

Cycling of colloidal organic carbon and nitrogen during an estuarine phytoplankton bloom

Christopher J. Gobler

Natural Science Division, Southampton College of Long Island University, Southampton, New York 11968

Sergio A. Sañudo-Wilhelmy

Marine Sciences Research Center, Stony Brook University, Stony Brook, New York 11794-5000

Abstract

To establish the influence of phytoplankton blooms on the cycling of dissolved and particulate species of organic carbon and nitrogen, we conducted a field study during a series of blooms in a coastal embayment on Shelter Island, NY. Using cross-flow filtration, we collected high- and low-molecular-weight (HMW and LMW) dissolved organic matter (DOM), along with particulate organic matter (POM). There was a significant and near equivalent enhancement in levels of particulate organic carbon (POC) and dissolved organic carbon (DOC) during phytoplankton blooms. HMW organic carbon was responsible for most (80%) of the DOC increase. In contrast, substantial amounts of organic nitrogen were produced in all size fractions (particulate organic nitrogen [PON], HMW, and LMW) during blooms. POC:PON and HMW C:N ratios exceeded Redfield stoichiometry and were well correlated with chlorophyll concentrations, which suggests that phytoplankton were the primary source of C-enriched particles and colloids in this system. DOM C:N ratios were higher during periods of elevated nitrate than during low nitrate conditions, which were dominated by phytoplankton with heterotrophic capabilities. This suggests that, in some coastal systems, the accumulation of C-enriched organic matter may be more dependent on algal species composition than ambient inorganic nitrogen levels. After the collapse of algal blooms, bacterial densities rose markedly, and all organic pools rapidly decreased to near prebloom levels. Despite substantial production and turnover rates of HMW organic carbon during blooms, longer residence times of other, more refractory, organic carbon pools such as the LMW fraction indicated that considerable portions of organic matter produced during estuarine phytoplankton blooms may be exported to continental shelves.

Coastal environments are regions of high biological productivity. It has been estimated that, although continental margins occupy <10% of the total surface area of the world ocean, up to one third of the global marine primary production occurs within these regions (Wollast 1991). The fate of this production (whether it is consumed by the shelf microbial communities, buried in the shelf sediments, or exported to deep ocean waters) is of considerable interest, particularly with regard to its impact on the global carbon budget (Hedges 1987; del Giorgio and Duarte 2002). Although recent mass balance estimates have suggested that the input of dissolved organic matter (DOM) from continental margins to the open ocean could be as much as 100 times greater than the contribution of material from surface waters (Bauer and Druffel 1998), the importance of coastal environments in the export of organic matter remains the subject of diverging opinions (e.g., Falkowski et al. 1988; Liu et al. 2000; del Giorgio and Duarte 2002). Our current understanding of the fate of the marine organic pools in coastal waters (e.g., ex-

port, burial, or consumption) has been hampered, in part, by the poor characterization of their composition and lability.

The photosynthetic fixation of inorganic carbon and nutrients into cellular material by phytoplankton is the primary source of organic matter to the world's oceans. Once fixed into particulate material (POM), organic matter synthesized by phytoplankton can be subsequently released to the dissolved phase (as DOM) by a variety of processes, including cell leakage (Mague et al. 1980), grazing (Nagata and Kirchman 1992), and viral lysis (Gobler et al. 1997). The release of DOM by marine phytoplankton has been shown to significantly affect nutrient cycling (Kirchman et al. 1991; Gardner et al. 1996), trace metal availability (Hutchins et al. 1999), bacterial growth (Cole et al. 1982), and microbial food webs (Kirchman et al. 1991). All of these processes and interactions may also strongly influence the net production and ultimate fate of the organic matter in coastal waters.

To refine our understanding of the cycling of organic carbon (OC) and organic nitrogen (ON) during coastal phytoplankton blooms, we conducted a field study in a small, shallow, enclosed embayment (West Neck Bay [WNB]; Fig. 1) on Shelter Island, NY. Using cross-flow filtration, we collected the high-molecular-weight (HMW; 0.2 μm –1 kDa) and low-molecular-weight (LMW <1 kDa) size fractions of DOM (<0.2 μm), along with POM (>0.7 μm), over the course of successive plankton blooms dominated by a mixture of algal species, a brown tide alga (*Aureococcus anophagefferens*), and heterotrophic bacteria. This time-series approach allowed us to establish the physical speciation and

Acknowledgments

We thank David Hirshberg for analytical assistance, K. Black for access to WNB, and Ed Himelblau for graphical assistance. We are grateful to Robert Bidigare, and two anonymous reviewers for useful comments on this manuscript.

This research was supported by NOAA's Coastal Ocean Programs award NA66 RG0368 for New York Sea Grant Institute to S.S.W. and by an award from the Southampton College of Long Island University Research Awards Committee to C.J.G.

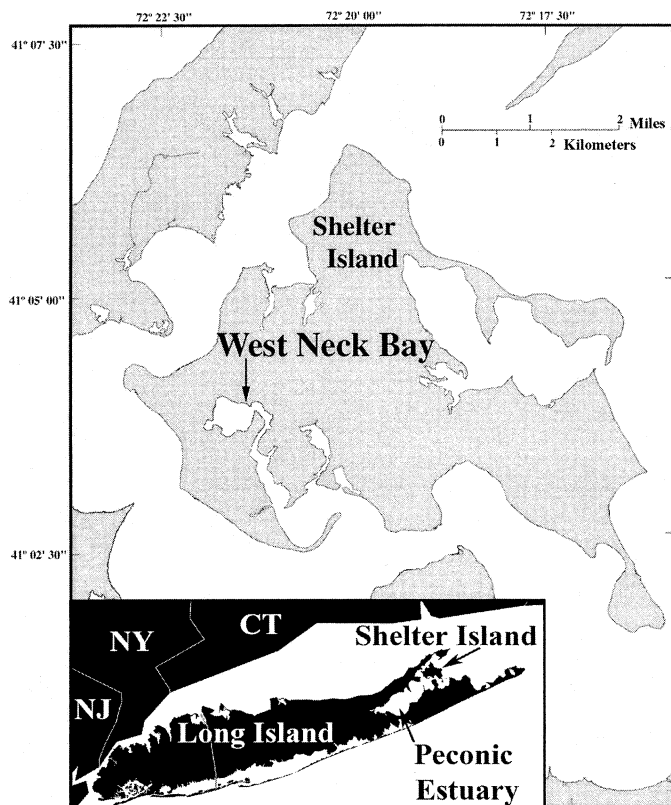


Fig. 1. Study site, West Neck Bay, Shelter Island, New York.

fate of organic matter produced during phytoplankton blooms.

Materials and methods

Study area—WNB is a small (1 km²), shallow (2–4 m), well-mixed, enclosed embayment on Shelter Island, within the Peconic Estuary of eastern Long Island, NY (Fig. 1). To the east, this estuary exchanges with Block Island Sound and the northwest Atlantic Ocean. WNB has a long, winding, restricted channel that exchanges with the Peconic Estuary. This circuitous conduit causes WNB to have a fairly long hydraulic residence time and recurrent phytoplankton blooms. Tidal exchange volumes calculated using a salt balance (Fischer et al. 1979) have indicated that WNB had a residence time of 15 d during our study, a value that is within the range of residence time previously calculated for this bay (10–15 d; J. L. DiLorenzo and R. V. Ram pers. comm.). The absence of tributaries and point-source anthropogenic inputs make this bay a relatively simple system, where in situ water column processes dominate over allochthonous inputs (Gobler et al. 2002). Moreover, the enclosed nature of WNB makes it a “natural mesocosm” ideal for documenting the cycling of organic matter during phytoplankton blooms.

Sample collection, processing, and analysis—Seawater samples from WNB were collected twice weekly to biweekly from April to October of 1998 using acid-washed Teflon tubing which extended 4 m from a pier to a depth of 1 m.

Duplicate particulate organic carbon and nitrogen (POC and PON) and triplicate Chl *a* samples were collected on pre-combusted GF/F glass fiber filters and stored frozen. Dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and nutrient samples were filtered with acid-cleaned, polypropylene capsule filters (0.2 μm; MSI) in the field and immediately stored on ice. Triplicate whole-water samples were preserved in 1% glutaraldehyde using a 10% solution made from 0.2-μm-filtered seawater for later quantification of microbial communities. Within 2 h of collection, DOC samples were acidified with quartz-distilled nitric acid and frozen along with DON and nutrient samples.

Cross flow filtration (CFF) with a 1-kDa Amicon polysulfone membrane (model S10N1) was used to separate DOC and DON into HMW (0.2 μm–1 kDa) and LMW (<1 kDa) fractions. Twenty liters of 0.2-μm-filtered seawater were collected with acid-cleaned polypropylene capsule filters (MSI) and stored in dark, acid-cleaned fluorinated carboys. Samples were kept cold (~5°C) and cross-flow filtered within 5 h of collection. The CFF membrane was stored in 0.1 N HCl between uses. The retentate and permeate sides of the CFF system were flushed with 20 liters of 0.1 N HCl and 20 liters of Milli-Q before and after processing each sample. Five liters of retentate and permeate were flushed and discarded before samples were processed. Samples were circulated within the CFF unit for 1 h before final processing commenced. A concentration factor (CF) of 10 was used to prevent the breaking of colloids and the resultant diffusion of constituents into the LMW fraction (Buesseler et al. 1996; Dai et al. 1998). Operating pressures were 40–50 psi at the inlet and 30–40 psi at the outlet, filtration rates were 10–15 L h⁻¹, and the filtration temperature ranged 20–25°C. Because cross flow filtration separates dissolved samples into a filtrate (LMW) fraction and a concentrated retentate (HMW and LMW) fraction, the actual concentration of HMW constituents were calculated using the equation [HMW] = ([retentate] – [filtrate])/CF, where CF was 10. To ensure that the cross flow filtration was not adding or removing DOC or DON, the following mass balance equation was used: percent recovery = ([total dissolved/HMW] + LMW) × 100. Quantitative (~95%) recoveries were obtained with this system for DOC and DON during this study.

DOC samples were analyzed in duplicate by high-temperature catalytic oxidation using a Shimadzu TOC-5000 Total Organic Carbon Analyzer (Benner and Strom 1993). Duplicate POC and PON samples were dried at 60°C before analysis on a Carlo Erba NA 1500 NCS system (Cutter and Radford-Knoery 1991). Total dissolved N (TDN) was analyzed in duplicate by persulfate oxidation techniques (Valderrama 1981), and DON was calculated by subtracting levels of nitrate, nitrite, and ammonium from concentrations of TDN. Chl *a* was analyzed in triplicate by standard fluorometric methods (Parsons et al. 1984). Within 2 weeks of collection nitrate, nitrite, ammonium, and phosphate were analyzed in duplicate by standard spectrophotometric methods using a 1- or 10-cm cell, depending on ambient concentrations (Jones 1984; Parsons et al. 1984). Measurements of J. Sharp’s (Univ. of Delaware) intercalibration DOC samples were within 5% of the consensus value. Recoveries (mean ± SD) of SPEX Certi-Prep standard reference material at

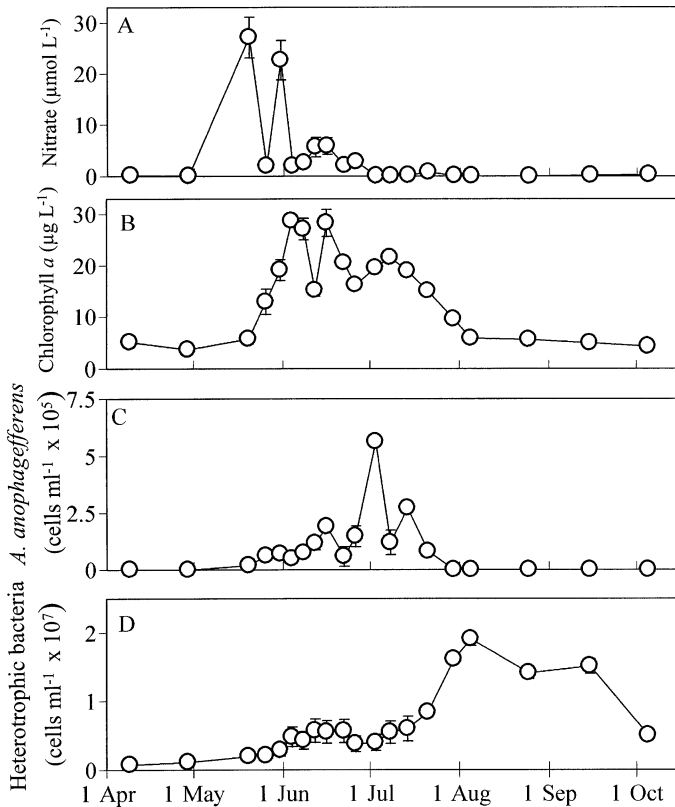


Fig. 2. Levels of (A) nitrate, (B) Chl *a*, (C) *A. anophagefferens*, and (D) bacteria in West Neck Bay, 1998. Error bars represent ± 1 SD of replicated measurements.

environmentally representative concentrations were $101\% \pm 7\%$ for nitrate and $96\% \pm 11\%$ for total nitrogen. Measurements of NIST 16326 standard reference material for POC were within 7% of certified values. Blanks for DOC, DON, POC, and PON were typically $<10\%$ of the lowest sample. *A. anophagefferens* and bacterial densities in preserved samples were determined by direct count methods that used fluorochromes and an epifluorescent microscope, as described in Gobler and Sañudo-Wilhelmy (2001a). The relative abundance of *A. anophagefferens* as a percentage of the total phytoplankton community was determined under the assumption of a Chl *a* per cell quota of 0.035 ± 0.003 pg (Gobler et al. 2002).

Results and discussion

Phytoplankton bloom progression—The late spring and early summer of 1998 on eastern Long Island were marked by an abnormally large amount of rainfall, which resulted in a late May/early June peak in the seepage of nitrate-enriched groundwater into WNB (Fig. 2A; Gobler and Sañudo-Wilhelmy 2001b). This substantial nitrate flux seemed to stimulate the phytoplankton bloom that subsequently developed—Chl *a* levels increased sixfold from $5 \mu\text{g L}^{-1}$ on 26 May to nearly $30 \mu\text{g L}^{-1}$ on 4 June (Fig. 2B). This bloom consisted of a mixed assemblage of small ($<5 \mu\text{m}$), unidentified, autotrophic picoflagellates and cyanobacteria, as well

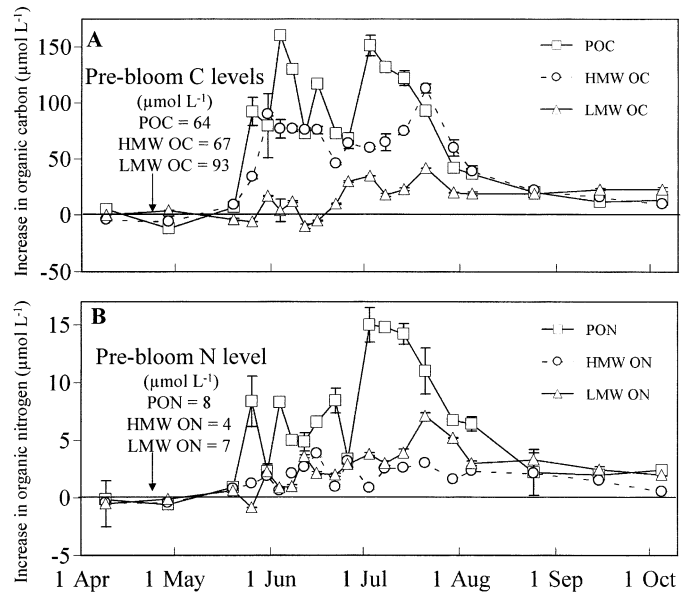


Fig. 3. Changes (Δ) in (A) organic carbon and (B) organic nitrogen in West Neck Bay, 1998. Error bars represent ± 1 SD of replicated measurements.

as modest levels of the brown tide species *A. anophagefferens* ($\sim 10^5$ cells ml^{-1} and $<20\%$ of total algal biomass; Fig. 2C). Although high chlorophyll levels ($>15 \mu\text{g L}^{-1}$) were sustained in WNB through mid-July (Fig. 2B), the phytoplankton community shifted from a mixed assemblage to domination by *A. anophagefferens* in late June and early July (Fig. 2C). On 3 July, the algal community became nearly monospecific—brown tide densities were $>5.5 \times 10^5$ cells ml^{-1} (Fig. 2C) and accounted for nearly 90% of algal biomass. At this time, nitrate levels were $<0.25 \mu\text{mol L}^{-1}$ for the first time since mid-May and remained low for the rest of the study period (Fig. 2A). After the early July bloom, *A. anophagefferens* cell densities and Chl *a* levels gradually dissipated, whereas heterotrophic bacteria levels increased through July (Fig. 2B–D), remained elevated during August, and declined in the fall. Levels of ammonium, nitrite, and phosphate were low ($<1 \mu\text{mol L}^{-1}$) throughout the study period.

Organic matter cycling—The succession of plankton communities in WNB appeared to influence the quality and quantity of organic matter produced during the blooms. When the mixed-species phytoplankton bloom started during late May (20 May–4 June), concentrations of POC increased (Δ OC = change in organic carbon) by up to $150 \mu\text{mol L}^{-1}$ and HMW OC concentrations increased by nearly $100 \mu\text{mol L}^{-1}$, whereas LMW OC remained relatively unchanged ($<5 \mu\text{mol L}^{-1}$ increase; Fig. 3A). ON dynamics seemed somewhat decoupled from OC as PON increased (Δ ON) by $9 \mu\text{mol L}^{-1}$ during this bloom, and levels of LMW and HMW ON did not change markedly ($<1 \mu\text{mol L}^{-1}$ each; Fig. 3B). During the initiation period of the *A. anophagefferens* bloom (26 June–3 July), levels of POC and HMW OC again increased to levels displayed during the earlier June bloom. In contrast to this earlier bloom, HMW ON,

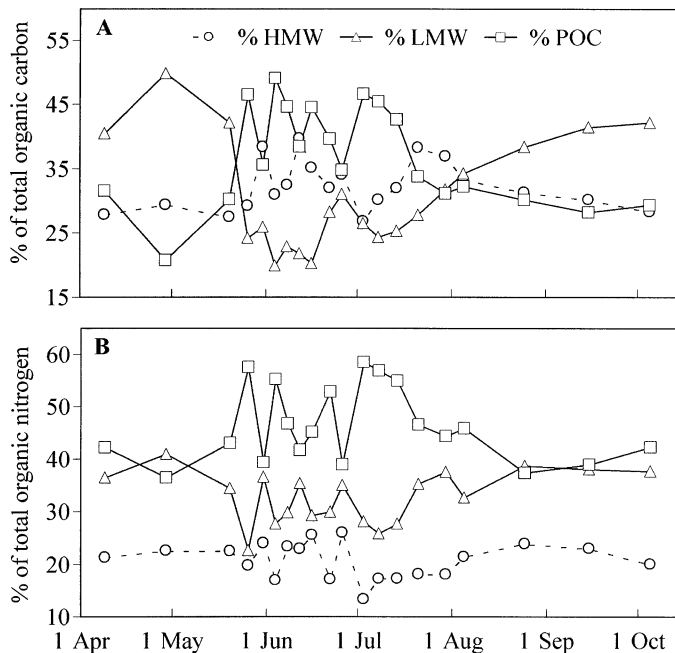


Fig. 4. (A) Percentage of the total organic carbon pool (TOC) represented by particulate, HMW OC, and LMW OC. (B) Percentage of the total organic nitrogen pool (TON) represented by particulate, HMW and LMW ON in West Neck Bay, 1998.

LMW ON, and LMW OC levels all increased during the *Aureococcus* bloom, and PON reached its annual peak (Fig. 3A,B). Paralleling the collapse of the phytoplankton blooms in WNB (Fig. 2B,C), all organic pools rapidly declined during July and August and ultimately leveled off at concentrations only slightly higher than prebloom levels during late August and September, which indicated that only small amounts of the freshly produced organic matter remained in the system (Fig. 3).

The relative abundance of each organic matter pool also changed with the occurrence of plankton blooms in WNB. Prior to the onset of phytoplankton blooms, LMW OC was the most abundant OC pool and accounted for 40%–50% of the total OC (TOC) pool, whereas POC and HMW OC each made up ~30% of TOC at that time (Fig. 4A). With the initiation of the first phytoplankton bloom (26 May), POC became the dominant OC pool and accounted for, on average, 45% of the TOC throughout all blooms (26 May–14 July; Fig. 4A). HMW OC also represented a larger portion of TOC during blooms, accounting for an average of 35% of TOC from 26 May through 14 July. Moreover, HMW OC became the largest OC pool after each peak in algal biomass (31 May, 12 June, and 21 and 30 July), during which HMW OC constituted up to 40% of TOC (Fig. 4A). LMW OC was the smallest OC pool during blooms, ranging between 20% and 30% of TOC during June and July (Fig. 4A). The cessation of algal blooms in WNB during August and September returned the distribution of the various OC pools to their prebloom status, as LMW OC again became the largest OC fraction (Fig. 4A).

The relative abundance of the ON was somewhat different than that of OC during the WNB phytoplankton bloom

events. For example, although most of the prebloom OC was LMW, most of the prebloom total organic nitrogen (TON) was in the particulate pools (~40%; Fig. 4B). Additionally, the LMW ON abundance was greater than HMW ON throughout our study period (Fig. 4B). As phytoplankton blooms burgeoned in WNB, the PON fraction became even more enriched (~55% of the TON), which somewhat resembled the distribution observed for POC (Fig. 4A). The percentages of LMW ON fluctuated between 20% and 35% of the TON during bloom conditions and appeared to be inversely related to the portion of TON represented by PON, which suggests an exchange of N between these two pools (Fig. 4B). Only small fluctuations in the relative abundance of HMW ON were detected during the blooms (15%–25% of TON). By the end of August (postbloom conditions), the percentages of the different pools of ON were similar to those measured during April prebloom conditions (Fig. 4B).

Seasonal variations in oceanic DOC concentrations typically correspond to changes in algal activity, with maximum levels often observed after periods of high primary production (Carlson et al. 1994; Williams 1995). Throughout the present study, levels of POC and HMW OC were strongly correlated with Chl *a* in WNB ($P < 0.0001$; $r^2 = 0.91$ and 0.77), whereas a correlation with LMW OC did not exist. These results, in conjunction with the observed enrichment of these pools during bloom events, indicate that phytoplankton blooms are a direct source of two distinct particle pools of carbon: POC and HMW OC. This conclusion is consistent with previous studies of colloidal organic matter made with larger molecular-weight cutoffs (10 kDa; Kepkay et al. 1997). Moreover, although previous reports have documented the formation of DOC during phytoplankton blooms (Kirchman et al. 1991; Carlson et al. 1994; Williams 1995), our study documented the formation of HMW OC with a 1-kDa cutoff and demonstrates that, in fact, most of the DOC produced by phytoplankton blooms is colloidal in nature (Fig. 3A). Concentrations of HWM ON were also correlated with Chl *a* levels during the present study, although at a much lower significance level ($P < 0.05$; $r^2 = 0.45$). This weaker correlation, along with a smaller absolute increase in the HMW ON pool, indicates that the production of OC and ON are somewhat decoupled, with phytoplankton blooms having a greater impact on OC pools relative to ON. This conclusion is consistent with the results of previous coastal investigations of phytoplankton blooms that have also indicated the production of C-enriched organic matter (Kepkay et al. 1997).

Carbon:nitrogen ratios—The onset of phytoplankton blooms in WNB also affected the ratios of OC:ON within dissolved and particulate organic matter pools (Fig. 5A). The mixed-species chlorophyll bloom during late May and early June was coincident with the annual peaks in C:N ratios for particulate (~14) and dissolved (~18) organic pools (Fig. 5A). The increase in the DOM C:N ratio was due entirely to HMW material, given that the HMW C:N ratio nearly doubled (from 15 to 28) during this period, whereas the LMW OC:ON ratio remained unchanged (9.9 ± 2.0) (Fig. 5B). As the blooms persisted through the summer, the HMW and POC:PON ratios remained elevated. Overall, the C:N

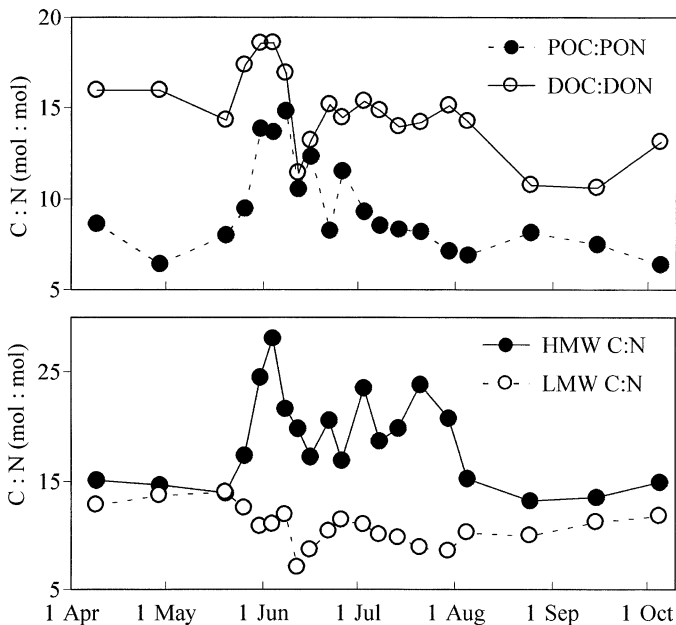


Fig. 5. Molar carbon:nitrogen ratios of (A) POM and DOM, (B) HMW organic matter, and LMW organic matter in West Neck Bay, 1998. Error bars represent ± 1 SD of replicated measurements.

ratios in all of the pools were consistently above the Redfield ratio of 6.6 (average \pm SD: HMW, 18.7 ± 4.2 ; DOM, 14.7 ± 2.5 ; POM, 9.5 ± 2.6 ; and LMW, 10.3 ± 1.7 ; Fig. 5A,B). A strong, positive correlation between the C:N ratios of POM and HMW organic matter and algal biomass (Chl *a*; $P < 0.0001$; $r^2 = 0.77$ and 0.73) during our study suggests that phytoplankton were the primary source of these C-enriched particles and colloids in WNB. This finding supports previous research that indicated that HMW organic matter is enriched in phytoplankton-derived carbohydrates and that such fresh DOM frequently has a C:N ratio that is significantly higher than the Redfield ratio (Amon and Benner 1994). We also observed a significant inverse correlation between bacterial densities and the C:N ratio of LMW organic matter ($P < 0.05$; $r^2 = -0.53$), as well as a significant correlation between LMW ON and bacterial densities during the present study ($P < 0.05$; $r^2 = 0.50$). These correlations, along with the lower C:N ratio of LMW organic matter, suggests that this pool was more enriched with small, labile, N-rich compounds such as amino acids (Bauer et al. 1996), which are capable of supporting robust bacterial growth (Gardner et al. 1996).

Previous studies have hypothesized that C-enriched DOM seasonally accumulates in marine surface waters during late summer, once ambient nitrate levels have been depleted (e.g., Williams 1995; Kahler and Koeve 2001). However, the results of our study demonstrate that, in coastal waters, DOM that is depleted in N relative to Redfield stoichiometry can accumulate in the water column, even when nitrate levels are relatively high (Figs. 2A, 5A). Our data also demonstrate that the release of C-rich colloidal material during algal blooms accounts for such anomalously high C:N ratios in bulk dissolved pools (Fig. 5B). Because phytoplankton species are known to vary considerably in their capacity to

produce (Biddanda and Benner 1997; Kepkay et al. 1997) or consume (Lewitus and Kana 1995) DOC or DON, it is possible that species composition of phytoplankton assemblages may also have a profound impact on the C:N ratio and quantity of DOM. For example, initial phytoplankton blooms in WNB in June occurred when nitrate levels were high (Fig. 2A) and were likely dominated by autotrophic phytoplankton species that produced C-enriched DOM. These initial blooms were succeeded by a bloom of *A. anophagefferens* in July (Fig. 1C), a species with well-documented heterotrophic capabilities (Gobler and Sañudo-Wilhelmy 2001a; Berg et al. 2002). It is likely that this population contributed to the both production and consumption of organic matter during its dominance and thus likely affected the DOC:DON ratio in a manner that differed from earlier, more autotrophic species. Hence, algal species composition may have a greater impact on DOM C:N ratios than ambient inorganic nitrogen levels, particularly in coastal systems, which can be organically enriched and dominated by heterotrophic phytoplankton (Glibert et al. 2001).

Recently, Lomas et al. (2001) also documented the impact of *A. anophagefferens* on DOM elemental ratios, specifically noting elevated DOC:DON ratios (>12) in New York embayments when *A. anophagefferens* densities were $>10^5$ cells ml^{-1} . We also observed higher DOC:DON ratios during bloom densities of *A. anophagefferens* (26 May–21 July, DOC:DON = 15 ± 2) compared with the postbloom period (30 July–5 Oct, 11 ± 2 ; Fig. 5A). However, during early June (26 May–8 June), when *A. anophagefferens* was a small component of the algal community (10%–20% of algal biomass), DOC:DON ratios were markedly higher (18 ± 1) than in early July, when *A. anophagefferens* was the dominant phytoplankton (15 ± 1 ; Figs. 2C, 5A). These results suggest that the relative abundance of *A. anophagefferens* within the phytoplankton community may also affect DOC:DON ratios. For example, higher DOC:DON ratios before the monospecific *A. anophagefferens* bloom could be indicative of a C-enriched DOM supply that supports bloom initiation by this mixotrophic species, a conclusion that is consistent with previous experimental observations we have made in WNB (Gobler and Sañudo-Wilhelmy 2001a). Alternatively, higher densities (and activities) of heterotrophic bacteria during the July bloom (Fig. 2D) could have also contributed toward DOC consumption and thus could have affected DOC:DON ratios as well (Soendergaard et al. 2000).

DOC turnover—OC-pool turnover rates for POC, DOC, HMW OC, and LMW OC were determined during the collapse of phytoplankton blooms in WNB (21 July–5 October; Table 1). In addition to microbial degradation, these turnover rates were also likely influenced by physical advection, and allochthonous inputs. However, the extended residence time and the dominance of autochthonous biogeochemical processes (Gobler et al. 2002) in this bay suggest that carbon losses due to advection and additions from allochthonous sources were likely small, relative to in situ processing. Our calculations demonstrate that all OC pools yielded rapid turnover rates during the first 2 weeks of decay and slower rates thereafter, which indicates components of assorted la-

Table 1. A comparison of organic carbon (OC) turnover rates during the collapse of algal blooms in West Neck Bay (WNB). OC pool turnover rates for particulate OC (POC), dissolved OC (DOC), high-molecular-weight (HMW) OC, and low-molecular-weight (LMW) OC were calculated from changes in the natural log of OC concentrations over time during the collapse of phytoplankton blooms in WNB (21 Jul–5 Oct; Kirchman et al. 1991). Short-term rates were determined over 0–15 d, whereas long term rates were as 15–75 d.

OC pool	Short-term turnover rates (d ⁻¹)	Long-term turnover rates (d ⁻¹)	Residence time of the short-term decay pool (d)	Residence time of the long-term decay pool (d)
POC	0.026±0.0027	0.0012±0.0021	38	830
DOC	0.025±0.0038	0.0036±0.0017	40	280
HMW OC	0.036±0.0052	0.0052±0.0009	28	190
LMW OC	0.014±0.0053	0.00073±0.00025	71	1,400

bilities within each physically fractionated pool (Berner 1980; Raymond and Bauer 2000). Over short time periods (2 weeks), DOC and suspended POC both turned over at similar rates (~0.025 d⁻¹; Table 1). In contrast, over both short (0–14 d) and long (15–75 d) time periods, the HMW OC pool turned over at rates approximately double the rates of the LMW OC pool (Table 1), which indicates the more rapid decay of colloidal carbon after its production by algal blooms. This observation is consistent with the results of previous research, which have demonstrated that HMW organic matter is highly labile and is preferentially used by bacteria over LMW organic matter (Amon and Benner 1994). It is of interest that the turnover rates for LMW OC were low, despite the relatively low C:N ratio (10.8 ± 1.8; Fig. 5), and thus potentially greater lability, of the LMW DOM pool. Such a discrepancy may reflect a decoupling of LMW OC and ON associated with the various compounds that make up this pool. For example, although N within LMW compounds such as amino acids turns over rapidly (Gardner et al. 1996), some refractory OC, which is likely LMW, can have an ocean residence time on the order of 10³ yr (del Giorgio and Duarte 2002).

Our turnover rates for all pools were lower than those obtained by Hopkinson et al (2002) within the Mid-Atlantic Bight for “very labile” DOM. Because our field observations were only made weekly, the measurement of such extremely short-term turnover rates of DOM was not possible. However, our short-term turnover rates (0–14 d; Table 1) were similar to those reported by Hopkinson et al (2002) for the pool they defined as “labile” DOM. Our OC turnover rates were notably higher than those observed by Raymond and Bauer (2000) in the York estuary, a river-dominated system. This difference could represent a greater importance of humic DOC in such a system, given that rivers typically contribute substantial levels of recalcitrant, humic DOC in estuaries, which turns over at a slower rate relative to fresh DOC produced by algal blooms (Moran and Hodson 1990).

The fate of carbon produced by estuarine phytoplankton blooms—Although coastal zones are more productive than the open ocean, the efficiency of the coastal ocean in sequestering CO₂ is unknown (del Giorgio and Duarte 2002) and is the focus of several major ongoing studies (Liu et al. 2000). Although some studies have determined the impact of sinking particles on the removal of carbon from the euphotic zone (Falkowski et al. 1988), little is known about

the fate of freshly produced DOM in coastal environments, despite its likely greater importance relative to sinking POM (del Giorgio and Duarte, 2002). We observed that most of the DOC produced during estuarine phytoplankton blooms was HMW (Fig. 3A) and turned over rapidly (Table 1). The quantification of phytoplankton and bacterial biomass during our study period has indicated that nearly all of the suspended POC in WNB was microbial biomass (Gobler and Sañudo-Wilhelmy 2001b), which suggests that the coagulation of HMW OC into POC (Honeyman and Santschi, 1989) was not a significant loss process. The rapid turnover rates for HMW OC (Table 1) and the bloom of bacteria (Fig. 2D) that occurred after the collapse of algal blooms in WNB suggests that a substantial portion of the DOM produced during our study may have been remineralized by microbial respiration. Specifically, the residence time of this bay (10–15 d) was closest to the residence time determined for the HMW OC short-term decay pool (28 d; Table 1), which suggests that only a fraction of this pool may have been exported from this system. By contrast, the significantly longer residence times of suspended POC and LMW OC (months to years; Table 1) suggests that substantial portions of these pools may have survived microbial decomposition in WNB and thus would serve as a net export of recently fixed carbon from this system. This conclusion is supported by the results of previous studies, which have found that a portion of DOM produced by marine phytoplankton is resistant to remineralization (Aluwihare et al, 1997). Our findings, coupled with Hopkinson et al.’s (2002) observed inverse correlation between DOM and salinity within the Mid-Atlantic Bight, suggest that estuaries are likely an important source of DOM to continental shelf ecosystems.

References

- ALUWIHARE L. I., D. J. REPETA, AND R. F. CHEN. 1997. A major biopolymeric component to dissolved organic carbon in surface sea water. *Nature* **387**: 166–169.
- AMON, R. W., AND R. BENNER. 1994. Rapid cycling of high-molecular weight dissolved organic matter in the ocean. *Nature* **369**: 549–552.
- BAUER J. E., AND E. R. M. DRUFFEL. 1998. Ocean margins as a significant source of organic matter to the deep open ocean. *Nature* **392**: 482–485.
- , K. K. RUTTENBERG, D. M. WOLGAST, E. MONAGHAN, AND M. K. SCHROPE. 1996. Cross-flow filtration of dissolved and

- colloidal nitrogen and phosphorus in seawater: Results from an intercomparison study. *Mar. Chem.* **55**: 33–52.
- BENNER, R., AND M. STROM. 1993. A critical evaluation of the analytical blank associated with DOC measurements by high-temperature catalytic oxidation. *Mar. Chem.* **41**: 153–160.
- BERG G. M., D. J. REPETA, AND J. LAROCHE. 2002. Dissolved organic nitrogen hydrolysis rates in axenic cultures of *Aureococcus anophagefferens* (Pelagophyceae): Comparison with heterotrophic bacteria. *Appl. Environ. Microbiol.* **68**: 401–404.
- BERNER, R. A. 1980. Early diagenesis: A theoretical approach. Princeton Univ. Press.
- BIDDANDA, B., AND R. BENNER. 1997. Carbon, nitrogen, and carbohydrate fluxes during the production of particulate and dissolved organic matter by marine phytoplankton. *Limnol. Oceanogr.* **42**: 506–518.
- BUESSELER, K. O. AND OTHERS. 1996. An intercomparison of cross-flow filtration techniques for sampling marine colloids. Overview and organic carbon results. *Mar. Chem.* **55**: 1–31.
- COLE, J. J., G. E. LIKENS, AND D. L. STRAYER. 1982. Photosynthetically produced dissolved organic carbon: An important carbon source for planktonic bacteria. *Limnol. Oceanogr.* **27**: 1080–1090.
- CARLSON, C. A., H. W. DUCKLOW, AND A. F. MICHAELS. 1994. Annual flux of dissolved organic carbon from the euphotic zone in the northwestern Sargasso Sea. *Nature* **371**: 405–408.
- CUTTER, G. A., AND J. RADFORD-KNOERY. 1991. Determination of carbon, nitrogen, sulfur, and inorganic sulfur species in marine particles, p. 57–63. *In* D. C. Hurd and D. W. Spencer [eds.], *Marine particles: Analysis and characterization*. Geophysical monograph 63. American Geophysical Union.
- DAI, M. H., AND OTHERS. 1998. Evaluation of two cross-flow ultrafiltration membranes for isolating marine organic colloids. *Mar. Chem.* **62**: 117–136.
- DEL GIORGIO, P. A., AND C. M. DUARTE. 2002. Respiration in the open ocean. *Nature* **420**: 379–384.
- FALKOWSKI, P. G., C. N. FLAGG, G. T. ROWE, S. L. SMITH, T. E. WHITLEDGE, AND C. D. WIRICK. 1988. The fate of a spring phytoplankton bloom: Export or oxidation? *Cont. Shelf Res.* **8**: 457–484.
- FISCHER, H. B., E. J. LIST, R. C. Y. KOH, J. IMBERGER, AND N. H. BROOKS. 1979. Mixing in inland and coastal waters. Academic Press.
- GARDNER W. S., R. BENNER, R. M. W. AMON, J. B. COTNER, J. F. CAVALETTI, AND J. R. JOHNSON. 1996. Effects of high-molecular weight dissolved organic matter on nitrogen dynamics in the Mississippi River plume. *Mar. Ecol. Prog. Ser.* **133**: 287–297.
- GLIBERT P. M., AND OTHERS. 2001. Harmful algal blooms in the Chesapeake and coastal bays of Maryland, USA: Comparison of 1997, 1998, and 1999 events. *Estuaries* **24**: 875–883.
- GOBLER C. J., J. R. DONAT, J. A. CONSOLVO, AND S. A. SAÑUDO-WILHELMY. 2002. Physico-chemical speciation of iron during coastal algal blooms. *Mar. Chem.* **77**: 71–89.
- , D. A. HUTCHINS, N. S. FISHER, E. M. COSPER, AND S. A. SAÑUDO-WILHELMY. 1997. Release and bioavailability of C, N, P, Fe, and Se following viral lysis of a marine chrysophyte. *Limnol. Oceanogr.* **42**: 1492–1504.
- , AND S. A. SAÑUDO-WILHELMY. 2001a. Effects of organic carbon, organic nitrogen, inorganic nutrients, and iron additions on the growth of phytoplankton and bacteria during a brown tide bloom. *Mar. Ecol. Prog. Ser.* **209**: 19–34.
- , AND ———. 2001b. Temporal variability of groundwater seepage and Brown Tide blooms in a Long Island embayment. *Mar. Ecol. Prog. Ser.* **217**: 299–309.
- HEDGES, J. 1987. Organic matter in sea water. *Nature* **330**: 205–206.
- HONEYMAN, B. D., AND P. H. SANTSCHI. 1989. A Brownian-pumping model for oceanic trace metal scavenging: Evidence from Th isotopes. *J. Mar. Res.* **47**: 951–992.
- HOPKINSON C. S., J. J. VALLINO, AND A. NOLIN. 2002. Decomposition of dissolved organic matter from the continental margin. *Deep-Sea Res. II* **49**: 4461–4478.
- HUTCHINS, D. A., A. E. WITTER, A. BUTLER, AND G. W. LUTHER. 1999. Specialized utilization of different organic iron species by marine phytoplankton taxa. *Nature* **400**: 858–861.
- JONES, M. N. 1984. Nitrate reduction by shaking with cadmium: Alternative to cadmium columns. *Water Res.* **18**: 643–646.
- KAHLER P., AND W. KOEVE. 2001. Marine dissolved organic matter: Can its C:N ratio explain carbon overconsumption? *Deep-Sea Res. I* **48**: 49–62.
- KEPKAY, P. E., J. F. JELLET, AND S. E. H. NIVEM. 1997. Colloidal organic carbon and phytoplankton speciation during a coastal phytoplankton bloom. *J. Plankton Res.* **19**: 369–389.
- KIRCHMAN, D. L., Y. SUZUKI, C. GARSIDE, AND H. W. DUCKLOW. 1991. High turnover rates of dissolved organic carbon during a spring phytoplankton bloom. *Nature* **352**: 612–614.
- LEWITUS, A. J., AND T. M. KANA. 1995. Light respiration in six estuarine phytoplankton species: Contrasts under photoautotrophic and mixotrophic growth conditions. *J. Phycol.* **31**: 754–761.
- LIU, K. K., K. ISEKI, AND S. Y. CHAO. 2000. Continental margins carbon fluxes. *In* R. B. Hanson, H. W. Ducklow, and J. G. Field [eds.], *The changing ocean carbon cycle*, p. 187–239. Cambridge Univ. Press.
- LOMAS M. W., P. M. GLIBERT, D. A. CLOUGHERTY, D. R. HUBER, J. JONES, J. ALEXANDER, AND E. HARAMOTO. 2001. Elevated organic nutrient ratios associated with brown tide algal blooms of *Aureococcus anophagefferens*. *J. Plankton Res.* **23**: 1339–1344.
- MAGUE, T. H., E. FRIBERG, D. J. HUGHES, AND I. MORRIS. 1980. Extracellular release of carbon by marine phytoplankton: A physiological approach. *Limnol. Oceanogr.* **25**: 262–279.
- MORAN, M. A., AND R. E. HODSON. 1990. Bacterial production on humic and nonhumic components of dissolved organic carbon. *Limnol. Oceanogr.* **35**: 1744–1756.
- NAGATA, T., AND D. L. KIRCHMAN. 1992. Release of macromolecular organic complexes by heterotrophic marine flagellates. *Mar. Ecol. Prog. Ser.* **83**: 233–246.
- PARSONS, T. R., Y. MAITA, AND C. M. LALLI. 1984. A manual of chemical and biological methods for seawater analysis. Pergamon Press.
- RAYMOND P. A., AND J. E. BAUER. 2000. Bacterial consumption of DOC during transport through a temperate estuary. *Aquat. Microb. Ecol.* **22**: 1–12.
- SOENDERGAARD, M., AND OTHERS. 2001. Net accumulation and flux of dissolved organic carbon and dissolved organic nitrogen in marine plankton communities. *Limnol. Oceanogr.* **45**: 1097–1111.
- VALDERRAMA, J. C. 1981. The simultaneous analysis of total nitrogen and phosphorus in natural waters. *Mar. Chem.* **10**: 109–122.
- WILLIAMS, P. J. LE B. 1995. Evidence for the seasonal accumulation of carbon-rich dissolved organic material, its scale in comparison with changes in particulate material and the consequential effect on net C/N assimilation ratios. *Mar. Chem.* **51**: 17–29.
- WOLLAST, R. 1991. The coastal organic carbon cycle: Fluxes, sources and sinks. *In* R. F. C. Mantoura, J. M. Martin, and R. Wollast [eds.], *Ocean margin progress in global change*, p. 365–381. Dahlem Workshop report. Wiley.

Received: 14 December 2002

Accepted: 9 June 2003

Amended: 17 June 2003