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Nitrogen uptake and primary productivity rates in the Mid-Atlantic Bight (MAB)

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ABSTRACT

Nutrient concentrations, primary productivity, and nitrogen uptake rates were measured in coastal waters of the Mid-Atlantic Bight over a two-year period that included measurements from all four seasons. In order to assess carbon productivity and nitrogen demand within the context of the physical environment, the region was divided into three distinct hydrographic regimes: the Chesapeake and Delaware Bay outflow plumes (PL), the southern Mid-Atlantic shelf influenced by the Gulf Stream (SS), and the mid-shelf area to the north of the Chesapeake Bay mouth (MS). Annual areal rates of total nitrogen (N) uptake were similar across all regions (10.9 ± 2.1 mol N m^{-2} y^{-1}). However, annual areal rates of net primary productivity were higher in the outflow plume region (43 mol C m^{-2} y^{-1}), than along the Mid-Atlantic shelf and in areas influenced by the Gulf Stream (41 and 34 mol C m^{-2} y^{-1}, respectively). Rates of net primary productivity were not well correlated with Chl *a* concentrations and were uncoupled with net N uptake rates. Seasonally averaged annual areal rates of net primary productivity for the Mid-Atlantic Bight measured in this study were higher than those calculated in previous decades and provide important validation information for biogeochemical models and satellite remote sensing algorithms developed for the region.

1. Introduction

While the global coastal ocean (<200 m) comprises less than 10% of the world's oceans, these highly productive regions are thought to account for more than 21% of total oceanic productivity (Gattuso et al., 1998; Jahnke, 2007). Primary production in most coastal and shelf systems is thought to be limited by nitrogen (N) (Dugdale and Goering, 1967; Ryther and Dunstan, 1971; Howarth and Marino, 2006), however these areas are impacted by adjacent landmasses and receive anthropogenic N inputs that can potentially alleviate this limitation. Consequently, productivity in these areas is often controlled by "new" N inputs [sensu Eppley and Peterson, 1979] from terrestrial sources such as rivers, overland and groundwater discharge, and from atmospheric deposition (Duce et al., 2008). Denitrification in freshwater, terrestrial, and estuarine sediments removes a substantial amount of reactive N (globally, between 80 and 90%) before it even enters the coastal zone and it is thought that most of the remainder is denitrified in continental shelf sediments (Galloway et al., 2008). In the Mid-Atlantic Bight (MAB), denitrification is thought to remove 90% of the total N entering the region by advection from the north and riverine sources (Fennel et al., 2006).

Because high denitrification rates in freshwater and estuarine systems effectively removes N before it is delivered to coastal systems, riverine and terrestrial run-off has less of an effect on primary productivity in the coastal zone than would otherwise be expected (Seitzinger et al., 2006). However, riverine N loading to the coastal U.S. has almost doubled over the past forty years and it is projected that these inputs will increase by another 30% over the next 30 years (Howarth et al., 1996, 2002). If denitrification in freshwater and estuarine sediments does not increase concomitantly with increasing N loads, the system may become saturated with reactive N and become a source of N to otherwise N-limited coastal systems off-shore (Galloway et al., 2008).

The N budget in the MAB is an important driver of primary production in this N-limited area, and therefore is tightly coupled to the carbon (C) budget (Howarth, 2004; Gruber and Galloway, 2008). Increases in primary productivity have been related to increases in anthropogenic N inputs into the coastal zone (Howarth et al., 2002; Paerl and Piehler, 2008; Conley et al., 2009). In particular, models used to predict algal growth and C draw down from nutrient loading often use simple conversion factors such as the Redfield ratio to estimate primary productivity from N uptake and vice versa (Fennel et al., 2006, 2008). Ratios of standing stocks of N and C may not be appropriate for relating N uptake to C productivity or turnover. In eutrophic environments, there may be shifts in the absolute amount and dominant source or form of N delivered to the coastal ocean from terrestrial sources (Cloern, 2001; Galloway et al., 2008), which

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in turn could effect photosynthetic activity and metabolism (Syrett, 1981; Syrett and Peplinska, 1988). For example, a shift from inorganic N to organic N loading may alter a community structure which could then affect net system trophic status or fuel algal blooms (Glibert et al., 1991, 2001). Mixotrophy also appears to be common in eutrophic environments (Burkholder et al., 2008; Heisler et al., 2008; Anderson et al., 2008) and both grazing and osmotrophic C uptake by phytoplankton mixotrophs can result in bicarbonate:N uptake rates that deviate from Redfield.

Large-scale shifts in circulation patterns and nutrient delivery to coastal regions due to sea level rise and changes in storm activity under projected climate change scenarios are likely to have great consequences for N delivery to coastal systems and coastal productivity (Stevenson et al., 2002; Alley et al., 2007). Physical processes controlling mixing are an important control on N availability and primary productivity and seasonal stratification/destratification; upwelling can dominate the annual cycle of productivity in the MAB (Flagg et al., 2002; Lentz, 2003; Rasmussen et al., 2005). Specifically, interactions between the flow of the cold Labrador current from the north and the warm oligotrophic Gulf Stream current from the south creates a complicated pattern of seasonal stratification and destratification that is highly dependent on wind speed, direction, duration, and eddy development (Flagg et al., 2002). In the Summer months, along the southern near shore section of the North American Mid-Atlantic coast, the water column is highly stratified, thus limiting vertical transport of nutrients to surface waters from depth and primary productivity is greater near the bottom of this shallow water column rather than in surface waters (O'Reilly and Zetlin, 1998; Flagg et al., 2002). Intrusions of saltier deep water from the slope increases during the Summer in the along-shelf direction (from north to south), thus leading to higher salinity surface waters, nutrient upwelling and increased biomass concentrations in subsurface waters (about 20–25 m) during this time (O'Reilly and Zetlin, 1998; Flagg et al., 2002; Lentz, 2003). In the Fall, surface waters cool and the water column turns over, due to wind-driven mixing, and there is higher productivity in the near shore surface waters and along the shelf (O'Reilly and Zetlin, 1998). The water column is usually well-mixed with generally low productivity during the Winter (Wright and Parker, 1976; Rasmussen et al., 2005). In the Spring, increased light availability leads to higher productivity in relatively nutrient enriched surface waters (O'Reilly and Zetlin, 1998).

In addition to physical forcing and anthropogenic N inputs, primary productivity in the MAB and other coastal areas may be affected by increasing atmospheric carbon dioxide (CO_2) concentrations and/or projected temperature rises in the future, as has been observed in the oligotrophic North Atlantic and in mesocosm experiments (Hein and Sand-Jensen, 1997; Riebesell et al., 2007). The sensitivity of coastal regions to increasing CO_2 and water temperature is largely unknown and so the future of these systems as sources or sinks of atmospheric CO_2 is in question (Riebesell et al., 2007). While ocean margins, including those associated with the MAB, are currently thought to be net sinks for atmospheric CO_2, it is unclear whether the MAB will be a net source or sink of atmospheric CO_2 in the future given the complex interactions affecting productivity in the region (Chavez et al., 2007). How N availability will affect primary production and the ocean's ability to continue to take up C is centered on understanding 'nitrogen-carbon-climate interactions' (Gruber and Galloway, 2008). Quantifying regional N dynamics at present will not only help resolve N budgets and primary productivity in coastal regions under present day climatic conditions, but will allow us to begin to project what the future might hold under evolving climate change scenarios (Howarth, 2004).

Like most oceanic systems, the MAB is under-sampled and so the N budget is poorly constrained. There are few measurements of N uptake in this coastal system and most models estimate N demand for primary productivity from nitrate (NO_3^-) and ammonium (NH_4^+) uptake (Fennel et al., 2006). However, uptake of these compounds is often lower than that of other N compounds such as nitrite (NO_2^-), urea, and dissolved free amino acid N (DFAA N) and uptake of these compounds can be particularly important in coastal regions where recycling is rapid (Lipschultz, 2008; Filippino et al., 2009). Multiple N forms are present at any given time, including inorganic and organic compounds, and phytoplankton and bacteria can compete for these N compounds, complicating our interpretation of uptake data (Mulholland and Lomas, 2008). In addition, many phytoplankton are mixotrophic and so the relationship between N uptake and photosynthetic C fixation can be complicated, particularly in coastal regions enriched in organic and inorganic N compounds. In this study we quantified ambient N concentrations, N uptake using a broad range of inorganic and organic N compounds, and photosynthetic C uptake with respect to the hydrographic regime. This information is essential for constructing and testing models, developing accurate algorithms to estimate productivity from ocean color, and predicting present day and future uptake of atmospheric CO_2 in this highly productive region.

2. Materials and methods

Five cruises were undertaken over two years (30 March–2 April 2005; 26–30 July 2005; 9–12 May 2006; 2–5 July 2006; 30 October–2 November 2006). Primary productivity rates, N uptake rates, and nutrient concentrations were measured during these 3–5 day sampling excursions. Stations included locations in the Chesapeake Bay mouth and its outflow plume [see also Filippino et al., 2009], the Delaware Bay outflow plume, waters influenced by the Gulf Stream, and the non-estuarine influenced continental shelf between the Delaware Bay and Chesapeake Bay (Fig. 1). Exact station locations varied between cruises due to meteorological,

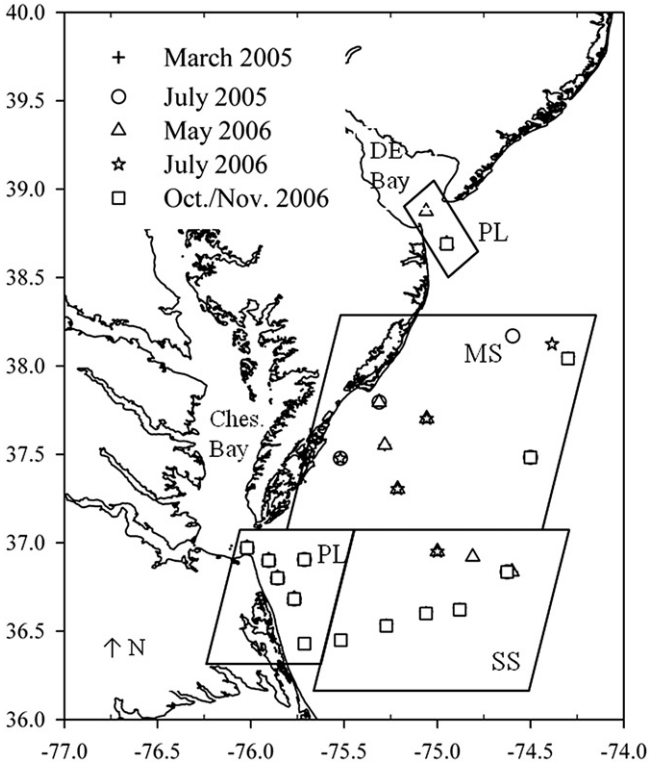

Fig. 1. Station locations for cruises conducted during March 2005 (plus signs), July 2005 (circles), May 2006 (triangles), July 2006 (stars), and October/November 2006 (squares).

tidal, and other constraints. Cruises were aboard the *R/V Cape Henlopen* (2005) or *R/V Hugh R. Sharp* (2006) and were generally comprised of on-shore to off-shore or off-shore to on-shore sampling transects each cruise day.

$$\text{Euphotic depth} = \frac{\ln(\text{surface light}) - \ln(\text{light at compensation depth})}{\text{K490}} \quad (1)$$

Hydrography was characterized at each station using a rosette-mounted conductivity, temperature, and depth (CTD) sensor (SeaBird electronics). Water samples were collected using rosette-mounted Niskin bottles at both the surface (D1: 0–2 m) and fluorescence maximum (D2: 4.5–18 m in the plume region; 10–50 m in the southern shelf; 5–53 m in the mid-shelf). When the water column was well-mixed or shallow, with no defined fluorescence maximum, samples were collected from the upper 2 m and 1 m above the bottom. Water samples collected for nutrient analyses were filtered through 0.2 μm polysulfone cartridge filters and placed into acid washed bottles and frozen until analysis. Particulate (N and C) and chlorophyll *a* (Chl *a*) samples were filtered onto precombusted (450 °C for 2 h) GF/F filters (nominal pore size of 0.7 μm), and the filters were placed into sterile cryovials and frozen until analysis.

Concentrations of NO_2^-, NO_3^-, urea, PO_4^{3-}, and SiO_4^{4-} were analyzed on an Astoria Pacific nutrient autoanalyzer according to manufacturer specifications using standard colorimetric methods (Parsons et al., 1984; Price and Harrison, 1987). The manual phenol–hypochlorite method was used for NH_4^+ analyses (Solorzano, 1969). Total dissolved nitrogen (TDN) was analyzed as NO_3^- after persulfate oxidation (Valderrama, 1981). DON was calculated as the difference between TDN and dissolved inorganic N (DIN). Dissolved free amino acids (DFAA) were measured by high performance liquid chromatography, (HPLC) [modified from Cowie and Hedges, 1992]. DFAA N concentrations were calculated based on the mole % composition of the individual amino acids and their N content. Chl *a* samples were analyzed fluorometrically within 5 days of collection (Welschmeyer, 1994).

N uptake and estimates of primary productivity were measured using stable isotopes as tracers. Whole water samples were placed into acid-cleaned 250 mL or 500 mL PETG incubation bottles. Experiments were initiated by adding 0.05–0.1 μmol N L^{-1} highly enriched (96–99%) ^{15}N tracers (or about 10% of the estimated ambient nutrient pool) of the tracer (Filippino et al., 2009). For bicarbonate uptake ($H^{13}CO_3^-$), 4-h or 24-h incubations were done to estimate integrated daily net bicarbonate uptake. Daily rates of photosynthesis were calculated directly from 24-h incubations; a 12-h photoperiod was used to calculate daily rates for the 4-h incubations. Volumetric uptake rates were calculated using a mixing model (Mulholland et al., 2006).

Areal rates of N and C uptake were calculated by averaging volumetric rates for the two sampling depths and then multiplying by the euphotic depth. The euphotic depth, typically defined as 1% of photosynthetic active radiation (PAR), was determined in three different ways during the five cruises; using: 1) PAR sensor data, 2) *in situ* radiometry readings, or 3) satellite imagery data. There was no single reliable or available measurement for all stations and all cruises. A PAR sensor interfaced to a Campbell Scientific CR-10X datalogger was used to measure the euphotic depth in some cases. *In situ* radiometry measurements of the water leaving irradiance at 490 and 555 nm (nLw490/nLw555) using the BioPro, in-water profiling spectroradiometer (Biospherical Instruments, Inc.; San Diego, CA) were also used to estimate the euphotic depth (Mannino et al., 2008). Finally, the diffuse attenuation coefficient at 490 nm (K490) from either SeaWifs or MODIS satellite imagery was obtained and the euphotic depth was estimated using NASA's algorithm for some stations (Eq. (1)):

Because the euphotic depth was determined using different methods depending on data availability, decision criteria were developed to select the most appropriate euphotic depth for each station. For most cruises, the euphotic depth was estimated in at least two ways and these estimates were in agreement. If no modeled or measured estimates (i.e. from PAR sensor, radiometry, or K490 data) were available and the fluorescence maximum was equal to the depth of the water column, then the depth of the water column was used as the euphotic depth, this was the case for 21% of the stations occupied during the five cruises. If only 1% PAR measurements were available or radiometry and/or K490 measurements did not agree with each other, then the depth at which 1% PAR was observed was used as the euphotic depth, and this occurred at 33% of the stations occupied. If the calculated or modeled depths were greater than the actual depth of the water column, the depth of the water column was used as the euphotic depth. This was the case for 23% of the stations occupied during the five cruises. If there was only radiometry or K490 measurements available, and they were not greater than the water column depth, either radiometry or K490 measurements were used to calculate the euphotic depth. This was the case at 8% of the stations occupied during the five cruises. Finally, if no modeled or measured estimates were available, than the base of the fluorescence maximum was used as the euphotic depth. This was the case for 15% of the stations occupied during the five cruises.

Areal rates of N uptake and primary productivity were averaged by region (PL, MS, and SS) and season for the two-year study to get annual rates. First, daily rates were calculated for each season: Winter (March 2005), Spring (May 2006), Summer (average from July 2005 and 2006), and Fall (October/November 2006). Daily rates for each season were then multiplied by 91.25 days (365 days per year divided by 4) and then added together to estimate a seasonally integrated annual N or C uptake rate for each region. Annual rates were calculated for each region using the surface area of each of the three regions (PL, MS, and SS). These surface areas were estimated based on the sampling boundaries during each cruise: for PL this was 37–36.4°N, 76° and the coastal land boundary along the eastern border; for SS this was 36.4–37.0°N, 75.5–74.4°W; and for MS this was 37–38.5°N and the coastal land boundary along eastern border to 74°W.

3. Results and discussion

3.1. Hydrographic regime

The hydrographic regime in the sampling region varied greatly between cruises (Fig. 2). Based on temperature, salinity, and density the study region was separated into three major hydrographic regions: plume influenced regions (PL), a mid-shelf region (MS) outside the influence of the plumes, and a southern shelf region (SS). The PL regions were largely influenced by inputs from the Chesapeake and Delaware Bays and often had large gradients in salinity. In the SS region, the Gulf Stream often introduced warm, salty water from the south while in the MS region north of the

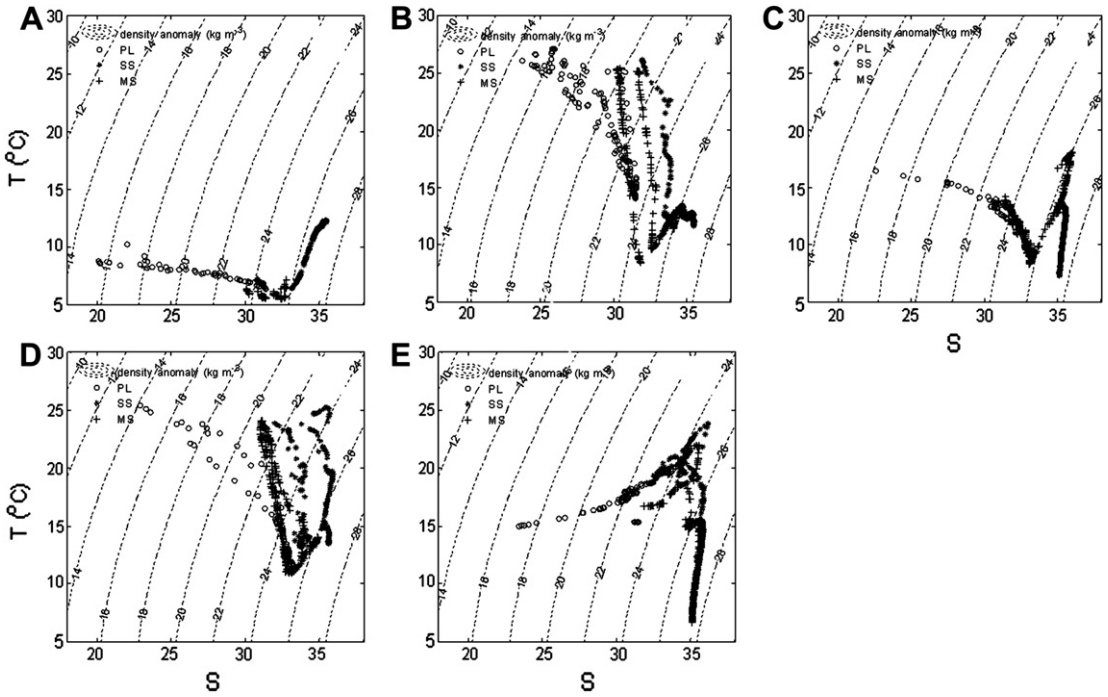

Fig. 2. Temperature–salinity diagrams for each cruise: A) March 2005, B) July 2005, C) May 2006, D) July 2006, E) Oct./Nov. 2006. Dashed lines are density anomaly contours.

Chesapeake Bay mouth, oceanic and coastal process converged and Gulf Stream and plume salinity and temperature signatures were not detected. Temperature–salinity diagrams show that the range in surface salinity was the greatest (between 22 and 31) for the PL region, as expected due to the influence of freshwater inputs and tidal fluctuations (Fig. 2). Overall, the plume region was generally stratified (Fig. 2A–E) and had the lowest surface salinities within the entire sampling region. During late Winter (March 2005), a jet-like plume of Bay water exiting South along the coastline was observed due to downwelling-favorable winds from the north. A jet-like plume was also observed during Spring (May 2006) when the field campaign was preceded by a period of strong and sustained winds from the north causing off-shore transport of surface water (Filippino et al., 2009). A diffusive plume with an estuarine influence was observed during Summer due to upwelling-favorable winds (July 2005 and 2006), while a more oceanic influence was observed during Fall (October/November 2006) (Filippino et al., 2009). Salinity in the SS and MS did not vary greatly, ranging between 29 and 36 in the SS and between 30 and 34 along the MS. The density anomalies for the SS and MS were also similar ranging between 22 and 28 kg m^{-3} and 20 and 28 kg m^{-3} for the SS and MS, respectively (Fig. 2A–F), and the water column in both regions was generally well-mixed.

A wide range of surface water temperatures was observed over the study period, with the lowest temperatures (6 °C) occurring during late Winter/early Spring 2005 and highest temperatures (27 °C) occurring during Summer 2005 in all three regions. There was an apparent Gulf Stream influence at SS stations during Summer (July 2006) when higher temperatures and salinities were observed at off-shore stations (Fig. 2D). Relative to Summer 2005, water temperatures were lower and salinity was higher in the MS region along the eastern shore of Virginia (north of the Chesapeake Bay mouth) during Summer 2006 suggesting upwelling of nutrient-rich waters. Upwelling-favorable winds coming out of the south were observed prior to the cruise.

3.2. Nutrient regime

Bulk DIN ($DIN = NH_4^+ + NO_3^- + NO_2^-$) concentrations were not significantly different between surface waters (0.1–4.3 μmol L^{-1}; mean = 1.0 ± 0.9 μmol L^{-1}) and the fluorescence maximum or near bottom sampling depth (0.2–4.2 μmol L^{-1}; mean = 1.2 ± 0.9 μmol L^{-1}), therefore DIN concentrations were averaged over both depths. When samples were averaged for each season, DIN concentrations (specifically NO_3^-) were greater in Fall and Winter compared to Spring and Summer ($p < 0.05$; Table 1). NH_4^+ concentrations were significantly greater in Winter compared to Spring, Summer, and Fall, and Fall and Summer concentrations were greater than Spring concentrations ($p < 0.05$; Table 1). NO_2^-

Table 1
Average concentrations for NH_4^+, NO_2^-, NO_3^-, DIN, urea, DFAA N, and DON by region and season. Standard deviations are in parentheses.

	# of observations	NH_4^+ (μmol N L^{-1})	NO_2^- (μmol N L^{-1})	NO_3^- (μmol N L^{-1})	DIN (μmol N L^{-1})	Urea N (μmol N L^{-1})	DFAA N (μmol N L^{-1})	DON (μmol N L^{-1})
PL	54	0.63 (0.34)	0.17 (0.13)	0.29 (0.42)	1.10 (0.75)	0.26 (0.20)	0.27 (0.24)	13.78 (5.45)
SS	24	0.48 (0.37)	0.15 (0.10)	0.70 (1.03)	1.33 (1.20)	0.20 (0.17)	0.22 (0.10)	7.89 (3.85)
MS	46	0.53 (0.36)	0.14 (0.15)	0.32 (0.46)	0.98 (0.75)	0.20 (0.20)	0.19 (0.14)	11.92 (7.55)
Spring	26	0.35 (0.04)	0.13 (0.06)	0.15 (0.40)	0.62 (0.45)	0.21 (0.10)	0.20 (0.06)	14.06 (7.72)
Summer	50	0.53 (0.25)	0.12 (0.09)	0.22 (0.30)	0.88 (0.44)	0.15 (0.18)	0.17 (0.12)	10.10 (6.15)
Fall	30	0.55 (0.48)	0.28 (0.16)	0.60 (0.80)	1.43 (1.09)	0.32 (0.17)	0.23 (0.13)	10.88 (5.29)
Winter	18	1.00 (0.25)	0.08 (0.06)	0.79 (0.89)	1.87 (1.09)	0.31 (0.27)	0.44 (0.36)	15.80 (4.48)

concentrations in Fall were significantly greater than in Winter, Spring, and Summer ($p < 0.05$; Table 1).

NH_4^+ was generally the proportion of the total measured dissolved N (NH_4^+, NO_2^-, NO_3^-, urea, and DFAA) pool at PL and MS stations (39% and 34% of measured dissolved N, at surface and at depth, respectively). However, NO_3^- was often the dominant N form at the SS stations at the fluorescence maximum (as high as 80% of measured dissolved N) particularly at the off-shore stations, suggesting possible upwelling of NO_3^- at the shelf/slope interface.

Urea concentrations ranged from below the limit of detection (0.05 μmol N L^{-1}) to 1.2 μmol N L^{-1} for all regions (Table 1) and no significant differences were observed between sample depths. When averaged across seasons, urea concentrations were significantly greater in Winter than in Spring and Summer, and concentrations in Fall were significantly greater than those observed in Summer ($p < 0.05$; Table 1). There were no significant differences in DFAA N concentrations between regions (D1: 0.27 ± 0.24 μmol N L^{-1}; D2: 0.39 ± 0.39 μmol N L^{-1}), but DFAA N concentrations were significantly greater in Winter compared to other seasons ($p < 0.05$; Table 1). DON concentrations were not significantly different between surface waters (D1: 12.1 ± 6.3 μmol N L^{-1}) and the fluorescence maximum or near bottom sampling depth (D2: 11.7 ± 6.6 μmol N L^{-1}). While there were no significant regional differences in average urea and DFAA N concentrations, DON concentrations were significantly higher in the PL and MS regions compared to the SS region ($p < 0.05$; Table 1) where the lowest concentrations of DON for the whole study area were observed in July 2006 (D1: 2.2–13 μmol N L^{-1}; D2: 3.3–8.3 μmol N L^{-1}). DON concentrations were significantly greater in Winter and Spring compared to Summer and Fall, and greater in Fall than in Summer ($p < 0.05$; Table 1).

Concentrations of PO_4^{3-} ranged from below the limit of detection (0.02 μmol L^{-1}) to 0.5 μmol L^{-1} and concentrations of SiO_4^{4-} ranged from 0.06 to 15 μmol L^{-1} for the pooled data set (Table 2). There was no significant difference in averaged PO_4^{3-} concentrations between regions ($p > 0.05$; Table 2). However, not surprisingly, SiO_4^{4-} concentrations were greatest in the PL region compared to the SS and MS regions ($p < 0.05$; Table 2). PO_4^{3-} concentrations were significantly greater in Winter than in any other season ($p < 0.05$; Table 2) while SiO_4^{4-} concentrations were significantly greater in Fall than in any other season ($p < 0.05$; Table 2). DIN:DIP ratios were most often less than 16, suggesting N limitation in the study region (Table 2), exceptions were the SS and PL stations during the Summer cruises when ratios were greater than 16. SiO_4^{4-} did not appear to be limiting to diatom growth (DIN:SiO_4^{4-} < 1; Table 2), except possibly during March 2005.

3.3. Biomass

Chl *a* concentrations were significantly greater at the PL stations than the SS and MS stations, ranging from 0.8 to 12 μg chl L^{-1} ($p < 0.05$; Table 3). Chl *a* concentrations in Winter were significantly greater than in Spring, Summer, and Fall ($p < 0.05$; Table 3). This is likely due to the timing of the Winter cruise during March when the Spring bloom normally occurs in the Chesapeake Bay (Boynton et al., 1982; Malone et al., 1988). The greatest differences in Chl *a* concentrations between the surface and fluorescence maximum (12.1 and 3.1 μg chl L^{-1}, respectively) were observed in the plume in March 2005 when there was strong, fresh, surface water outflow, and the water column was highly stratified (Filippino et al., 2009); likely due to washout of Chl *a* from the Chesapeake Bay Spring bloom (Boynton et al., 1982; Malone et al., 1988). On average, Chl *a* concentrations in water collected from the surface and fluorescence maximum were not significantly different ($p > 0.05$) in the PL region. In contrast, the overall average Chl *a* concentrations at the fluorescence maximum in the MS and SS regions (MS: 1.44 ± 0.79 μg chl L^{-1}; SS: 1.23 ± 0.66 μg chl L^{-1}) were significantly greater than the average surface concentrations (MS: 0.79 ± 0.66 μg chl L^{-1}; SS: 0.67 ± 0.54 μg chl L^{-1}; $p < 0.05$).

Similar to Chl *a*, PN and PC concentrations were significantly greater at the PL stations compared to the SS and MS stations ($p < 0.05$; Table 3). When PN and PC concentrations were averaged for each season, there were no significant differences in PN concentrations between seasons, but PC concentrations were significantly greater in Spring than in Fall ($p < 0.05$; Table 3). Average PN and PC concentrations were not significantly different between surface water and the fluorescence maximum ($p > 0.05$).

Table 2
Average concentrations for PO_4^{3-}, SiO_4^{4-}, DIN:DIP, and DIN:SiO_4^{4-} by region and season.

	# of observations	PO_4^{3-} (μmol L^{-1})	SiO_4^{4-} (μmol L^{-1})	DIN:DIP	DIN:SiO_4^{4-}
PL	54	0.15 (0.09)	3.32 (3.53)	7.23 (0.91)	0.33 (1.26)
SS	24	0.13 (0.12)	1. 10 (0.98)	9.69 (1.29)	1.22 (1.27)
MS	46	0.15 (0.12)	1.46 (1.14)	6.41 (1.11)	0.67 (1.09)
Spring	26	0.11 (0.05)	0.91 (0.29)	5.76 (0.87)	0.68 (0.81)
Summer	50	0.12 (0.11)	2.37 (2.72)	6.58 (1.02)	0.36 (1.38)
Fall	30	0.15 (0.07)	3.86 (3.47)	9.66 (0.89)	0.37 (1.17)
Winter	18	0.27 (0.12)	0.84 (0.32)	7.23 (0.78)	2.37 (0.73)

Table 3
Average concentrations for Chl *a*, PN, and PC by region and season.

	# of observations	Chl *a* (μg L^{-1})	PN (μmol L^{-1})	PC (μmol L^{-1})
PL	54	3.22 (2.10)	5.74 (2.76)	48.99 (21.46)
SS	24	0.94 (0.69)	1.95 (1.09)	16.93 (5.95)
MS	46	1.10 (0.78)	2.57 (1.20)	25.20 (10.67)
Spring	26	2.11 (1.62)	4.47 (3.13)	44.19 (25.91)
Summer	50	1.50 (1.32)	3.80 (2.75)	34.19 (19.07)
Fall	30	2.32 (1.42)	3.39 (1.50)	26.08 (12.22)
Winter	18	3.12 (3.61)	3.80 (3.02)	32.18 (23.68)

3.4. Volumetric primary productivity and N uptake rates

Primary productivity rates (volumetric and Chl *a* normalized) were not significantly different between the surface and fluorescence maximum throughout the study area ($p > 0.05$; Fig. 3). Volumetric bicarbonate uptake rates were significantly greater in the PL region compared to the SS and MS regions for the combined data ($p < 0.05$), there were no significant differences in Chl *a* normalized primary productivity rates between regions ($p > 0.05$). Volumetric primary productivity rates were not significantly different between seasons ($p > 0.05$), however, average Chl *a* normalized primary productivity rates were significantly greater in Summer than in Fall and Winter ($p < 0.05$).

During March 2005, volumetric primary productivity rates ranged between 0.9 and 12.4 μmol C L^{-1} d^{-1} and Chl *a* normalized rates ranged between 0.2 and 3.9 μmol C μg chl^{-1} d^{-1} (Fig. 3A). During the first Summer cruise (July 2005) volumetric and Chl *a* normalized rates had the largest ranges (4.1–31.6 μmol C L^{-1} d^{-1} or 5.8–42.0 μmol C μg chl^{-1} d^{-1}; Fig. 3B). In July 2005, volumetric rates were significantly greater in the plume and coastal regions of the mid-shelf while Chl *a* normalized rates were greatest in the MS region, both near the coast and off-shore (Fig. 3B). Volumetric and Chl *a* normalized primary productivity rates in Spring 2006 ranged between 1.8 and 18.4 μmol C L^{-1} d^{-1} and 0.7 and 11.3 μmol C μg chl^{-1} d^{-1}, respectively (Fig. 3C). Rates were similar throughout the study area, with only slightly higher volumetric rates

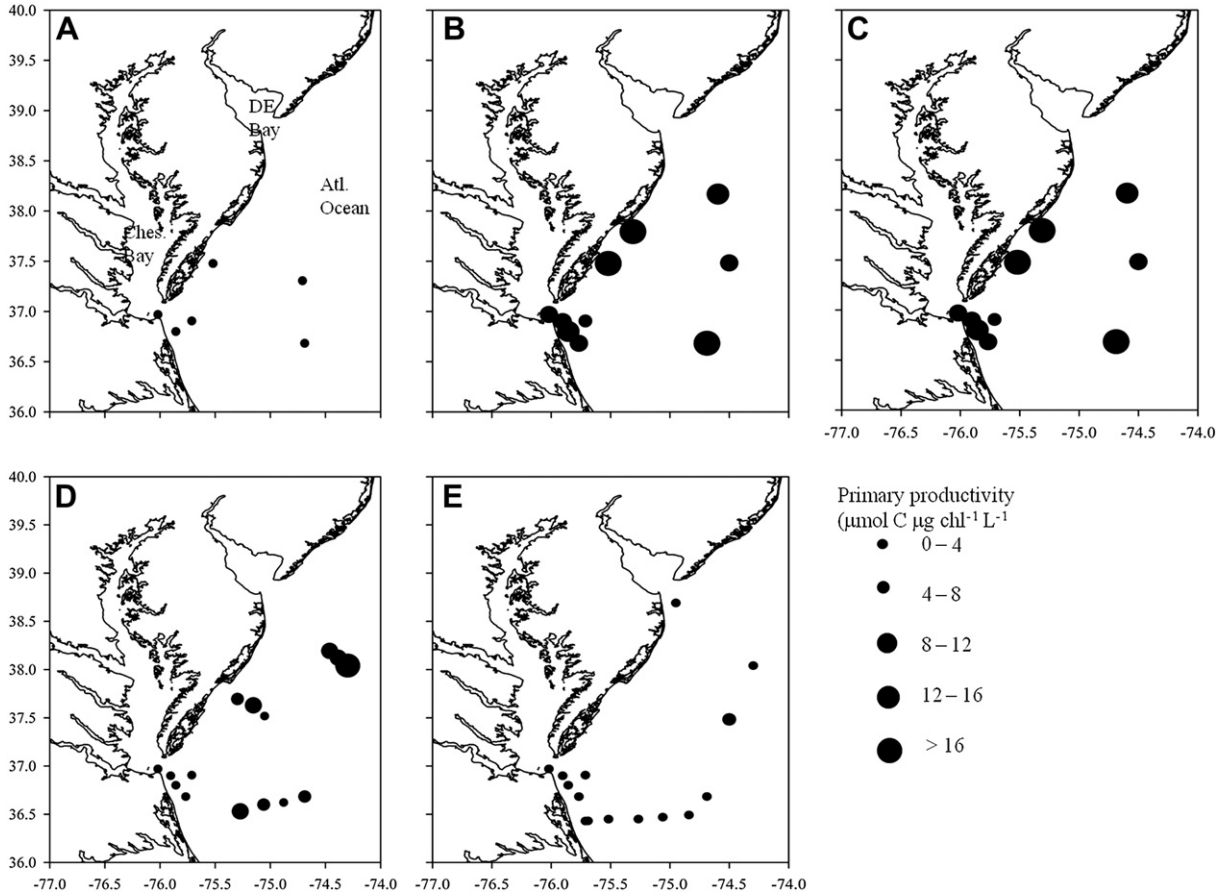

Fig. 3. Chl *a* normalized primary productivity rates (μmol C μg chl^{-1} d^{-1}) during A) 30 March–1 April, 2005, B) 27–30 July 2005, C) 8–12 May 2006, D) 2–5 July 2006, and E) 30 October–2 November 2006. Rates are averages from surface and the fluorescence maximum.

observed in the two plume regions. In July 2006, volumetric and Chl *a* normalized primary productivity rates were lower than during the first Summer cruise and ranged between 0.8 and 10.8 μmol C L^{-1} d^{-1} and 1.6 and 16.1 μmol C μg chl^{-1}vd^{-1}, respectively (Fig. 3D) and there were no significant differences in productivity between regions. During October 2006, volumetric and Chl *a* normalized primary productivity rates were as low as those observed in March 2005 and ranged from 1.6 to 12.2 μmol C L^{-1} d^{-1} and 1.0 to 5.4 μmol C μg chl^{-1} d^{-1}, respectively (Fig. 3E).

Volumetric primary productivity rates were not well correlated with Chl *a* concentrations for the pooled data set ($R = 0.367$) or when averaged over region, similar to what was observed in a more detailed study of the Chesapeake Bay outflow plume (Filippino et al., 2009). There was a significant positive linear relationship between average volumetric primary productivity and Chl *a* concentration during Spring ($R = 0.659$; $p < 0.05$; Fig. 4A) and in Fall ($R = 0.882$; $p < 0.05$; Fig. 4A). If only the lower range of primary productivity (<10 μmol C L^{-1} d^{-1}) and Chl *a* (<5 μg chl L^{-1}) are considered, a significant relationship was also observed in Fall ($R = 0.907$; $p < 0.05$; Fig. 4B) but not for Spring (Fig. 4B). During Fall, there were significant negative linear relationships between volumetric primary productivity rates and salinity ($R = -0.794$; $p < 0.05$) and temperature ($R = -0.728$; $p < 0.05$; data not shown). These relationships suggest that cool (15 °C), fresher (s = 24), estuarine outflow waters are more productive than warm (24 °C), salty (s =36), oceanic waters. There were also significant positive linear relationships between primary productivity and TDN concentrations ($R = 0.634$; $p < 0.05$), PO_4^{3-} concentrations ($R = 0.649$; $p < 0.05$), and SiO_4^{4-} concentrations ($R = 0.759$; $p < 0.05$) during Fall but not during any other season.

Similar to primary productivity results, there were no significant differences between total volumetric N uptake rates at the surface or the fluorescence maximum, therefore rates reported here are depth-averaged. Total measured volumetric N uptake rates were significantly greater in the PL region (0.01–0.63 μmol N L^{-1} h^{-1}), and NH_4^+ uptake rates on average were significantly greater ($p < 0.05$) than uptake of the other N compounds measured and often represented over 50% of the total measured N uptake (Fig. 5). Only in off-shore stations in the SS region were uptake rates of NO_3^- (0.013–0.029 μmol L^{-1} h^{-1}) greater than uptake rates of NH_4^+ (0.002–0.007 μmol L^{-1} h^{-1}). Although total N uptake rates were greatest in the PL region, where Chl *a* biomass was also highest (Table 3) (Fig. 5A), total N uptake rates did not significantly correlate to Chl *a* concentrations in the PL region ($p > 0.05$). There was no significant linear relationship between Chl *a* and total N uptake or between Chl *a* and uptake of individual N compounds ($R = 0.056$; $p > 0.05$) in the study area. In fact N uptake was fairly uniform over a range of Chl *a* concentrations. For example, NH_4^+ uptake rates were nearly identical (0.34 and 0.35 μmol N L^{-1} h^{-1}) at PL stations with Chl *a* concentrations of 2.2 and 9.1 μg chl L^{-1}, respectively.

Total N uptake rates were significantly greater in Summer compared to Fall and NH_4^+ comprised 60% of the total N uptake rates (Fig. 5B). One reason for this may be retention of bacteria on GF/F filters. Between 20 and 80% of bacteria can be retained on these filters (Taguchi and Laws, 1988) and bacteria also take up the inorganic and organic compounds used here (Mulholland and Lomas, 2008). DFAA N uptake rates were significantly greater during Winter when DFAA concentrations were higher than in Spring, Summer, and Fall (Fig. 5B). No significant differences in NO_3^- and NO_2^- uptake rates were observed between seasons.

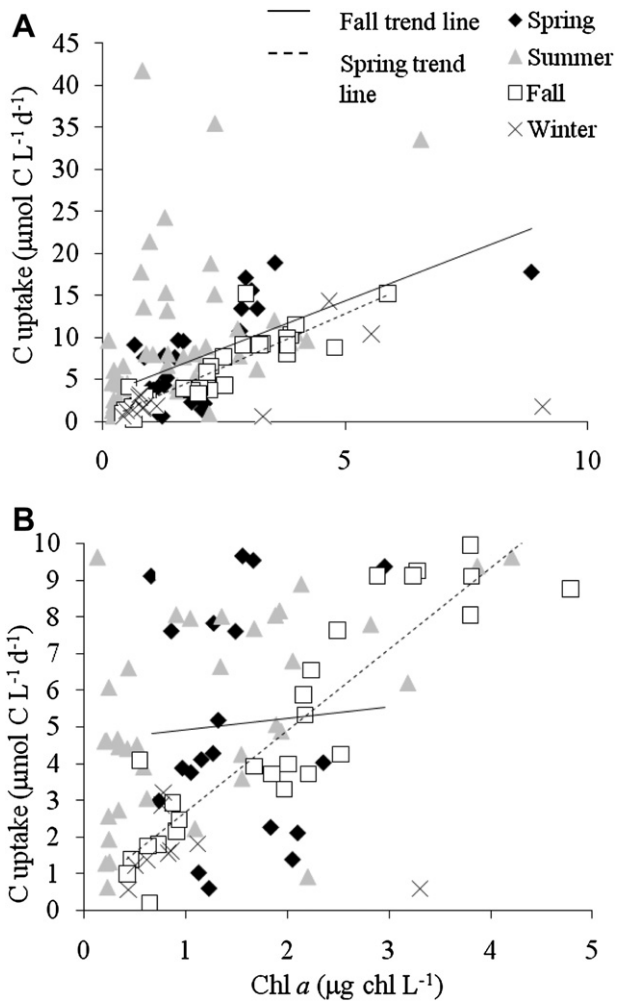

Fig. 4. Volumetric primary productivity rates versus Chl *a* concentrations for A) the entire range of Chl *a* during Spring, Summer, Fall, and Winter and for B) Chl *a* concentrations less than 5 µg chl L^{-1}.

3.5. Annual areal primary productivity and N uptake rates

Using the assumptions and parameters provided in the methods, we estimate an average annual areal primary productivity rate of 39.6 ± 4.2 mol C m^{-2} y^{-1} and an average annual areal N uptake rate of 10.9 ± 2.1 mol N m^{-2} y^{-1} (Table 4) for the study region. Annual areal primary productivity rates for the Gulf Stream-influenced SS stations (5.8–45.1 mol C m^{-2} y^{-1}; Table 4) were at the lower range of published estimates of primary productivity for Gulf Stream intrusions (54 ± 20 mol C m^{-2} y^{-1} during Spring and Summer; Table 5) (Lohrenz et al., 2002). This may be because we measured net rather than gross bicarbonate uptake. While there were no significant differences between seasonal averages of areal primary productivity (Table 6), during Summer and Spring there were larger ranges in rates, with some stations having rates as high as 0.44 mol C m^{-2} d^{-1}. During Fall and Winter, the highest rates at any station were only 0.22 mol C m^{-2} d^{-1}. Annual areal rates of primary productivity and total N uptake rates (mol y^{-1}) were 3.4 and 4.2 times greater in the MS area than in the PL and SS regions, respectively, primarily due to the larger surface area (Table 4).

4. Conclusions

There are very few, direct measurements of primary productivity for the coastal MAB region, and most literature estimates are based on data from at least a decade ago, models, or inferred from satellite data and relationships between Chl *a*, nutrients, and productivity (Table 5). The most comprehensive study (Marine Resources Monitoring, Assessment, and Prediction program – MARMAP) with *in situ* ^{14}C bicarbonate incubations was conducted from 1977 to 1988 (Campbell and O'Reilly, 1988). Since that time, much has changed with regard to methodology and our understanding of human impacts on the environment and global climate change. Many of the published productivity estimates were derived from modeled data; the majority of these estimates calculated lower primary productivity rates than those found in our study (Table 5). For example, primary productivity rates calculated from mixed layer depth (based on temperature), phytoplankton community and Chl *a* data from the MARMAP program, and nitrate concentrations from the World Ocean Atlas 2001 (Mouw and Yoder, 2005) were much lower than those estimated here and in most of the other studies. Model assumptions included relationships between nitrate concentrations and photosynthesis (Mouw and Yoder, 2005), however, our results showed no correlation between nitrate concentrations and either nutrient uptake or primary productivity rates in the coastal waters of the MAB. Early attempts to model primary productivity using satellite imagery and optical properties of phytoplankton concluded that these measurements are not sufficient for accurately modeling primary productivity, and that better parameterizations of the chemical and physical constraints on phytoplankton growth and photosynthesis are imperative for estimating primary productivity using models (Behrenfeld and Falkowski, 1997). This highlights the need for more observations and coupled measurements of nutrient concentrations, primary productivity, and N uptake rates for validating models on both local and regional scales.

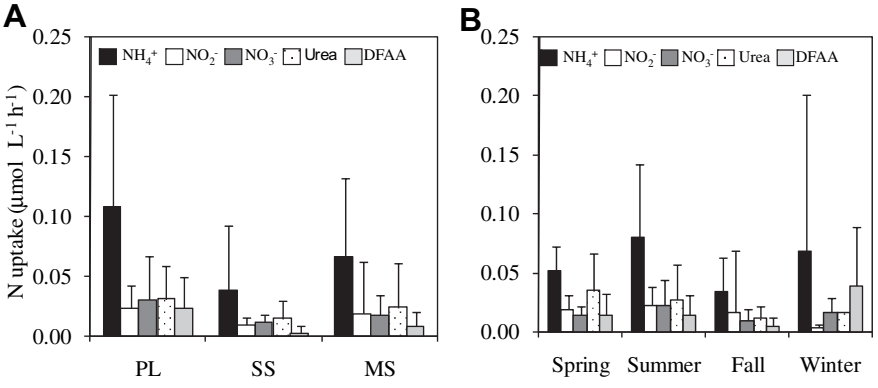

Fig. 5. Volumetric N uptake rates averaged for A) each region and B) each season.

Table 4
Summary table of surface area of each hydrographic regime calculated from cruise maps, average euphotic depth, daily volumetric primary productivity rates, daily total N (TN) uptake rates, areal primary productivity rates calculated from the depth of the euphotic zone and averaged over surface and fluorescence maximum, and integrated seasonally, areal total N uptake rates, annual C uptake due to primary productivity, annual total N uptake, and annual C:N uptake ratios. Values are averages of all stations for each region across all seasons for both years and surface and fluorescence maximum rates with ranges in parentheses.

	Surface area (km^2)	Euphotic depth (m)	Daily primary productivity ($\mu mol\ C\ L^{-1}\ d^{-1}$)	Daily TN uptake ($\mu mol\ N\ L^{-1}\ d^{-1}$)	Annual areal primary productivity ($mol\ C\ m^{-2}\ y^{-1}$)	Annual areal total N uptake ($mol\ N\ m^{-2}\ y^{-1}$)	Annual C uptake ($mol\ C \times 10^9\ y^{-1}$)	Annual N uptake ($mol\ N \times 10^9\ y^{-1}$)	Annual C:N uptake
PL	1200	12	10.8 (0.6–35.5)	2.6 (0.2–7.5)	43.0 (14.8–79.4)	11.1 (3.3–21.5)	52 (18–95)	14 (4.0–26)	3.9
SS	6300	38	3.1 (0.6–9.6)	1.0 (0.1–2.7)	34.9 (5.8–45.1)	8.7 (3.5–11.9)	220 (37–284)	55 (22–75)	4.0
MS	22,450	27	6.2 (0.2–41.8)	1.6 (0.2–6.5)	40.9 (14.0–84.0)	12.9 (5.7–20.9)	918 (313–1890)	289 (128–469)	3.2
Total	29,950						1190 (368–2270)	358 (154–569)	

4.1. Inferring primary productivity rates from N uptake rates

The ratio of annual areal primary C productivity, measured as net bicarbonate uptake, to total measured annual areal N uptake ranged from 3.2:1 to 4.0:1, much lower than that expected based on the widely applied Redfield ratio of 6.6 (Table 4). This low ratio suggests that primary productivity rates and N uptake rates are not tightly coupled on the short timescales on which measurements are made (hours to days), there are unquantified C sources, or that cellular N and C stoichiometry is a poor indicator of the relative uptake of these elements. This could be due to unbalanced growth, underestimates of gross C fixation, or overestimates of N uptake by autotrophs on GF/F filters. Unbalanced growth can result from nutrient limitation, light limitation, and variations in temperature (Eppley, 1980, 1981; Cullen et al., 1992). We measured net bicarbonate uptake using ^{13}C without accounting for release of recently fixed C as dissolved organic C (DOC). Finally, we used GF/F filters with a nominal pore size of 0.7–0.8 μm. These filters have been shown to retain a variable fraction of the bacterial population (Taguchi and Laws, 1988). We know that phytoplankton and bacteria compete for both inorganic and organic N sources in nature and this makes it hard to attribute uptake to any one group, consequently, N uptake may be overestimated if a significant fraction of the N uptake was due to bacteria retained on the GF/F filters (Mulholland and Lomas, 2008). Better methods for determining taxa-specific N uptake are necessary.

Unlike many previous studies, we measured uptake of both organic and inorganic N compounds during this study. If only DIN uptake is considered, C:N uptake ratios increased to 4.1–5.4:1, closer to but still below Redfield. The Redfield ratio has been used to

Table 5
Published areal rates of primary productivity including a description of the study area, areal rate, method, number of observations (or years for modeled data), and source for each estimate.

Study area	Areal rates of primary productivity ($mol\ C\ m^{-2}\ y^{-1}$)	Methods	# of observations or # of years for modeled data	Reference
PL	43.0 ± 13.8	^{13}C bicarbonate incubations	$n = 54$	This study
SS	34.9 ± 5.5		$n = 24$	
MS	40.9 ± 14.2		$n = 46$	
MAB	20.4	ROMS model with denitrification	5 years	(Fennel et al., 2008)
	23.7	ROMS model, without denitrification		
MAB	17	3-Dimensional biogeochemical model (ROMS)	5 years	(Fennel et al., 2006)
New Jersey coast to Bermuda:		Productivity model using *in situ* data, satellite imagery, previously published data, and photosynthesis/irradiance relationship over 33.4 km^2 study areas, depth integrated. Data shown is a range for the 5-year study period of a hybrid of water column/satellite-derived productivity.	5 years	(Mouw and Yoder, 2005)
Shelf	18.9 ± 0.7			
Shelf break	15.9 ± 2.8			
Slope	16.9 ± 0.6			
Gulf Stream	25.2 ± 2.0			
Cape Hatteras Shelf (Spring and Summer estimates)	29.5 ± 21.6	^{14}C bicarbonate incubations, depth integrated	$n = 21$	(Redalje et al., 2002)
Cape Hatteras Shelf (Spring and Summer estimates)	54 ± 20	Wavelength resolved photosynthesis-irradiance model	$n = 25$	(Lohrenz et al., 2002)
	30 ± 22	^{14}C Bicarbonate incubations	$n = 7$	
Northwest Atlantic Shelf		^{14}C Bicarbonate incubations	$n = 1047$	(Campbell and O'Reilly, 1988; O'Reilly and Busch, 1984; O'Reilly et al., 1987)
Shelf	23			
Shelf break	25			
Slope	23			
Atlantic Ocean (assume surface area of $77*10^{12}$ m^2)	12.6	Ocean color model	6 months	(Carr et al., 2006)
Global continental shelf (40 different regions; 70% of global continental shelf)	18	Average of 40 different studies	$n = 40$	(Walsh, 1988)
Global continental shelf	16.7–18.3	Average estimates		(Wollast and Billen, 1981; Wollast, 1991)

Table 6
Average, minimum, and maximum daily primary productivity rates for each season at each region. Ranges are in parentheses below the averages (n.d. = no data).

Region	Spring ($mol\,C\,m^{-2}\,d^{-1}$)	Summer ($mol\,C\,m^{-2}\,d^{-1}$)	Fall ($mol\,C\,m^{-2}\,d^{-1}$)	Winter ($mol\,C\,m^{-2}\,d^{-1}$)
PL	0.16 (0.03–0.28)	0.16 (0.05–0.40)	0.10 (0.08–0.13)	0.04 (0.01–0.06)
SS	n.d.	0.11 (0.03–0.18)	0.06 (0.03–0.09)	0.22 (n.d.)
MS	0.14 (0.02–0.29)	0.19 (0.05–0.14)	0.10 (0.05–0.14)	0.04 (0.02–0.05)

calculate either C or N uptake, one from the other, in model simulations and to construct C and N budgets for the region (Seitzinger and Giblin, 1996; Fennel et al., 2006). Our results suggest that using Redfield assumptions may bias estimates of N uptake or primary productivity when estimating one from the other. Further, model simulations often use only DIN uptake, specifically NO_3^-, to infer net primary production (Mouw and Yoder, 2005; Fennel et al., 2006). However, in this study, the average hourly ratio of primary productivity to NO_3^- uptake was much greater than 6.6 (PL: 36 ± 31, SS: 14.5 ± 9.5, MS: 52 ± 97) and other forms of N contributed substantially to total N uptake. Prior research in the Chesapeake Bay plume similarly reported the ratios of hourly primary productivity to NO_3^- uptake rates deviated from Redfield ranging from 0.9 to 276 (Malone and Ducklow, 1990; Glibert and Garside, 1992). Using only DIN or NO_3^-, uptake rates or concentrations, may bias estimates of primary productivity rates upwards because primary producers can use a wide variety of N sources to support their growth (Mulholland and Lomas, 2008) and these compounds can dominate the dissolved N pool, particularly in coastal waters where inputs from terrestrial systems and atmospheric deposition are significant (Howarth and Marino, 2006).

4.2. Eutrophication and climate change

It is not known whether continental margins across the globe, including the coastal MAB, are currently net sources or sinks for anthropogenic CO_2 and N (Verity et al., 2002; Crossland et al., 2005; Chavez et al., 2007; Fennel et al., 2008; Chen and Borges, 2009; Fennel and Wilkin, 2009), mainly because consistent measurements in these very large and complicated systems are lacking. The region could be a source or a sink based on many different processes that are occurring simultaneously. For example, if N inputs due to eutrophication alleviate N limitation in the coastal system and the excess production is grazed and ultimately contributes to fish production (Nixon and Buckley, 2002), this could be a positive outcome of enhanced primary productivity, and thus the region would be a CO_2 and N sink. If, on the other hand, more organic material sinks to the sediments, increasing oxygen demand in the sediments, resulting in coastal hypoxia or anoxia (such as has been observed north of our study area on the MAB shelf of New Jersey (Glenn et al., 2004; Frazer et al., 2006)), the region could be a CO_2 source. It is possible that increased total N loads or increased atmospheric CO_2 could cause an increase in net primary productivity and it is important that we determine the likely fate of the resulting organic matter (Verity et al., 2002).

In addition to understanding the effects of increased nutrients and CO_2 on primary productivity, the effect of changes in productivity on higher trophic levels or on biogeochemical feedbacks such as N losses through denitrification must also be examined. If denitrification is currently limited by the supply of organic matter, then an increased rain of particulate matter from above could result in enhanced rates of denitrification (Codispoti et al., 2001) and N losses from the system, perhaps even compensating for anthropogenic N inputs. Estimates of daily sedimentary denitrification rates are currently about 2% of primary productivity rates [e.g. Seitzinger and Giblin, 1996]. However, if denitrification rates increase commensurately with increased productivity thereby maintaining a N-limited coastal system, then anthropogenic N inputs can be counterbalanced with N losses through denitrification and this area could be an important anthropogenic C sink. On the other hand, if primary productivity decreases in the future due to global climate change or natural climate variability, denitrification might decrease due to C limitation of denitrifying microbes as less organic material is delivered to the sediments (Fennel et al., 2006; Fulweiler et al., 2007). Sedimentary denitrification rates might also be limited by something else preventing denitrification rates from increasing with increasing organic matter deposition. This might cause N to accumulate in the MAB sediments where it might be buried or be a source of N fueling benthic productivity. Alleviating N limitation in this system might also simply shift the system toward limitation by another element in short supply such as phosphorus or iron (Codispoti et al., 2001). However, since the main source of these elements to aquatic systems is terrestrial, this seems unlikely in coastal waters with riverine and estuarine inputs.

N and C dynamics are affected not only by the physical and biological environments, but also by human perturbations of these elemental cycles on both short and long timescales. Although satellite imagery is becoming a widely used tool to relate surface productivity with remotely sensed parameters, present and past results suggest that satellite data should be interpreted carefully and validation with measurements is necessary, as rates of primary productivity do not always correlate well with Chl *a* biomass and there are differences in productivity with depth that may not be related in a predictable way to biomass estimates (Hoffman et al., 2008). Coastal algorithms relating primary productivity and ocean color are still poor predictors of productivity in marine coastal waters primarily due to interferences from other dissolved or particulate constituents in the water and the lack of robust validation with direct measurements (Hoffman et al., 2008). Equally important, better relationships between primary productivity and N uptake rates need to be elucidated to reconcile global C and N budgets, and to more accurately extrapolate one from the other. We demonstrate that nutrient concentrations and uptake of one or two particular compound (e.g. NO_3^-) are not good predictors of productivity in this coastal system. Resolving these issues in the coastal zone is crucial for parameterizing biogeochemical models that are necessary for a whole ecosystem approach to understanding the N and C dynamics.

The results from this study also suggest that better seasonal resolution is important for making accurate annual assessments of primary productivity in this region. Long-term trends in productivity due to coastal eutrophication and large-scale indices of climate variability, such as the North Atlantic Oscillation and El Niño Southern Oscillation, are only beginning to be observed in data records and our short satellite record is not yet sufficient to observe the full extent of these patterns and trends. Our observations have shown that coastal productivity is highly sensitive to physical forcing and that N uptake and primary productivity rates can be uncoupled. Taking this into account will be crucial for generating next-generation satellite-based productivity models for the region. Further, better agreement between models, satellite data and observations are critical for projecting how climate variability impacts coastal productivity and for accurately assessing both long and short-term trends in coastal productivity.

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