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Dissolved Organic Carbon as a Component of the Biological Pump in the North Atlantic Ocean [and Discussion]

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Dissolved organic carbon as a component of the biological pump in the North Atlantic Ocean

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SUMMARY

The North Atlantic is characterized by strong seasonality in mixed layer depths, resulting in winter recharge of surface layer nutrients and the spring phytoplankton bloom. This is the classical textbook model of seasonal cycles of oceanic biogeochemical processes, but in fact the North Atlantic is the exception rather than the rule. In much of the temperate and subpolar regions of the basin, the vernal accumulation of biomass is accompanied by a marked drawdown of inorganic carbon in the water column and pulses of particle flux to the seafloor. In the classical model, the decline of the CO_2 is balanced by accumulation of biogenic carbon and particle export. The main export mechanisms include sinking of ungrazed but possibly senescent phytoplankton and zooplankton grazing and egestion.

Carbon budgets based on observations from the Joint Global Ocean Flux Study North Atlantic Bloom Experiment and Bermuda Atlantic Time Series cannot be closed using the elements of the classical model. That is, the CO_2 drawdown cannot be balanced by biomass accumulation and exports estimated by sediment traps. There are at least three possible routes toward reconciliation: (i) trap estimates are in error and systematically biased; (ii) spatial variability aliasses the observations making budgeting impossible without recourse to coupled three-dimensional models; and/or (iii) the classical model must be abandoned and replaced by a concept in which the accumulation and export of dissolved organic carbon assumes a major role in the North Atlantic carbon balance.

At Bermuda, where the most complete data set exists, the weight of the evidence favours the first and third possibilities.

1. INTRODUCTION

The 'biological pump' is an export resulting from the collective actions of the production and consumption of organic matter in plankton foodwebs (Longhurst & Harrison 1989) and contributes to the maintenance of the vertical gradient of dissolved inorganic carbon (Sarmiento & Siegenthaler 1992). The North Atlantic ocean represents the model paradigm of the classical biological pump, characterized by vernal phytoplankton blooming, depletion of nutrient stocks and seasonal deposition of sedimenting particulate organic matter on the seafloor (Billett *et al.* 1983; Lampitt 1985; Deuser 1986). The episodic particle output is generally held to be the major factor supporting mesopelagic and benthic life (Krogh 1934) and regulating the chemistry of the deep sea (Watson & Whitfield 1985; Anderson & Sarmiento 1994). The highly seasonal nature of deep mixing in the North Atlantic results in uncoupling of production and removal processes leading to accumulations of biogenic matter. We can learn about the mechanisms governing the biological pump by recognizing the special nature of the North Atlantic and asking why it supports periodic cycles of organic matter accumulation and export.

Over the past decade great effort has been directed toward a better understanding of the relationships among primary production, its consumption by grazers and microbes, and particle export from the ocean surface. Since the publication of the seminal paper by Eppley & Peterson (1979), it has commonly been assumed that new production is balanced by particle sedimentation in the upper ocean (e.g. Vinogradov *et al.* 1992). Establishing this balance has proven to be difficult and controversial. Sediment traps used to estimate export fluxes appear to be imprecise at best (Buesseler 1991), and reliable annual estimates of new production are still rare (e.g. Harrison *et al.* 1992) or incompatible in scale and not readily comparable with export estimates (Spitzer & Jenkins 1989).

In 1988, the Joint Global Ocean Flux Study (JGOFS) initiated a program of coordinated measurements of primary and new production, carbon stocks and export fluxes in a variety of exemplary ocean regimes. The emerging body of JGOFS observations enables us to judge the current status of oceanic carbon budgets. One interesting outcome of JGOFS has been a renewal of interest in another term in the ocean carbon budget, dissolved organic carbon (DOC). DOC comprises the largest reservoir of organic matter in the sea and is comparable in size to the reservoir of organic

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matter in soils in the terrestrial biosphere. Early determinations of DOC concentrations made near Bermuda by Krogh (1934) were too high by a factor of about 2–4, but he correctly concluded that the large DOC pool was not an important source of nutrition for deep sea biota other than microbes (Jorgensen 1976). We are still seeking the correct function of this enormous, slowly cycling pool. Duursma (1962) provided the first modern observations of DOC variations in time and space in the North Atlantic, showing, for example that DOC varied seasonally in the open ocean. He estimated that the annual production of DOC in the surface waters of the open North Atlantic was 52 g C m^{-2} (4.3 M m^{-2}). The chemistry, biology and oceanography of DOC were reviewed by Williams (1975). Neither Duursma (1962) nor Williams (1975) considered the potential role of DOC as a balancing term in the upper ocean carbon budget, a possibility raised by Eppley & Peterson (1979).

In this paper, we present data from the JGOFS North Atlantic Bloom Experiment (NABE) and Bermuda Atlantic Time Series (BATS), showing that seasonal removal of dissolved inorganic carbon (TCO_2) from the upper water column cannot presently be balanced by observed particle fluxes and air–sea exchange of CO_2 (e.g. Bates *et al.* 1995; Michaels *et al.* 1995). There is not a satisfactory data set for DOC from the NABE experiment, but new observations on the annual cycle of DOC near the BATS station (Carlson *et al.* 1995) suggest that the export of DOC equals or exceeds the particle export caught in traps. Similar observations have been made in the Mediterranean by Copin-Montegut & Avril (1993) in the French JGOFS program DYFAMED.

2. METHODS AND DATA SOURCES

The data presented in this paper were collected during the two US JGOFS ATLANTIS II cruises near 47° N, 20° W in the northeastern Atlantic during NABE in April–May 1989, and at the US JGOFS BATS site near 31° 50′ N, 64° 10′ W in the northwestern Sargasso Sea during 1988–1993. Most of the data reported here are published in the US JGOFS NABE and BATS data reports, or in publications by the originating PI's cited herein. Many of these data are now available online through the US JGOFS Data Management System, accessible via MOSAIC. Specific method protocols are described in the data reports or published articles by the PI's.

There is no reliable data set on DOC for the NABE program. Samples for DOC were collected on regular BATS cruises, supplemental regional survey cruises and Hydrostation S cruises, all in the vicinity of the BATS site, and analysed at the Horn Point Environmental Laboratory, using a modified Dohrmann DC-190 TOC Analyzer according to the method described in Carlson & Ducklow (1995). These data are described in Carlson *et al.* (1995).

3. RESULTS

(*a*) *Budgets of TCO_2 and particles*

At both the NABE and BATS sites there is a marked removal of total dissolved inorganic carbon (DIC or TCO_2) from the upper ocean following restratification in spring. In the northeastern Atlantic, the depletion is sudden and brief, with a net removal of 60 μM kg^{-1} over 30–45 days (see figure 1; Chipman *et al.* 1993; Takahashi *et al.* 1994). In the seasonal, but markedly more oligotrophic regime of the northern Sargasso Sea however, the process is more gradual, showing removal of 35–40 μM kg^{-1} over ca. 100 days (see figure 2; Michaels *et al.* 1994; Bates *et al.* 1995). The mean net removal rate of TCO_2 in the mixed layer (upper 35 m) at the NABE site was 43 mM m^{-2} d^{-1} between 25 April and 31 May 1989. The mean observed removal of DIC over 0–150 m was 9.4 mM m^{-2} d^{-1} for April through November 1992 and 1993. (Michaels *et al.* 1995). Note that in both regimes, with contrasting wintertime nitrate levels (ca. 1 μM at Bermuda and 10 μM in the NABE area) and removal rates, the total amount of DIC removed from the surface is about the same. The reasons for this coincidence are not well understood.

The TCO_2 cycle is driven by the annual cycles of primary production and temperature. Chipman *et al.* (1993) showed that net removal of TCO_2 from the mixed layer was equivalent to the net primary production rate (83 mM C m^{-2} d^{-1} for 25 April–8 May 1989). The five-year record of primary productivity at BATS (see figure 3) shows annual net primary production ranging from 109–179 g C m^{-2} a^{-1} (mean 11.9 M C $m^{-2}a^{-1}$; Michaels *et al.* 1994), substantially higher than the old estimates of 60–80 g C m^{-2} a^{-1}(Menzel & Ryther 1960). The synoptic record of particle flux into floating sediment traps at 150 m ranges from 7.3–9.3 g C m^{-2} a^{-1} (see figure 3; mean 0.71 M C $m^{-2}a^{-1}$) or just 6% of the mean annual

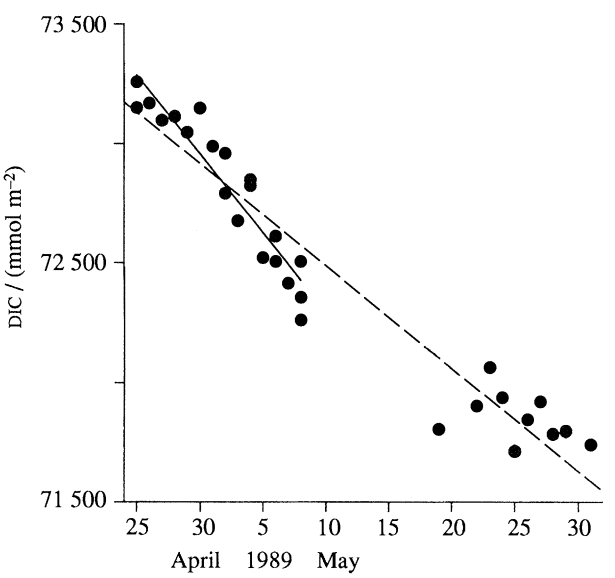

Figure 1. Stocks of dissolved inorganic carbon (TCO_2) in the upper 35 m at the NABE site (47° N, 20° W) during April–May 1989. The regression lines show the mean rates of decline for the 25 April–8 May and 25 April–31 May observation periods, respectively.

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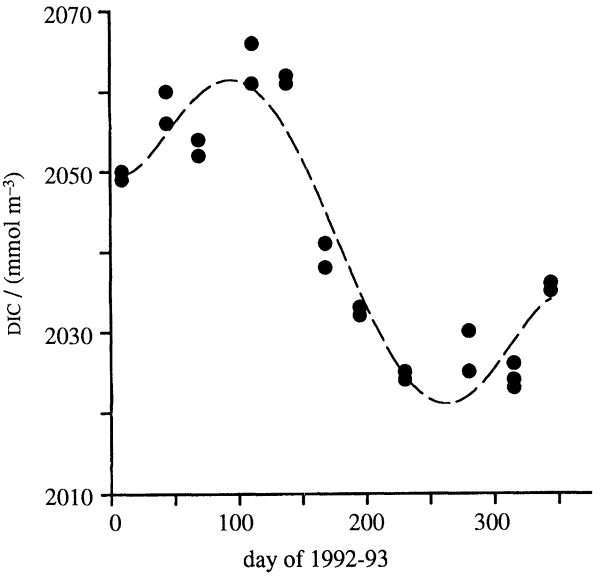

Figure 2. Seasonal cycle of dissolved inorganic carbon (TCO_2) in the upper 35 m at the Bermuda Atlantic Time Series site (32° N, 64° W) during 1992–1993.

production. At the NABE site particle flux from the mixed layer was determined from the disequilibrium between particle-reactive ^{234}Th and its soluble parent species ^{238}U to range from 5–41 mM C m^{-2} d^{-1} (Buesseler *et al.* 1992) or 6–46 % of the mean primary production of 90.4 mM m^{-2} d^{-1} (Martin *et al.* 1993). Martin *et al.* (1993) present an empirical function to extrapolate the flux from 150 m (their shallowest trap) to shallower depths. This function yields a flux of 39 mM C m^{-2} d^{-1} from the base of the mixed layer (35 m), similar to the high end of the ^{234}Th estimate.

CO_2 evasion through the air–sea interface was estimated from meteorological observations and calculated pCO_2 at each site, averaging 0.3 mM C m^{-2} d^{-1} at Bermuda (Bates *et al.* 1995) and 3.8–10.2 mM m^{-2} d^{-1} at the NABE site (Chipman *et al.* 1993). The contribution of horizontal advection to these carbon budgets (see tables 1, 2) is discussed by Michaels *et al.* (1994) and Chipman *et al.* (1993). In both cases the artifact derived from the one-dimensional consideration undertaken here is assumed to be small, but not well constrained.

(*b*) *The cycle of* DOC *at Bermuda*

DOC is potentially an important vehicle for carbon export. In contrast to particles, its transport is limited to water motions. DOC was measured on several NABE cruises, but a reliable record is not available, owing to the incomplete state of development of analytical procedures at the time of the study. The high-

Table 1. *One-dimensional carbon budget for the mixed layer (0–35 m) at the North Atlantic Bloom Experiment (NABE) site (47° N, 20° W), 25 April– 31 May 1989.*

process	flux mM C m^{-2} d^{-1}	reference
net CO_2 decline	43	figure 1
particle flux (floating traps)	39	Martin *et al.* (1993)
particle flux (^{234}Th)	5–41	Buesseler *et al.* (1992)
sea–air transfer	3–10	Chipman *et al.* (1993)
DOC export	(−8–51)[a]	—

[a] Size of DOC export flux required to balance carbon budget.

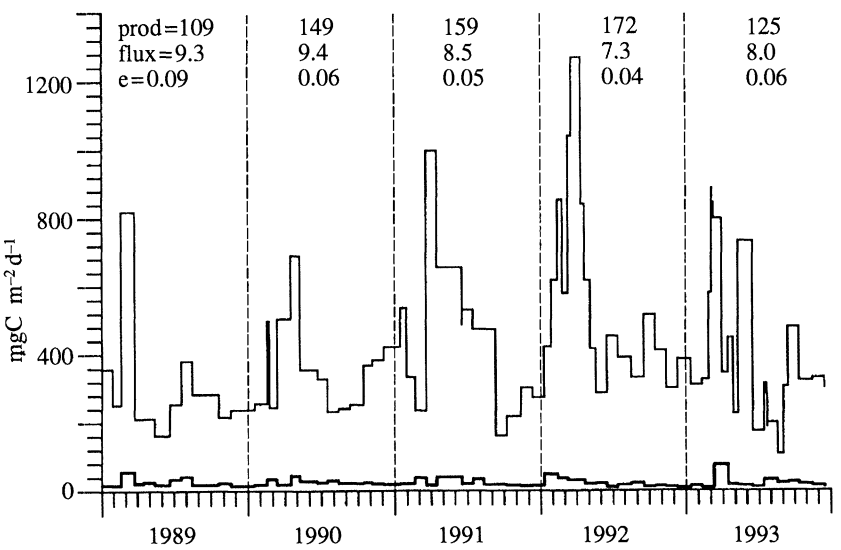

Figure 3. Primary production (upper curve) and particle flux into floating sediment traps (lower curve) at 150 m, at the Bermuda Atlantic Time Series site (32° N, 64° W) during 1988–1993. The numbers above each panel give the annual primary production and annual particle flux (g C m^{-2} a^{-1}), and the export (e-) ratio of the two annual rates.

Table 2. *One-dimensional carbon budget for the upper 150 m at the Bermuda Atlantic Time Series site (32° N, 64° W), April–November 1992–1993.*

process	flux / mM C m^{-2} d^{-1}	reference
net CO_2 decline	9.4	Michaels *et al.* (1995)
particle flux (floating traps)	2	Michaels *et al.* (1994)
particle flux (^{234}Th)	1.5–8.9	Michaels *et al.* (1995)
sea–air transfer	0.3	Bates *et al.* (1995)
DOC export	*ca.* 0[a]	—

[a] DOC declines in the 0–100 m and 100–250 m layers during April–November (see figure 5), and thus is not exchanged between layers at this time.

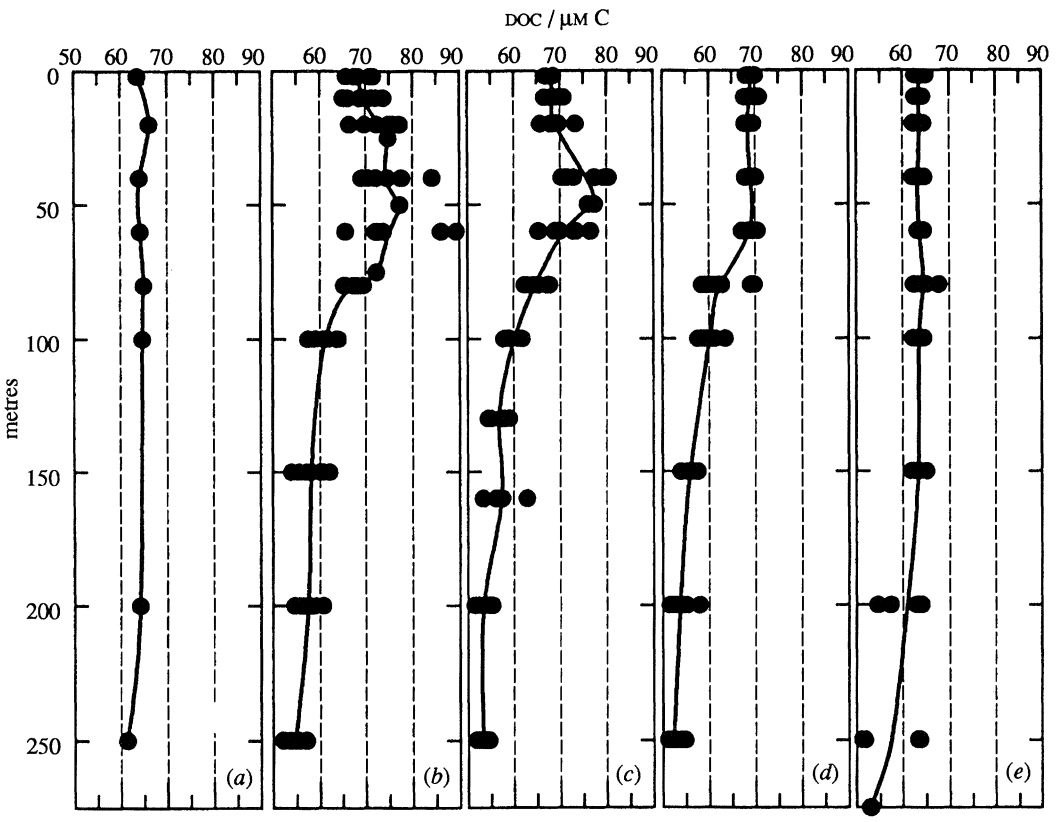

Figure 4. Vertical profiles of dissolved organic carbon (DOC) collected near the Bermuda Atlantic Time Series site (32° N, 64° W) during 1992–1993. The lines show the mean of all samples (symbols) collected at each depth during the dates indicated: (*a*) 24 March 1992; (*b*) 8–26 April 1992, eight profiles; (*c*) 29 June–14 July 1992, seven profiles; (*d*) 4–16 November 1992, nine profiles; (*e*) 25 February–11 March 1993, six profiles.

temperature catalytic oxidation method was refined subsequently (Sharp *et al.* 1993) and high precision analyses of DOC are now available for the BATS site during 1992–1993 (Carlson *et al.* 1995). DOC distributions and stocks follow the seasonal cycle of production and mixed layer development (see figures 4, 5). Vertical profiles were nearly uniform over 200 m in late winter following homogenization by convective mixing, with concentrations averaging ca. 65 μM C (figure 4*a*). After restratification of the upper water column, a subsurface DOC maximum is formed (see figure 4*b*,*c*), with concentrations enhanced over mixed layer levels by 5 and 10 μM C, respectively. Concentrations below the pycnocline decline from spring through autumn as microbial activity consumes DOC. Vertical mixing deepened the mixed layer in autumn, as continued biological activity reduced DOC concentrations further (see figure 4*d*). During the late winter, net DOC production associated with the spring bloom (see figure 3) is mixed down by convection completing the annual cycle (see figure 4*e*).

The simultaneous processes of DOC production and consumption occurring during the seasonal cycle of vertical mixing and stratification combine to produce the annual buildup and decline of DOC stocks shown in figure 5. In the upper 100 m, DOC stocks are highest in spring following the bloom, then decline throughout the summer and are exported by winter mixing. Carlson *et al.* (1995) estimate that the annual export of DOC from the upper 100 m was 1.0–1.2 M m^{-2} in 1992–1993, or about 50% greater than the particle flux caught in sediment traps. In the lower 100–250 m layer, stocks are highest in the late winter after import from the upper layer, and decompose throughout the

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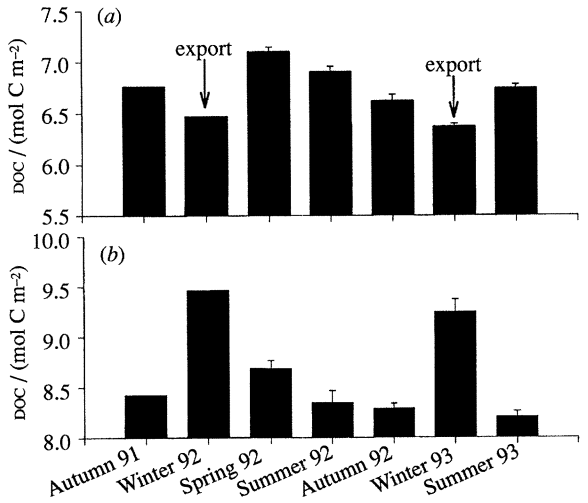

Figure 5. Annual cycle of DOC stocks in the (*a*) 0–100 m layer and (*b*) 100–250 m layer at the Bermuda Atlantic Time Series site (32° N, 64° W) during 1992–1993. Means (bars) and standard deviations of the stocks were determined by integration of the profiles shown in figure 4.

rest of the year before recharge the following winter. These observations suggest that upper ocean DOC has a component of biologically semi-labile compounds which accumulate in winter and spring and are decomposed and respired in summer and autumn, with apparent turnover times of ca. 250 days.

4. DISCUSSION

Budgets of carbon stocks at the NABE and BATS sites given in tables 1 and 2 suggest that in both regions, the total of the particle flux plus air–sea transfer may be much less than the net removal of TCO_2. These two removal processes accounted for 19–118% of TCO_2 removal in NABE and 19–98% at Bermuda. In the best case, the observed TCO_2 removal and estimates of particle export and air–sea exchange are about equal at NABE, and within a factor of two at Bermuda. However the particle flux estimates appear uncertain by a factor of 5–8, and air–sea flux estimates, though small, are uncertain by a factor of about two, due mainly to the range of uncertainty in gas transfer coefficients. In the worst case, the observed removal exceeds the summed removal processes by a factor of 5, suggesting that our current capability to estimate carbon fluxes from the upper ocean is inadequate to balance even local one–dimensional budgets. Three possible reasons for the discrepancy are discussed in turn below.

1. Particle flux estimates may be biased and lead to underestimates of particle exports at each site. The comparison between the trap and ^{234}Th-based estimates of particle flux given in table 2 suggests that the trap estimates do not account for all the particle export at Bermuda. Other comparisons of the two approaches suggest that traps are inaccurate by a factor of three (Buesseler *et al.* 1991), although in that study, the trap estimates were both less than and greater than the independent estimates from ^{234}Th. The ^{234}Th-based estimates of carbon flux themselves are still uncertain, owing to the need to convert the measured ^{234}Th fluxes into carbon flux estimates (Buesseler 1992). Particle solubilization by biological activity after deposition in traps is another possible loss term, but should be minimized in the poisoned traps employed at Bermuda. Finally, hydrodynamic biases caused by shears resulting from drag on trap mooring and float lines may also result in biased catches (Gust *et al.* 1992), though the bias may be minimized near Bermuda by apparent velocities of 10–15 cm s^{-1} (Michaels *et al.* 1995).

2. Horizontal variability in TCO_2 fields and horizontal advection might also account for some of the discrepancies. Watson *et al.* (1991) reported substantial meso- and smaller-scale patchiness in TCO_2 related to temperature and chlorophyll distributions (Weeks *et al.* 1993; McGillicuddy *et al.* 1995). This spatial variability, combined with stirring by eddies and other water motions may have contributed to the apparent removal of TCO_2 shown in figure 1, but the tightness of the fit suggests that the observed removal reflected a larger-scale process related to the regional-scale bloom (Bender *et al.* 1992). However, it was not possible to form a budget for the 0–150 m layer in NABE because mesoscale variability in the TCO_2 field precluded a meaningful regression, yielding apparent removal rates in excess of 1 M m^{-2} d^{-1}, impossible to reconcile with *in situ* processes. Michaels *et al.* (1995) concluded that lateral advection could not explain the entire discrepancy in the budget for BATS because the DIC field in the northern Sargasso Sea is more uniform than the scale of the seasonal fluctuations.

3. A third possibility is that carbon removal from the upper layer is not solely in the form of particles, with some substantial fraction being exported in dissolved organic matter. This possibility has already been explored in modeling studies (Bacastow & Maier-Reimer 1991; Najjar *et al.* 1992). Recently Copin–Montegut & Avril (1993) calculated from a seasonal time series of DOC profiles made in the western Mediterranean Sea that DOC export was equal to or greater in magnitude than the measured particle flux. DOC export cannot be the explanation for the observed removal of TCO_2 at Bermuda between April and November, because DOC is declining during this entire period in both the 0–100 and 100–250 m layers. Thus the TCO_2 removed during the period did not appear as DOC. But over the annual cycle, DOC export makes a large contribution toward reconciling the geochemical estimates of new production (3–4 M C m^{-2} a^{-1}; Spitzer & Jenkins, 1989) with observed export rates. Carlson *et al.* (1994) calculate that DOC export during winter mixing is ca. 1 M C m^{-2} a^{-1} at Bermuda, also greater than the particle export. Because we have no acceptable DOC data from NABE, it is not possible to suggest the importance of DOC in the carbon budget there. Bender *et al.* (1992) could only account for 0.39 mmol C of a measured net production of 0.68 mmol C m^{-2} over 13 days at the NABE site, and suggested that at least some of the remainder might have been stored as DOC. The lower end of the range of DOC export fluxes required to balance the NABE budget (i.e. 15–25 mmol m^{-2} d^{-1}; see table 1) is an acceptably low fraction of observed primary pro-

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duction rates, which commonly exceeded 100 mM m^{-2} d^{-1} during the observation period.

5. CONCLUSIONS

We can now state with some confidence resulting from recent advances in DOC analytical technique, that DOC undergoes seasonal cycles of accumulation and export in at least two ocean sites, where it also contributes as much or more to the carbon budget than particle sedimentation. Such observations are not entirely new. Duursma (1962) observed that DOC increased from ca. 0.5 to 1 mg kg^{-1} between April and September, 1958 along a transect south of Greenland (50° N, 40° W). The concentrations measured by Duursma (40–105 μM C) are in the range of recent determinations, and the changes he observed are not unreasonable for an area experiencing deep mixing and strong phytoplankton blooms. Duursma (1962) shows that the layer of elevated DOC in November extends to 200–300 m, suggesting that he in fact observed DOC export during winter mixing.

Both the older and more recent vertical profiles show elevated concentrations of DOC in the upper 100 m, and consistently low concentrations below the main thermocline. This pattern shows unequivocally that oceanic DOC originates in the upper layer, and at least in the seasonal regimes studied to date, is derived from biological production during the spring bloom. Areas of the ocean which experience spring phytoplankton blooms have seasonal accumulations of dissolved, as well as particulate organic matter. The particulate matter is exported by episodes of sinking during and shortly after the bloom, whereas the dissolved stocks decay slowly *in situ*, and the remainder is exported by vertical mixing in the fall and winter. This pattern of DOC accumulation, decomposition and export suggests that the relative rates and phasing of DOC production by phytoplankton and zooplankton, and DOC decomposition by microbial populations together determine the amounts of DOC returned to the upper water column as TCO_2, and the amount exported.

Little is known about these processes as they relate to the bulk DOC pool. The bulk pool is still largely uncharacterized with respect to the identity of component compounds. It is biologically reactive, supporting bacterial growth (Kirchman *et al.* 1991; Amon & Benner, 1994), and decays at variable rates depending on temperature, location, nitrogen availability and other factors. DOC is produced by a complex array of processes, such that its flows appear to dominate model reconstructions of plankton foodweb data (Jackson & Eldridge 1992). Post-bloom accumulations of DOC leading to export later in the year might result from lags between phytoplankton and bacterial growth, and production of semi-refractory DOC during microbial attack of phytoplankton polymers (Smith *et al.* 1992). Further studies of DOC distribution, production and utilization in contrasting oceanic regimes are required to evaluate the role of DOC in the biological pump. As a first step, a repeat study of Duursma's pioneering (1962) research in the North Atlantic seems appropriate.

APPENDIX 1.

Calculation of DOC turnover time

calculation	equation details	value
100 m stock April 1992/ (M m^{-2})		7.09[a]
100 m stock November 1992/(M m^{-2})		6.61
background concentration/ (M m^{-2})	(65 μM/100 m)	6.5
summer labile stock/ mM	(7090–6500 mM)	590
net decomposition rate/ (mM m^{-2} d^{-1})	(7.09–6.61)/214 d	2.24
turnover rate/d	590/2.24	263

[a] Mean concentration = 70.9 μM.

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Discussion

T. Jickells (*UEA, Norwich, U.K.*). If labile DOC is rapidly degraded to a background inert level, can this be a route for organic carbon to reach the deep ocean?

H. W. Ducklow. No. The labile DOC that we observe in the 0–100 m layer degrades in a few weeks and could not move far from its source. But even in the upper 250 m, DOC concentrations of *ca.* 55–60 μM are greater than deep ocean values of 40–45 μM. This less labile fraction also originates in the upper layer and might reach deeper into the water column.

P. J. Le B. Williams (*School of Ocean Sciences, University of Wales, Bangor, U.K.*). The dissolved organic matter is not constrained as to its C:N ratio, as is the particulate fraction. Thus, a major export of carbon in the form of DOC would disconnect the export of carbon from that of nitrogen. Would Professor Ducklow like to comment on the significance of this?

H. W. Ducklow. We have no reliable, recent information on complementary analyses of DOC and DON on the same samples. However, it seems likely that DOM might be enriched in C relative to POM. If so, N-based estimates of export might underestimate C removal.

I. N. McCave (*Department of Earth Sciences, University of Cambridge, U.K.*). The significant under-trapping Professor Ducklow reports suggests there may be other biasses in the material collected. Does he have any information relating to actual or potential bias in the relative collection efficiency of traps with respect to, for example, marine snow, faecal pellets, foraminifera, fine particles, e.t.c.?

H. W. Ducklow. The question was referred to Dr A. Michaels (Bermuda Biological Station for Research). No. There is no standard for comparison with the material the traps *do* catch. Biasses for ^{234}Th range over a factor of 3–7.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES