCP during the bloom accumulates as DOC, compared to the much lower NCP-normalized accumulation of DOC in the Ross Sea and the Equatorial Atlantic and Pacific. Community compositions and their responses to physical dynamics vary between these systems, and the answer likely lies in those variables (Carlson *et al.,* 1998; Hansell and Carlson, 1998b).

B. Regional and Global Estimates for Net Production of DOC

As mentioned in the introduction to this Section, the value of normalizing the DOC accumulation rates to NCP is that NCP is a variable for which there is high data density. We can use the findings developed here on net DOC production, along with existing estimates for new (nitrate-based) production in various ocean regions (Chavez and Toggweiler, 1995), to estimate annual rates of DOC accumulation (Table I). The ratio of net DOC production to new production for each ocean region was assigned given what is known for the few systems (reviewed above) in which data exist. As would be expected, the regions of highest new production, such as tropical and coastal upwelling areas, contribute most to net DOC production globally. The weakest sites for the entrainment of nitrate to the

Table I

Estimates of Annual Net DOC Production Based on Regional Estimates of New Production (Chavez and Toggweiler, 1995)

Region	New production (pg C year^{-1})	ΔDOC:NP	Net DOC production (pg C year^{-1})
Tropical open ocean			
Upwelling	1.5 (21%)	0.2	0.3 (24.6%)
Turbulent Mixing	0.7 (9.5%)	0.1	0.07 (5.7%)
Southern ocean	1.1 (15.5%)	0.12	0.13 (10.8%)
Subarctic gyres	0.3 (4%)	0.15	0.04 (3.7%)
Coastal upwelling	0.8 (11%)	0.2	0.16 (13.1%)
Monsoonal	0.4 (5.5%)	0.2	0.08 (6.6%)
Subtropical gyre	0.5 (7%)	0.1	0.05 (4.1%)
Continental margins			
Western boundary currents	0.7 (9.5%)	0.2	0.14 (11.5%)
Estuarine influenced shelves	1.2 (17%)	0.2	0.24 (19.7%)
Total	7.2		1.2 (17% of total NP)

Note. Values in parentheses represent percentages of the global estimate. Adapted with permission from Hansell and Carlson (1998b).

surface (such as the subtropical gyres) are the weakest in DOC net production. Net DOC production, based on this analysis, is the sink for about 17% of global new (nitrate based) production each year. A recent estimate for global new production is ~7 Pg C year^{-1} (Chavez and Toggweiler, 1995; Fung *et al.*, 2000; Lee, 2001), so net DOC production in the global ocean could be ~1.2 Pg C year^{-1}. This estimate is for nitrate-based new production, thus excluding other forms of new production such as nitrogen fixation. We do not at present know the fraction of carbon fixed by active diazotrophs accumulating as DOC.

C. Nutrient Depletion and Net Production of DOC

One apparent axiom of net DOC production has been that nutrient depletion drives high rates of DOC production. This perception was based on numerous batch phytoplankton culture experiments where nutrients were allowed to run to very low values. When nutrients were present, and the plants were in the exponential growth phase, DOC release was very small; when nutrients were depleted and the plants went into stationary phase, carbon fixation exceeded the N stocks available to support biomass growth, so C-rich DOC was released (e.g., Goldman *et al.*, 1992). Because of these results, it has been assumed that nutrient depletion forces high levels of DOC production everywhere in the ocean. It would follow

that high levels of DOC in oligotrophic systems were expected because of nutrient limitation. Such arguments can be tested for relatively oligotrophic systems using the time-series data from the Sargasso Sea (Fig. 6). As outlined above, net DOC production took place largely while rates of primary production were highest (the spring bloom period). During the summers, when nutrients were most depleted, there was no further accumulation of DOC; nor was there a major enhancement in bacterial respiration rates relative to primary productivity to indicate high release of labile DOC (Carlson *et al.*, 1996). The data from the Sargasso Sea indicate that nutrient depletion alone does not drive high rates of DOC production. Indeed, Parsons *et al.* (1970) reported DOC accumulation during the summer in the Strait of Georgia, but without depletion of the macronutrients (nitrate went as low as 7 μM only).

Where the culture experiments fail to reflect nature is in their inability to support reasonable changes in community composition. In nature, new assemblages of autotrophs will develop given changes in the nutrient forcing, and the stress of nutrient depletion on the summer population will be dissimilar to that felt by the spring bloom population. It is apparent that nutrient depletion alone is not adequate to force significant net production of DOC in the open ocean.

IV. CONTRIBUTION OF DOC TO THE BIOLOGICAL PUMP

A. Evidence for DOC Export

DOC plays perhaps its most important role in the biogeochemistry of the ocean carbon cycle when it contributes to the biological pump (Copin-Montégut and Avril, 1993; Carlson *et al.*, 1994; Ducklow *et al.*, 1995). The export of sinking biogenic particles has long been understood to drive respiration in the ocean interior and to help maintain the ocean's strong vertical gradient of inorganic carbon. The contribution of DOC to the biological pump has been debated for several decades, and is only now being resolved. Menzel (1970) stated that deep-ocean changes in oxygen and nutrients could not be attributed to the long-term *in situ* decomposition of dissolved organic matter. He acknowledged that some published data suggested that 15% of the total oxygen consumption was due to oxidation of DOC, but he thought this value to be unrealistic. Craig (1971), in a direct counter to these findings, suggested that one-third of the oxygen consumption in recently formed North Atlantic Deep Water could be due to DOC oxidation. While he did not have faith in the accuracy of the DOC data available at the time, and he used calculations that he described as "brute force," he was satisfied that deep DOC oxidation was substantive. Ogura (1970) took a refined approach to the question. He evaluated property/property plots of DOC and apparent oxygen utilization (AOU) along

isopycnal surfaces in the western North Pacific, reporting that one-third of the AOU was due to DOC consumption. He noted that the contribution was restricted to the upper ocean (<500 m); DOC oxidation was not resolvable in the deep waters. Kähler and Koeve (2001) argued that DOC is unlikely to be substantial in the export of biogenic material to the deep sea; otherwise the deep-ocean C:N ratios should deviate from Redfield stoichiometry as required by the input of C-enriched dissolved organic matter.

The export of DOC in the ocean is a consequence of its accumulation in the surface ocean (Fig. 2), redistribution with the wind-driven circulation, and eventual transport to depth with overturning (thermohaline) circulation at high latitudes and subduction in the subtropical gyres. Thermohaline circulation refers to the vertical movement of water that takes place when its density increases by a significant change of temperature or salinity. The most important sites for ventilation of the intermediate and deep ocean are located in the North Atlantic (Labrador Sea Intermediate Water and North Atlantic Deep Water formation sites), the North Pacific (site of North Pacific Intermediate Water formation), the area around Drake Passage (Antarctic Intermediate Water formation), and around Antarctica (Antarctic Bottom Water formation) (Fig. 8). Water mass formation at these sites occurs primarily during winter. Subduction occurs year round in subtropical gyres due to Ekman pumping of the surface layer. The upper thermocline ventilates by this process. Because the mixed layer density and depth reach their local maxima at late winter, the water subducted into the permanent thermocline has properties that are strongly biased toward the late winter values (Stommel, 1979). As a rule, DOC export with ventilation of the ocean occurs if there is a vertical DOC concentration gradient at the onset of overturn. In such a situation, DOC accumulated at the surface undergoes net transport downward. Where vertical DOC gradients are weak or absent, there is little net downward movement of DOC with overturn and subduction.

1. Export into the Upper Pycnocline

The main thermoclines of the major ocean basins ventilate following buoyancy loss (via cooling) in DOC-enriched warm water previously transported poleward in the western boundary currents. Equatorward subduction beneath the less dense surface waters results in the export of DOC along isopycnal surfaces, a process evaluated by Ogura (1970), Doval and Hansell (2000), and Abell *et al.* (2000). Establishing the contribution of DOC to export is perhaps best examined by normalizing the gradients in DOC concentrations to the gradients in AOU. AOU derives from the mineralization of sinking biogenic particles and subducted DOC and so reflects the total oxidation of biogenic carbon along specified surfaces. A representative isopycnal surface along 170°W in the western South Pacific is that of σ_θ26–26.5 (Doval and Hansell, 2000). DOC concentrations along that isopycnal decreased away from the sea surface commensurate with an increase in AOU,

such that oxidation of DOC drove ≈40% of the AOU. Mineralization of sinking biogenic particles formed overhead in the euphotic zone drove the balance of the AOU. In the isopycnal surfaces lying between σ_θ23.5 and 27.0 along 170°W, 21–47% of the AOU was driven by DOC oxidation (Doval and Hansell, 2000). Like Ogura's (1970) findings in the North Pacific, DOC oxidation along 170°W was restricted to the upper 500 m; at greater depths, only biologically refractory DOC remained in the water column so sinking particles alone drove additional AOU development. Guo *et al.* (1994) similarly found that 20–30% of AOU may be due to DOC mineralization in the Gulf of Mexico.

Subtropical mode water formation is a strong form of subduction ventilating the upper thermocline primarily during winter at mid-latitudes. Such a process is important to ventilation of the western North Atlantic in the north Sargasso Sea. The waters of the Sargasso Sea near Bermuda are strongly stratified through much of the year. During the fall and winter months, regular storm fronts deliver cold, dry winds that cool the surface water, causing a deepening of the mixed layer by convective overturn. Overturn of the water column, when deep enough (~250 m), ventilates Worthington's (1976) 18° Mode Water. DOC near Bermuda is present at its highest concentrations during the long warm (summer) periods (Fig. 7). At overturn, DOC concentrations and stocks at depths >100 m increase (Fig. 7), reflecting the downward mixing of the carbon; its disappearance with time at those depths reflects net microbial mineralization and removal by horizontal advection and mixing into mode water. During the overturn periods of 1992–1998, DOC export near Bermuda ranged from 0.4 to1.4 mol C m^{-2}, rates representing 15 to 41% of the total biogenic carbon mineralized annually in the upper 400 m of the water column (Carlson *et al.*, 1994; Hansell and Carlson, 2001a).

2. Export into the Deep Pycnocline

Ventilation of the deep pycnocline occurs with the formation of intermediate water masses. At present few data exist for evaluating DOC export during this process. An exception is DOC export with North Pacific intermediate water (NPIW) formation (Hansell *et al.*, 2002). NPIW forms by brine rejection in the Sea of Okhotsk north of Japan. It is delivered to intermediate depths (400–1000 m and bounded by σ_θ26.6–27.4) of the subtropical North Pacific as a mixture of recently ventilated, relatively fresh subpolar (Oyashio) water and older, more saline subtropical (Kuroshio) water of the same density range. New NPIW is transported eastward from the site of subduction east of Japan as a low-salinity tongue, with eventual circulation into the intermediate layers of the subpolar and subtropical gyres, thus replenishing those systems (Talley, 1997). Data collected at 1000 m (≈27.4 σ_θ), between 10 and 45°N along 152°/158°W (Fig. 1), demonstrate the export of DOC-enriched subpolar water and its impact on DOC distribution in the NPIW of the subtropical gyre (Fig. 9). The samples were from deep in the

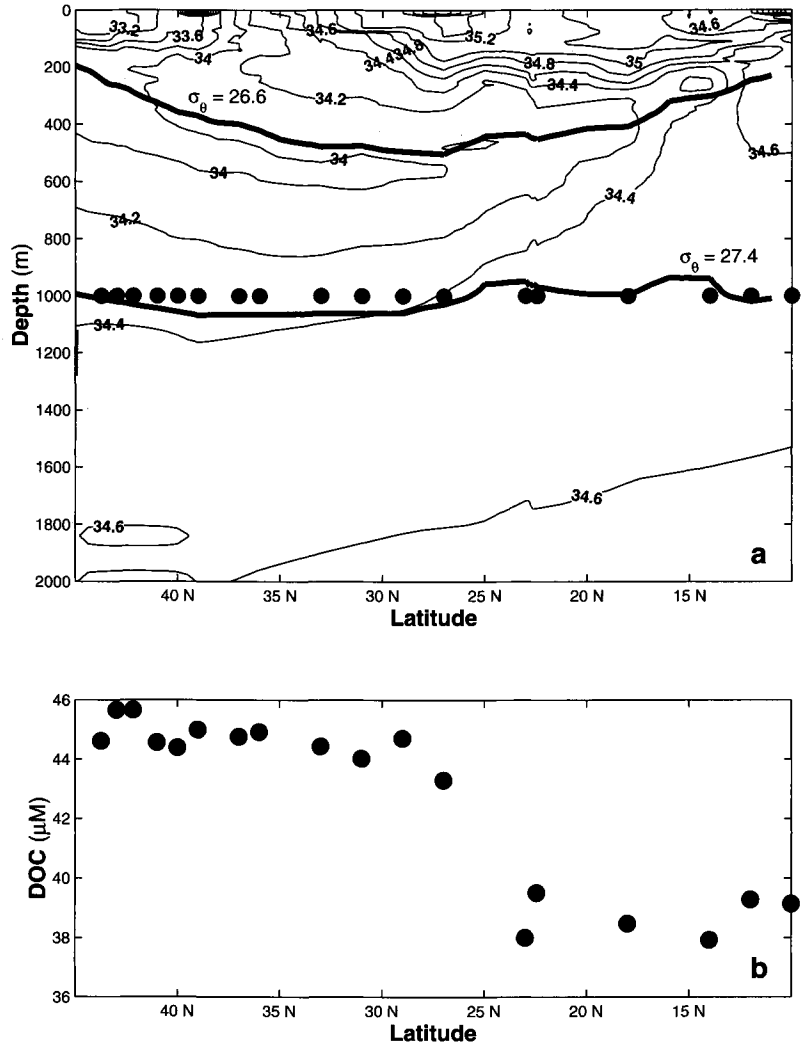

Figure 9 Evidence for the export of DOC with formation of new North Pacific intermediate water. (a) Salinity contours in the upper 2000 m along 152°/158°W in the North Pacific, overlain (bold) by σ_θ surfaces (26.6 and 27.4) indicating the upper and lower bounds of NPIW. Filled circles indicate sample locations for DOC (b) along the section. Note the freshening of the water column to the north, where the influence of new NPIW is strongest.

NPIW, across a salinity gradient of high subpolar (fresh) water influence in the north and high subtropical (saline) water influence in the south (Fig. 9a). Samples comprising subtropical water (south of 25°N and salinity >34.4) had a mean DOC concentration of 38.7 ± 0.7 μM (Fig. 9b). Waters to the north, with a greater subpolar contribution (salinity <34.4), had a mean of 44.7 ± 0.6 μM, for a 15% enrichment. The evidence for DOC export with NPIW formation is clear.

3. Export to the Deep Ocean

Removal of carbon from exchange with the atmosphere is greatest with DOC export associated with deep- and bottom-water formation. Evidence for the export of DOC with NADW formation is the strong meridional gradient in deep-water DOC, along the proximal path of the deep western boundary current (Fig. 5; Hansell and Carlson, 1998a). Data from 75°N in the deep Greenland Sea are presently our best representation for concentrations of DOC in the source water for NADW formation (48 μM). NADW overrides and entrains northward-flowing Antarctic bottom water (AABW), of a largely Weddell Sea source and with a DOC concentration of 41 μM (Fig. 5). Mixing of these two source waters, along with microbial degradation, results in a DOC concentration gradient in the Atlantic Ocean.

AABW forms in the cyclonic gyres that develop south of the Antarctic Circumpolar Current system, particularly the Weddell and Ross Sea gyres. The contribution of AABW formation to DOC export appears to be very small. The best studied of the high-latitude cyclonic gyre systems with regard to DOC distributions is the Ross Sea (Carlson *et al.*, 1998, 2000). During the 1997 austral summer season in the Ross Sea, DOC concentrations in the surface 50 m reached >20 μM above background in certain areas. By the time of winter overturn in fall, biological mineralization of the DOC reduced the concentrations to a mean of <5 μM above background. The vertical export of this material, if still remnant at the time of complete overturn, would contribute to only 2% of the annual export of particulate plus dissolved organic carbon in the Ross Sea (Sweeney *et al.*, 2000). Mineralization of the DOC prior to overturn prevented it from making a major contribution to export in this system.

Evaluating horizontal gradients of DOC in the deep layers between the Ross Sea and the circumpolar deep water is a second test for DOC export with AABW formation. Because DOC exported with NADW formation demonstrated a strong gradient along the path of advection, so too should a gradient be present from the sites of AABW formation to the deep circumpolar waters if export is significant. The deep Ross Sea (data from 76°S in the Pacific sector of Fig. 5) has a DOC concentration (42 μM) that is indistinguishable from the concentration in the circumpolar water to the north at 60°S (Fig. 5). The lack of a gradient suggests the absence of DOC export.

B. Exportable DOC

We see from the analyses presented here that the export of DOC contributes in a significant way at some, but not all, sites of water mass formation. The water masses formed in the Northern Hemisphere, as well as those formed in the low- to mid-latitudes of the Southern Hemisphere, carry with them significant DOC loads for export. NADW, formed in the region of 60–70°N of the North Atlantic, exports DOC at $\approx$32 Tg C year^{-1} and contributes to 40–50% of AOU in the deep northern North Atlantic (Hansell and Carlson, 1998b; Hansell *et al.,* 2002). NPIW, formed at 40°N in the western North Pacific, exports $\approx$13 Tg C year^{-1}, driving 30% of oxygen utilization near the site of formation (Ogura, 1970; Hansell *et al.,* 2002). Overturn at 32°N in the Sargasso Sea exports DOC adequate to drive 15–40% of AOU in the underlying waters (Hansell and Carlson, 2001a). Similarly, ventilation of the South Pacific and Indian Ocean main thermoclines delivers DOC adequate to drive 20–45% of AOU (Doval and Hansell, 2000). In contrast, DOC export does not take place with AABW formation. Export with Antarctic intermediate water formation, a poorly resolved process, is likely low as well.

In order for DOC export to occur its concentration must be elevated at the surface relative to the deeper water into which mixing takes place. This excess DOC at the surface must be present at the onset of overturn. *Exportable* DOC is the term used here to refer to DOC present at overturn that is in excess of the DOC concentrations at the depth to which vertical mixing takes place. It is the fraction of DOC whose lifetime exceeds the season of production and is therefore transportable to sites of water mass formation by surface currents. (So as to avoid confusion, some comments about the terminology used here and in the Introduction must be made. The *exportable* DOC introduced here is approximately the same fraction of DOC as the "semilabile" pool given in the Introduction. In this Section, though, the DOC pool is resolved into fractions that describe their export functionality. Terms such as "semilabile" DOC highlight the functional nature of DOC relative to microbial turnover of the various fractions.)

Significant amounts of *exportable* DOC appear to be absent at high latitudes in the Southern Ocean. Sharp fronts in a variety of properties separate the Antarctic Circumpolar Current System (ACCS) from the DOC-enriched subtropical gyres, as evidenced by the abrupt shifts in DOC concentrations south of the gyres (Fig. 2). It is likely to be in the gyres that *exportable* DOC is stored. Certainly it is in these waters that this fraction is resident year round (Fig. 6). The primary hydrographic front separating the subtropical and subantarctic water masses in the Southern Ocean is the Subtropical Front (also known as the Subtropical Convergence). Where subtropical gyre waters serve as precursors for water mass formation, we expect DOC export to be important. Where high-density waters of the Southern Ocean are the primary source for water mass formation (such as for AABW formation), DOC export appears to be negligible. Kähler *et al.* (1997), Wiebinga and

de Baar (1998), and Carlson *et al.* (1998, 2000) noted the apparent lack of DOC export in the Southern Ocean. Kähler *et al.* (1997) highlighted the absence of the *greater-than-seasonal* fraction of DOC, a fraction they described as being of intermediate stability and one that is defined here as making up the *exportable* fraction of DOC.

The distribution of the world ocean's primary sites for water mass formation (Talley, 1999), when overlain by the proposed global distribution of *exportable* DOC, indicates where DOC export is likely to be of consequence (Fig. 8). Excluded from this map are the zones of subduction in the subtropical gyres, which will force a relatively shallow (<500 m) export of DOC. Hansell and Carlson (2002 b) hypothesize that the primary sites of formation for *exportable* DOC are the subtropical gyres and the equatorial/coastal upwelling regions. It is in the gyres that *exportable* DOC is present year round, that this fraction has ample residence time in the euphotic zone to accumulate, and from which surface water is exported to higher latitudes as precursor for water mass formation. Further evidence for this hypothesis is that the *exportable* fraction is absent at high southern latitudes missing inputs of subtropical water (i.e., the Southern Ocean). Given this, high-latitude regions replenished by subtropical gyre waters via western boundary currents, such as the northern North Pacific and northern North Atlantic, will have *exportable* DOC present at the time of overturn. High-density water masses formed in high northern latitudes (NADW, NPIW, and likely Labrador Sea intermediate water), but fed by subtropical water, will export DOC. In contrast, DOC export in high-density water masses formed in the high-latitudes of the Southern Hemisphere will not contribute to the total export of biogenic carbon. The presence of the strong frontal systems in the ACCS prevents the DOC-enriched subtropical water from serving as source water during convection. The absence, as well, of locally produced *exportable* DOC at high southern latitudes precludes the process. Formation of Antarctic intermediate water (AAIW) should support a more variable export of DOC, dependent on the ratio of high-latitude and subtropical waters serving as precursor to this widely distributed water mass. Much more work is required to quantify DOC export with AAIW formation.

Hansell and Carlson (2002 b) have estimated the global, annual export of DOC. Export with intermediate, deep, and bottom water was estimated at $\sim 9.8 \times 10^{12}$ mol C year^{-1}, or ~10% of the total export (oxygen utilization) to depths >500 m. The contribution of DOC to exported C oxidized at depths <500 m is elevated relative to the deep ocean. DOC contributes 15 to 41% of oxygen utilization at the BATS site in the Sargasso Sea (Hansell and Carlson, 2001a) and 25 to 45% in the main thermoclines of the South Pacific and Indian Oceans (Doval and Hansell, 2000). The global contribution of DOC to export must lie between the ~10% value of the deep ocean and the ~30% value of the main thermocline. The contribution of DOC to global export in the open ocean, then, must fall in the range of $20 \pm 10\%$.

As referenced above, 7 Pg C year^{-1} is the recent estimate for global new production, so total DOC export is 1.4 ± 0.7 Pg C year^{-1}. DOC export to depths >500 m is only 0.13 Pg C year^{-1}, so most of the global export of DOC takes place through the many paths of shallow subduction. This rate of export is about the same as the earlier estimate of global net production of DOC (1.2 Pg C year^{-1}), suggesting that most of the annual net production of DOC is exported. The sites of production are spatially distinct from the sites of export; surface currents provide the essential connectivity.

V. RESEARCH PRIORITIES

In this chapter, a holistic picture of DOC in the ocean carbon cycle was developed. DOC was evaluated in the context of its wide-scale distribution (i.e., spatial and temporal variability), net production, and export. Evaluating DOC in this way was possible through collection of high quality data at key ocean sites. Unfortunately, our data density remains far too small to generate a higher resolution picture of the system. Many of the details await discovery and, the conceptual models and hypotheses, critical testing.

The major constraint on improving data density in the past has been that most of the DOC data generated by the international community were not referenced against common materials. Data from within a laboratory could be used to quantify, for example, wide-scale spatial variability, but data could not be combined from several laboratories for a similar analysis. The analytical differences between laboratories often exceeded the natural variability assessed, thus precluding such data compilations. The solution is increasing dedicated use of standardized reference materials for DOC analysis, now available to the ocean science community through funding by the U.S. National Science Foundation.

One important issue not covered in this chapter is the oceanic transport of carbon as DOC with surface currents. We evaluated DOC production and export, but we did not physically connect the processes with an evaluation of transport. What is required is a strong analysis of DOC transport with the surface-ocean, wind-driven circulation. The data now in existence are inadequate for extensive analyses of transport. Some efforts can be made in the North Atlantic where zonal sections have been completed (Fig. 4).

The distribution of DOC, with highest concentrations in the low to mid-latitude gyres, suggests that the subtropical gyres and low to mid-latitude upwelling systems are important sources of DOC for export at higher latitude sites of ocean ventilation. The strong western boundary currents carry the warm, saline subtropical water to higher latitudes, where cooling drives overturn of the water column. The subtropical waters are DOC-enriched, so the boundary currents must be important for the net transport of DOC as well. Little fieldwork or data analysis exists

to understand or quantify this process for the various ocean basins. The assessment made here that much of the net DOC production occurs in coastal and equatorial upwelling sites in turn suggests that the gyres must serve as a reservoir for that DOC produced. From these ocean systems, the DOC is transported to the high latitudes for export. This model will be evaluated over the next decade. Changes in the circulation and net DOC production patterns with ocean climate change will modify the importance of the system described.

One form of DOC export not considered in this chapter is vertical diffusive mixing into the water column. This process is likely important on a global scale but it has not been adequately evaluated. Loh and Bauer (2000), Emerson *et al.* (1997), Guo *et al.* (1995), Christian *et al.* (1997), and Vidal *et al.* (1999) provide recent calculations for downward diffusive flux of DOC. One major uncertainty with this method is the choice of the vertical diffusion coefficient, which may be uncertain by an order of magnitude. Also, it is difficult to test the vertical diffusive flux calculations independently. Confidence in rate estimates comes with independent evaluations. Clearly, this mechanism of export needs a good deal more analysis. Modeling efforts may prove the most useful test of the reported findings.

Other issues requiring high-priority effort include understanding controls on the variability in surface DOC concentrations between the various major subtropical gyres. DOC in the subtropical North Pacific, for example, may be elevated relative to the North Atlantic (Fig. 6), but we do not know why. Will the size of the marine reservoir of organic carbon vary with climate-induced changes in the unknown controls on the reservoir? Further, we do not know the factors controlling the NCP-normalized net production of DOC, such that the rate is high in the Sargasso Sea and lower in the areas with higher nutrient loads. In the deep ocean, we do not understand the processes causing the variability seen in Fig. 5. What are the mechanisms for removal of DOC along the entire path, and what are the mechanisms for introducing DOC in the low-latitude southern hemisphere? We also need to identify the truly important mechanisms of DOC production. Many times in publications a "laundry list" of mechanisms is presented (phytoplankton exudation, sloppy feeding, viral lysis, particle dissolution, etc.), but in truth we do not know which are significant and when. We know just as little about the processes involved in DOC decomposition. Progress is required here.

While a great deal of field work is still needed, certainly we can make more significant headway by modeling DOC dynamics, particularly when performed in the context of ocean physics. Advances in understanding processes such as DOC export will be made whole when models are employed to expand our understanding of how the system works. Meanwhile, it is important to collect high-quality data and to interpret these in the context of the biological and physical conditions present at collection.

VI. SUMMARY

In this chapter an understanding for the role of DOC in the ocean carbon cycle was developed. Net DOC production is a function of net community production in the ocean, so where NCP is highest, net DOC production is high as well (Table I). The coastal and equatorial upwelling environments are particularly important in this regard. DOC produced at mid-latitudes, given sufficient lifetime, converges by surface currents into the subtropical gyres. The gyres, as the recipients of the DOC enriched waters and as sites of strong vertical stability, have the highest year-round concentrations and stocks of DOC in the global ocean. Subduction in the gyres carries DOC into the upper pycnocline. The western boundary currents are important in the transport of the DOC from the gyres to higher latitudes, where DOC export occurs at sites of deep-water mass ventilation. Where the western boundary currents reach high latitudes, both intermediate and deep water formation carries exported DOC. Where western boundary currents are impeded from reaching high latitudes by frontal systems, such as in the Southern Ocean, DOC export is minimal. Annually, net DOC production represents about ~20% of net community production and ~20% of export production. Surface currents connect the sites of net production and export.

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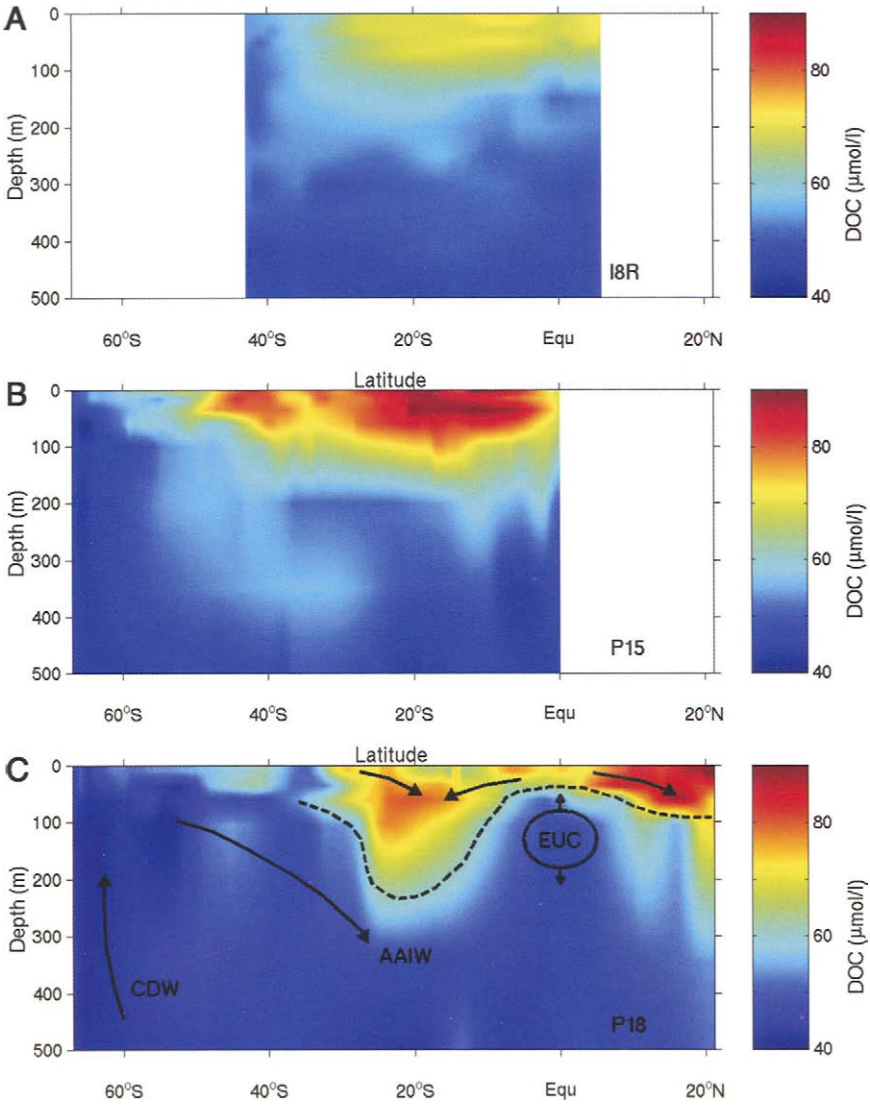

Figure 2 Meridional sections of DOC in the Southern Hemisphere. (A) the central Indian Ocean nominally along 80°E; (B) the western South Pacific along 170°W; and (C) the eastern South Pacific along 105°/110°W. Note the uplifting of contours in the Equatorial Pacific and surface accumulations in the subtropical gyres. See Fig. 1 for locations of sections. Labels on the figures indicate ocean section designations by the World Ocean Circulation Experiment (WOCE). In the section from the eastern South Pacific (C), the location of the Equatorial Undercurrent and its contribution to equatorial upwelling and downwelling is indicated. The approximate position of the main thermocline is indicated by the dashed line, and the general circulation patterns are shown by the arrows [low DOC Circumpolar Deep Water (CDW) upwells to the surface; Antarctic Intermediate Water (AAIW) subducts toward the equator; convergence in the gyres leads to downwelling of DOC enriched surface waters].

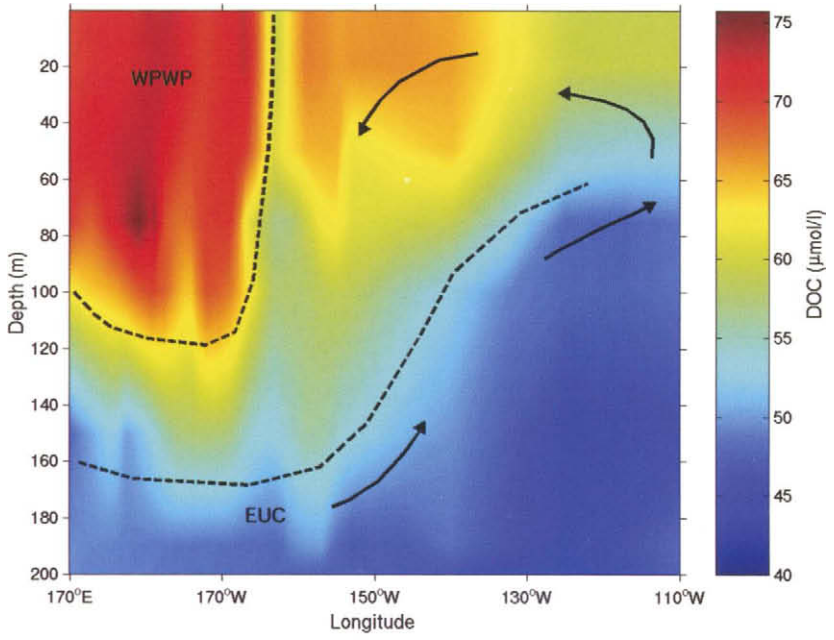

Figure 3

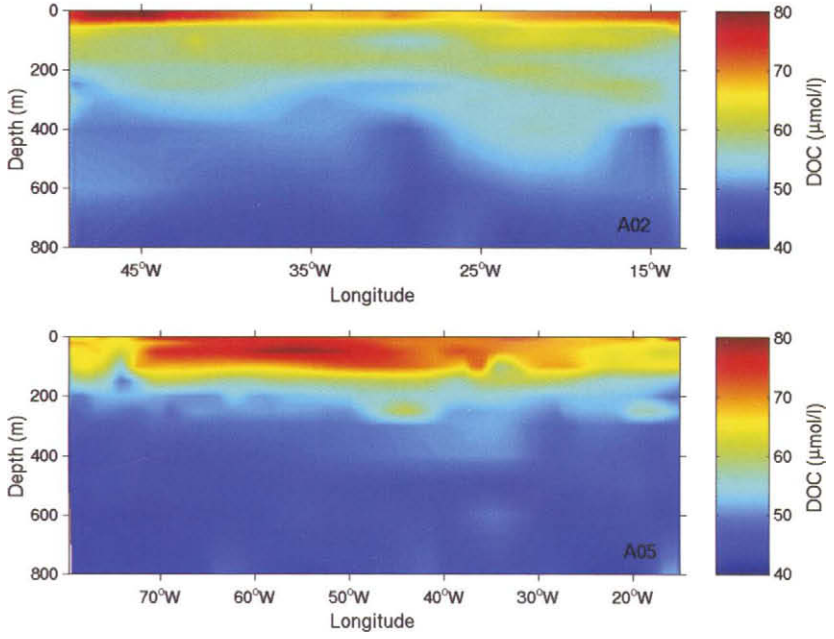

Figure 4

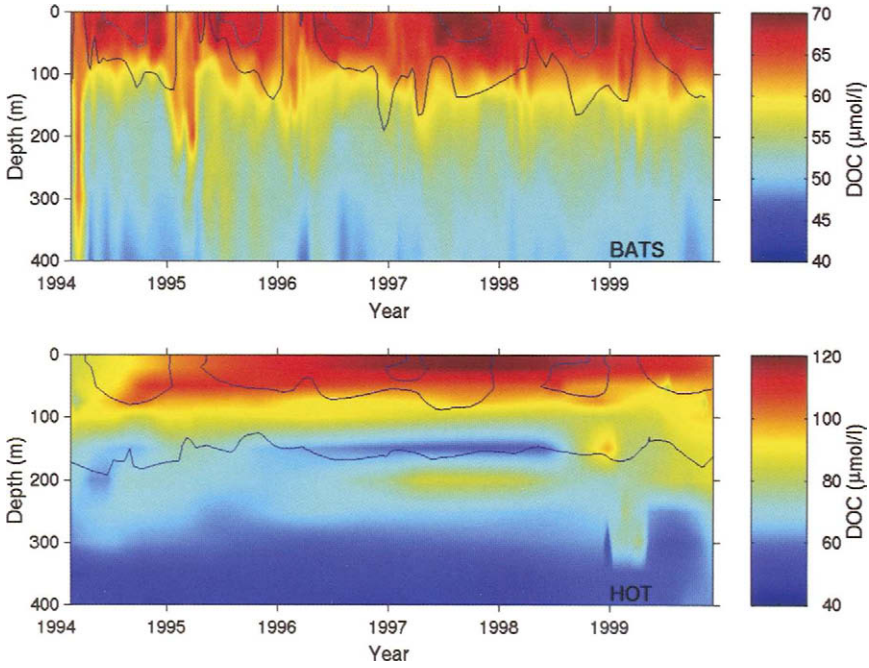

Figure 6 Time-series of DOC in the western Sargasso Sea near Bermuda (top) and the North Pacific near Hawaii (bottom). Note the differences in DOC contour scales. Seasonality in the Sargasso Sea is evident both in the DOC and temperature contours (shallow contour is 24°C; deeper contour is 20°C), while DOC seasonality is absent near Hawaii. Data from the Bermuda Atlantic Time-series Study (BATS) and Hawaiian Ocean Time-series (HOT) programs, respectively.

Figure 3 Zonal section of DOC along the equator in the Pacific Ocean. The data are a compilation collected in Autumn 1992 (Peltzer and Hayward, 1996; 110°W to 140°W) and in Autumn 1994 (Hansell *et al.*, 1997b; 150°W to 170°E), during similar ENSO states. Note the shoaling of low DOC, Equatorial Undercurrent (EUC) to the east. The high concentrations west of the dateline are associated with the Western Pacific Warm Pool (WPWP). The dashed lines serve to delineate the various water masses described.

Figure 4 Zonal sections of DOC in the North Atlantic Ocean, along 43°–49°N (top) and 24°N (bottom). Labels on the figures indicate ocean section designations by WOCE.

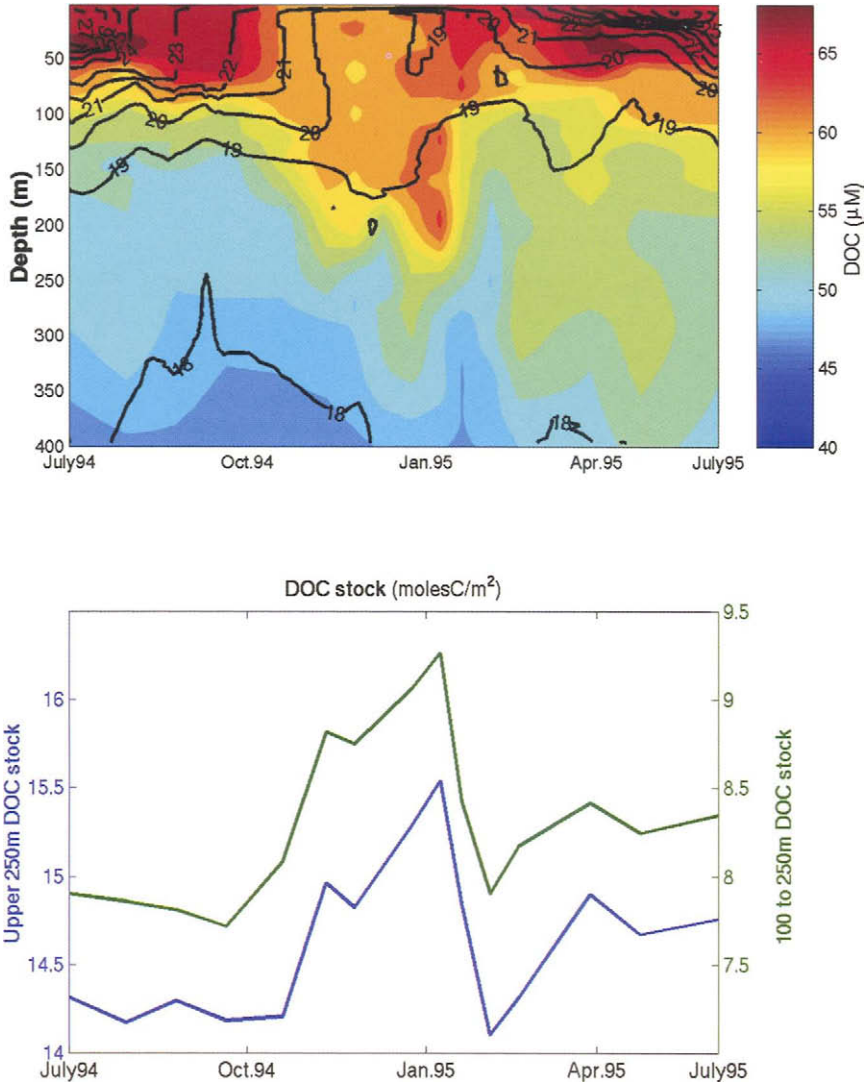

Figure 7 Top: DOC, overlain by isotherms, during 12 months (July 1994–July 1995) in the Sargasso Sea at the BATS site. Note the seasonal overturn of the water column, the downward mixing of DOC, and the summer maximum in DOC associated with high water column stability. Bottom: DOC stocks (moles m^{-2}) during the period. Note the increase in DOC stock during the period of overturn, both over the upper 250 m (reflecting total net DOC production) and at 100–250 m (reflecting export of DOC to those depths).

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