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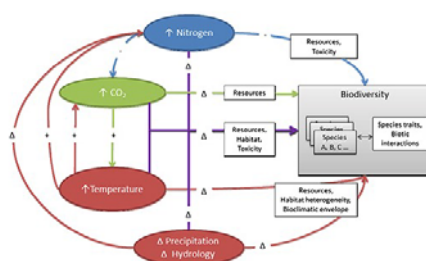
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Metabolism of a nitrogen-enriched coastal marine lagoon during the summertime

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Abstract We measured metabolism rates in a shallow, nitrogen-enriched coastal marine ecosystem on Cape Cod (MA, USA) during seven summers using an open-water diel oxygen method. We compared two basins, one directly receiving most of the nitrogen (N) load (“Snug Harbor”) and another further removed from the N load and better flushed (“Outer Harbor”). Both dissolved oxygen and pH varied greatly over the day, increasing in daylight and decreasing at night. The more N-enriched basin

frequently went hypoxic during the night, and the pH in both basins was low (compared to standard seawater) when the oxygen levels were low, due to elevated carbon dioxide. Day-to-day variation in gross primary production (GPP) was high and linked in part to variation in light. Whole-ecosystem respiration tended to track this short-term variation in GPP, suggesting that respiration by the primary producers often dominated whole-system respiration. GPP was higher in the more N-loaded Snug Harbor. Seagrasses covered over 60 % of the area of the better-flushed, Outer Harbor throughout our study and were the major contributors to GPP there. Seagrasses covered 20 % of the area in Snug Harbor for the first 5 years of our study, and their contribution to GPP was relatively small. The seagrasses in Snug Harbor died off completely in the 6th year, but GPP remained high then and in the subsequent year. Overall, rates of phytoplankton GPP were relatively low, suggesting that benthic micro- and macro-algae may be the dominant primary producers in Snug Harbor in most years. Net ecosystem production in both Snug Harbor and the Outer Harbor was variable from year to year, showing net heterotrophy in some years and net autotrophy in others, with a trend towards increasing autotrophy over the 7 years reported here.

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Introduction

The past few decades have seen a large increase in nutrient pollution and coastal eutrophication globally, leading to widespread hypoxia and anoxia, habitat degradation, alteration of food-web structure, loss of biodiversity, and increased frequency, spatial extent, and duration of harmful algal blooms (NRC 2000; Rabalais 2002; Conley et al. 2009). A majority of estuaries in the US are degraded as a result (Bricker et al. 2007). Shallow lagoons and coastal bays are particularly sensitive to eutrophication, and also have highly valuable habitat that can be severely degraded (Nixon et al. 2001; Hughes et al. 2002; McGlathery et al. 2007). During early phases of eutrophication of shallow lagoons, seagrasses are commonly overgrown by epiphytes and by macro-algae. When severe enough, seagrasses are lost and replaced as the dominant primary producers in the system by macro-algae and benthic micro-algae. If the water residence time is sufficiently long to allow for phytoplankton blooms, phytoplankton begin to dominate the primary producer community (Swaney et al. 2008). Habitat quality is severely degraded with these changes, biodiversity decreases, and production of fish and shellfish falls (Hughes et al. 2002; McGlathery et al. 2007). Although these general trends are well known, relatively few studies have characterized rates of whole-ecosystem metabolism in nutrient-enriched coastal lagoons, and fewer yet in ecosystems with well-characterized nutrient loads and over multiple growing seasons (D'Avanzo et al. 1996; Nixon et al. 2001; Caffrey 2003; Giordano et al. 2012).

The current conceptual model of eutrophication in coastal lagoons describes a change in biological structure but little change in rates of ecosystem metabolism (Duarte 1995; McGlathery et al. 2007). The relative contribution of the different primary producers changes as these systems become more eutrophic, but available evidence from both mesocosm experiments (Nixon et al. 2001) and cross ecosystem comparisons (Borum and Sand-Jensen 1996) suggests that total primary productivity may not greatly change once some relatively low threshold level of nitrogen (N) loading is exceeded. If generally true for shallow marine ecosystems, this contrasts sharply with deeper systems where primary production by phytoplankton tends to increase as a linear function of increasing N load (Nixon et al. 1996).

Here, we report rates of gross primary production (GPP), whole-ecosystem respiration (R), and net ecosystem production (NEP) in a shallow, N-enriched lagoon, West Falmouth Harbor on Cape Cod, Falmouth, MA, USA. This estuary is the site of an unplanned whole-ecosystem nutrient-addition experiment. Due to groundwater contamination by a municipal wastewater treatment facility, the N load to West Falmouth Harbor increased some threefold since the mid to late 1990s, gradually increasing through 2003 or so, and then remaining high and relatively constant through at least 2012 (Hayn 2012; Hayn et al. 2013). The metabolism data we present in this paper for the period 2005 through 2011 are part of a larger study on the ecological and biogeochemical responses of West Falmouth Harbor to the elevated N load. We concentrated on metabolism during the summer months when metabolism rates are highest and seagrasses are most sensitive to N pollution because of temperature stress, greater potential for hypoxia and anoxia, and increased likelihood of shading by phytoplankton, epiphytic algae, and macro-algae. We present data for two discrete sections of the estuary: an inner basin called Snug Harbor which directly receives most of the elevated N load, and the better flushed Outer Harbor adjacent to the outlet to Buzzards Bay and further from the source of the N pollution (Fig. 1). The seagrass *Zostera marina* was present in both of these parts of West Falmouth Harbor through 2009. Seagrass beds persisted in the Outer Harbor in 2010 and 2011 as well but largely disappeared from Snug Harbor between late July and early-mid August 2010. As such, our data on GPP, R, and NEP encompass the periods before, during, and for the first year after the precipitous seagrass die-off event.

Site description

Salinities in most of West Falmouth Harbor generally exceed 28 ppt. The tidal range is 1.1 m, and at mean water the estuary has an average depth of 1.9 m and an area of 71 ha (Hayn et al. 2013). Both Snug Harbor and the Outer Harbor also have average depths of 1.9 m at mean water, as do the specific sites for our metabolism measurements (Fig. 2a). The water exchange between West Falmouth Harbor and the coastal waters of Buzzards Bay occurs through a

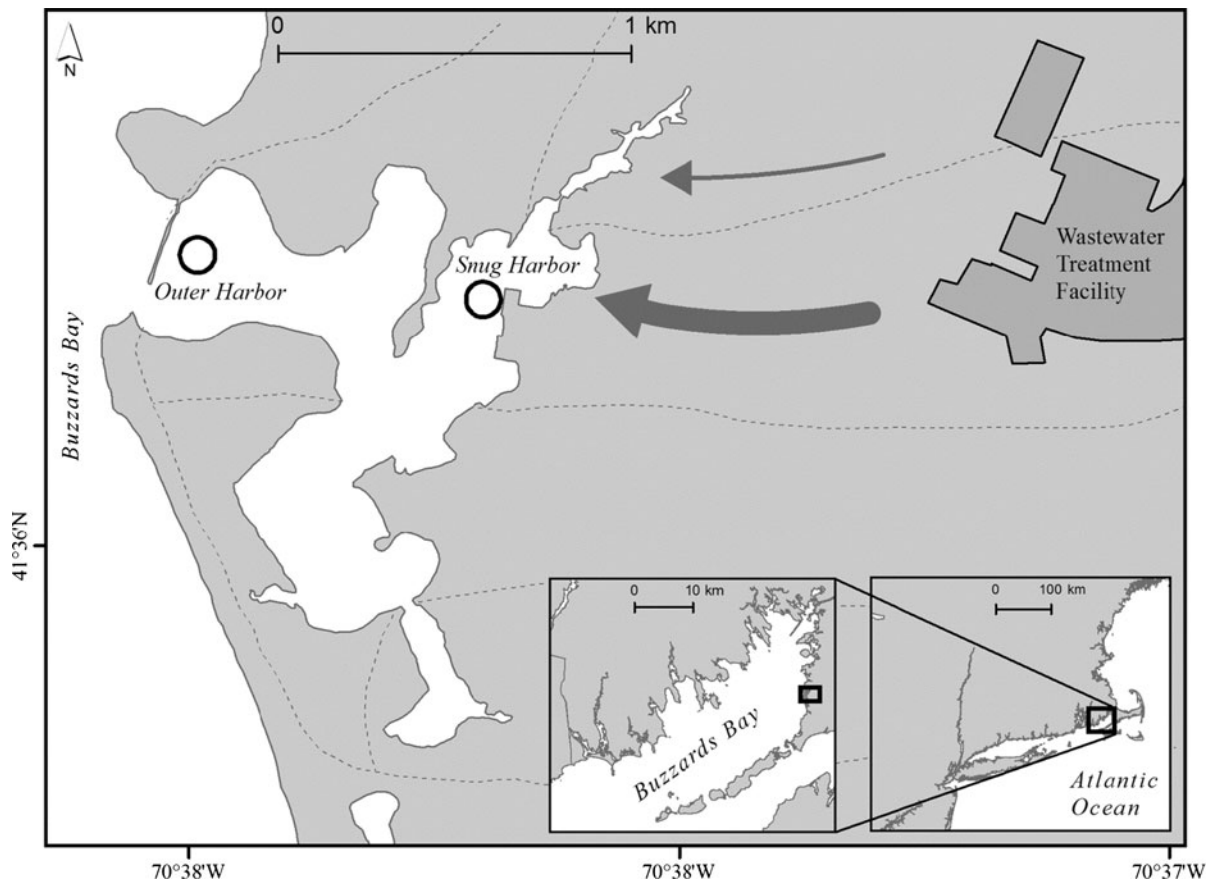


Fig. 1 West Falmouth Harbor and its location adjoining Buzzards Bay on Cape Cod. Deployment sites for measurement of DO and pH shown by circles in Snug Harbor and the Outer Harbor. Snug Harbor receives a large N load from contaminated

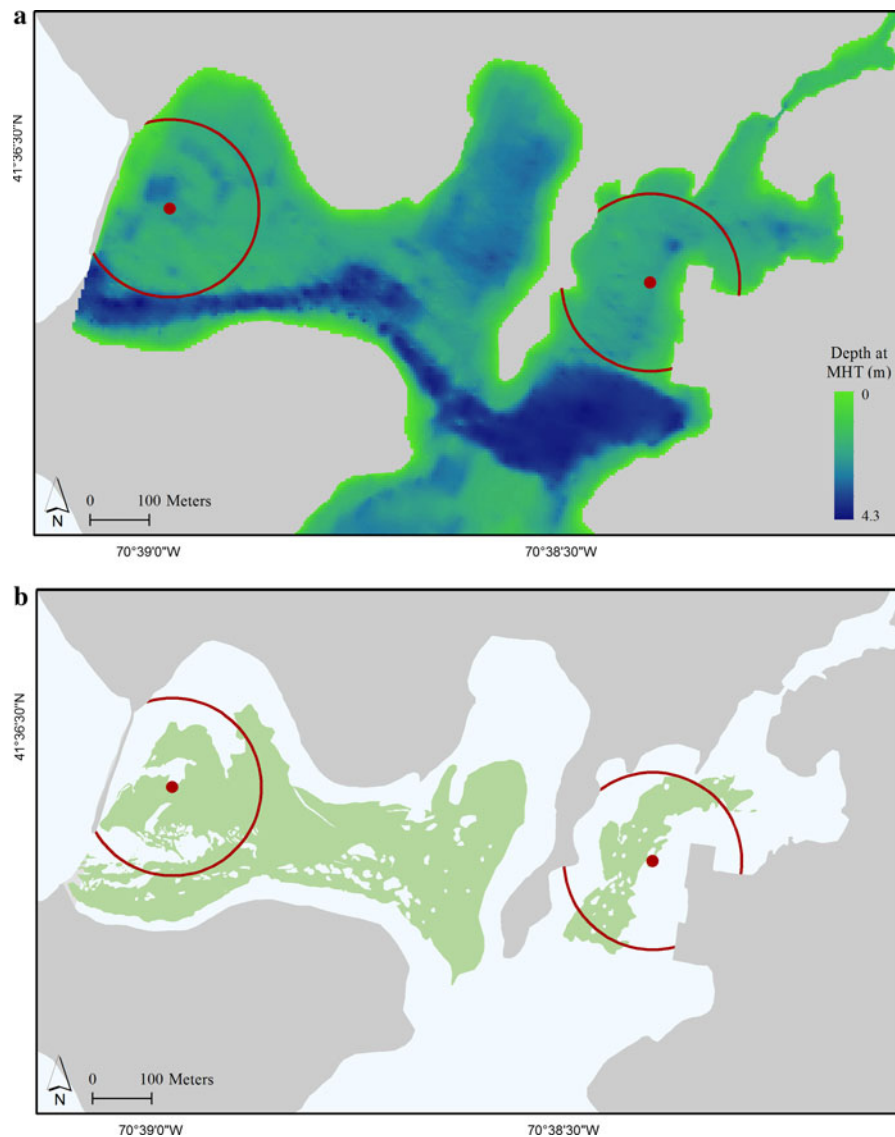
groundwater flowing from a wastewater treatment facility. West Falmouth Harbor exchanges water with Buzzards Bay through a single outlet on the western edge of the Outer Harbor

single inlet on the western edge of the Outer Harbor (Fig. 1). West Falmouth Harbor is rarely stratified, particularly at the sites we studied for this paper. Water residence times are estimated to be less than 1 day in the Outer Harbor (Howes et al. 2006). To estimate residence times in Snug Harbor, we used the ROMS model of Ganju et al. (2012), implementing the integrated particle tracking routine with 4,200 particles randomly spaced in the vertical in Snug Harbor; particles were advected using modeled velocities and vertical mixing, and assigned neutral buoyancy. Using a standard e-folding time estimate (Monsen et al. 2002), we estimate the mean residence time for Snug Harbor as 0.85 day during spring tides, and 1.75 days during neap tides. The mean tidal velocity in both Snug Harbor and the Outer Harbor is 0.125 m s^{-1} , with peak velocities of 0.25 m s^{-1} (Ganju et al. 2011).

Seagrasses covered $\sim 20 \%$ of the area in Snug Harbor between 2005 and the die-off in 2010 and $\sim 63 \%$ in the Outer Harbor (Fig. 2b; Hayn 2012).

The external N load for all of West Falmouth Harbor from the atmosphere and from land sources as determined in 2010 was $4.2 \text{ mmol N m}^{-2} \text{ day}^{-1}$ (Hayn et al. 2013). During the summer months, the harbor imported an additional net $0.7 \text{ mmol N m}^{-2} \text{ day}^{-1}$ from the coastal waters of Buzzards Bay; there was a net export of N from the harbor to Buzzards Bay in other seasons (Hayn et al. 2013). We are not including this net summer import in the external N loading estimates used in this paper, since such information is seldom available in other ecosystems. The total N inputs to West Falmouth Harbor during the summer months including this import from Buzzards Bay are 15 % greater than the external load alone.

Fig. 2 Bathymetric chart with depths relative to mean high tide (**a**, *top*) and seagrass distribution (**b**, *bottom*) in the northern part of West Falmouth Harbor. The *red dots* show the sites at which sondes were deployed in the Outer Harbor (to the *left*) and in Snug Harbor (to the *right*). The *red circles* show a 150 m radius around the sondes, representing the distance a parcel of water would on average travel to or from the sonde in the 20 min between oxygen measurements, based on an average tidal current of 0.125 m s^{-1} . Seagrass distribution data are for May 2010, before the die-off in Snug Harbor (Hayn 2012)



Of the $4.2 \text{ mmol N m}^{-2} \text{ day}^{-1}$ from land sources and the atmosphere, 66 % is attributable to inputs from the aquifer contaminated by the municipal wastewater treatment facility (Hayn et al. 2013). All of the N from this contaminated aquifer enters West Falmouth Harbor through Snug Harbor. The wastewater facility was built in 1986 and takes sewage from outside of the watershed of West Falmouth Harbor. Effluent from the plant was at first sprayed onto forest land and then later injected directly into the groundwater. Total discharge of effluent was low at first, increased over time, and reached a steady rate by the mid 1990s (Howes et al.

2006; Town of Falmouth 2011). The treatment facility is approximately 1.5 km uphill from Snug Harbor (Fig. 1), and the estimated travel time for groundwater from the facility to Snug Harbor is 7–10 years (Kroeger et al. 2006). Thus, the input to Snug Harbor of N in the contaminated plume was relatively constant over the time of the study we report here, from 2005 to 2011. The wastewater treatment facility instituted advanced N-removal technology in late 2005, so by late 2015, we expect the N load to Snug Harbor to decrease as the contaminated aquifer is flushed through; as of early 2013, the N load remained high (Hayn et al. 2013).

To estimate the N load attributable to the wastewater-facility-contaminated aquifer, Hayn et al. (2013) multiplied the groundwater flow into Snug Harbor (Ganju et al. 2012) by the nitrate concentration in that groundwater as estimated from a mixing curve of nitrate against salinity on water sampled along transects in Snug Harbor during winter when biological uptake was low. The rest of the N load from the watersheds was estimated by Kroeger et al. (2006) and Howes et al. (2006) based on land-use models. West Falmouth Harbor also receives some N from direct deposition onto the water surface, which is included in the estimate of $4.2 \text{ mmol N m}^{-2} \text{ day}^{-1}$; the direct deposition contributes less than 10 % of this total load (Hayn et al. 2013).

We can separately estimate the total N load directly into Snug Harbor, which consists of the contaminated groundwater plume ($1.9 \text{ kmol N day}^{-1}$ during 2010; Hayn et al. 2013) and the portion of the background load from other sources to West Falmouth Harbor that enters through Snug Harbor ($0.35 \text{ kmol N day}^{-1}$; Howes et al. 2006; Kroeger et al. 2006; Hayn et al. 2013). Summing these and dividing by the area for Snug Harbor at mean tide (13.2 ha), we estimate the Snug Harbor N load as $17 \text{ mmol N m}^{-2} \text{ day}^{-1}$ in 2010, with 84 % of this attributable to the contaminated groundwater plume. There is some inter-annual variation in this load, which is driven largely by variation in groundwater head between the wastewater treatment facility and Snug Harbor. Using data on groundwater levels from monitoring wells run by the Town of Falmouth (unpubl. data), and assuming groundwater flow is directly proportional to the head gradient, we estimate the N load to Snug Harbor during the summer as $15 \text{ mmol N m}^{-2} \text{ day}^{-1}$ in 2008, 2009, and 2011, $16 \text{ mmol N m}^{-2} \text{ day}^{-1}$ in 2005 and 2007, and $17 \text{ mmol N m}^{-2} \text{ day}^{-1}$ in 2006 and 2010.

Methods

We measured GPP, R, and NEP using a version of the open-water in situ diel oxygen technique originally pioneered by Odum in the 1950s (see reviews by Howarth and Michaels 2000 and Kemp and Testa 2011). Conceptually, R is estimated from the rate of decrease in dissolved oxygen (DO) overnight in the dark after correction for atmospheric exchange, and GPP is estimated from the rate of DO increase during

daylight hours, again corrected for atmospheric exchange and also adding a term for the consumption of DO during daytime respiration. We assume that R as estimated in the dark also applies during daylight, an assumption we discuss further below. NEP is calculated by subtracting R from GPP. Note that in some other estuarine studies, NEP is referred to as net ecosystem metabolism (NEM; Caffrey 2003) or net community production (NCP; Barron et al. 2004). We prefer the term NEP, which is more generally used in both aquatic and terrestrial ecology (Chapin et al. 2006).

In this paper, we report all of our measurements made during July and August over the years 2005 through 2011. We made measurements in other months as well (mostly May, June, and September), but our sampling in every year concentrated on the months of July and August, as this was the time of highest rates of GPP and R and the time of greatest potential impact from eutrophication. We used YSI 6-series and Hydrolab 4- and 5-series automated multi-parameter data sondes to measure DO, water temperature, salinity, and pH at two sites: one in Snug Harbor and one in the Outer Harbor (Figs. 1, 2a, b). We deployed the sondes during July and August over the 7 years for a total of 109 days in the Outer Harbor and 101 days in Snug Harbor. We had sondes deployed simultaneously at both locations for 77 of these days, and much of the data we report here is only for these concurrent sampling periods to facilitate comparisons across the basins. Deployments were generally for continuous periods of between 7 and 10 days, with each sonde recording data at 20-min intervals.

For each 20-min interval at each site, we calculated the change in the mass of DO in the water column per area as follows:

$$\Delta O_{x_{total}} = [(d_i + d_{i-1})/2] \times (C_i - C_{i-1}) / (t_i - t_{i-1}) \quad (1)$$

where $\Delta O_{x_{total}}$ ($\text{moles m}^{-2} \text{ h}^{-1}$) is the change in mass of DO over the water column depth during the 20-min period, d_i is the depth (m) at the station at the end of the 20-min period, d_{i-1} is the depth at the start of the interval, C_i is the concentration of DO (moles m^{-3}) at the end of the 20-min period, C_{i-1} is the concentration of DO at the start of the 20-min period, t_i is the time in hours at the end of the 20-min period and t_{i-1} is the time at the start of the interval.

We routinely deployed our sondes at a single depth, suspended ~ 0.5 m below the surface of the water. Changes in DO over depth were very small in comparison to changes over time, as expected given the general lack of water-column stratification. Figure 3 illustrates a series of vertical profiles in the morning (between 06:00 and 08:00 local time) and the afternoon (between 16:30 and 18:00) on three typical days, in this case in July 2005. The low value observed at 1.5 m depth on the morning of July 15 is probably a result of our disturbing bottom sediments with the sonde. The relatively small variation in DO with depth and the general lack of stratification at our sampling sites during several summers give us confidence to use single-depth sonde deployments to estimate metabolism rates.

From 2007 through 2011 we collected a continuous record of water level elevation in the harbor using a vented, pressure-compensated tide gauge. Prior to 2007, we estimated water level elevation from predicted tides at the mouth of the harbor from the Wtides software package (<http://www.wtides.com>), which we corrected using offsets derived from a comparison of these predictions with observations from our water level gauge in 2007. We then estimate d_i from these water levels and the detailed bathymetry at our deployment sites, using the average depth within 150 m of our deployment coordinates (Fig. 2a).

In our application of the free-water approach to West Falmouth Harbor, we assumed that the changes in DO measured at each site are driven by metabolism and

atmospheric exchange, with relatively little influence from advection of adjacent water masses. This is reasonable, since during the 20 min between sonde measurements, the water masses moved on average 150 m and at most 300 m, given the mean and peak tidal currents of 0.125 and 0.25 m s^{-1} (Ganju et al. 2011); the distribution of seagrasses and the bottom topography were reasonably similar in the vicinity of the sonde deployment sites in both Snug Harbor and the Outer Harbor at this spatial scale (Fig. 2a, b). The assumption that the single point measurements accurately reflect these larger areas is evaluated later in this paper.

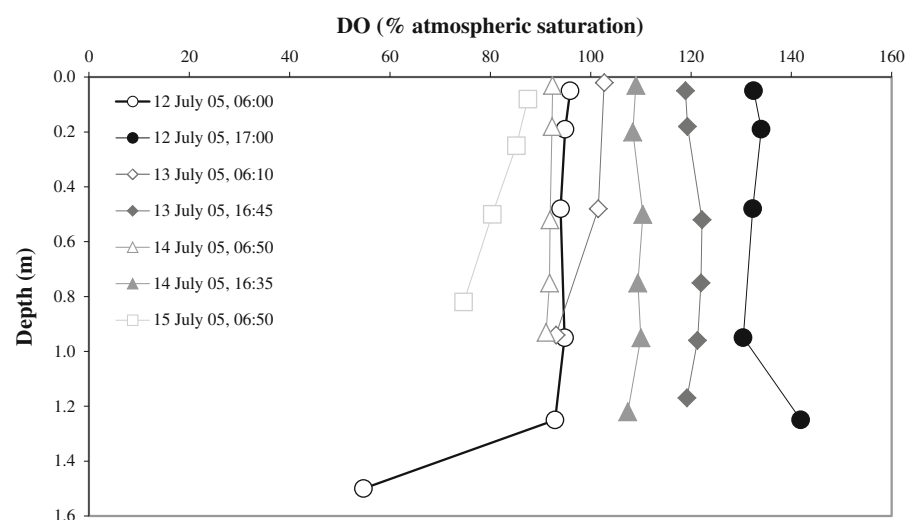
The sondes recorded DO as percent of atmospheric saturation. We used Eq. 2 from Benson and Krause (1984) to calculate the actual DO concentration in units moles m^{-3} at the observed salinity and temperature for each observation.

We calculated the change in DO attributable to metabolism by correcting for the atmospheric exchange of oxygen:

$$\Delta O_{x_{met}} = \Delta O_{x_{total}} + F_{atm} \quad (2)$$

where $\Delta O_{x_{met}}$ is the change in DO over the 20-min period ($\text{moles m}^{-2} \text{h}^{-1}$) as a result of metabolic activity and F_{atm} is the exchange of oxygen between the water and atmosphere ($\text{moles m}^{-2} \text{h}^{-1}$), with a positive value representing a net flux from water to the atmosphere. We used a transfer-velocity model to estimate F_{atm} as the product of a gas transfer coefficient (k) and the partial pressure gradient for oxygen between the water and the atmosphere:

Fig. 3 Dissolved oxygen, expressed as percent of atmospheric saturation, over depth in the Outer Harbor at 7 time points measured over three typical days, in this case during July 2005



$$F_{atm} = k \times [(C_i + C_{i-1})/2 - DO_{sat}] \quad (3)$$

where DO_{sat} is the concentration (moles m^{-3}) of oxygen in water in equilibrium with the atmosphere at the observed temperature and salinity (Benson and Krause 1984). We estimated k over each sampling period as a function of wind velocity during that same period, using the mean regression for all aquatic ecosystems included in Fig. 4a from Marino and Howarth (1993). Wind data came from a privately maintained observation station on Chapoquoit Beach (between West Falmouth Harbor and Buzzards Bay) or from Otis Air National Guard Base, approximately 10 km to the northeast, when data from Chapoquoit Beach were not available. Wind velocity was normalized to a 10-m height as in Marino and Howarth (1993).

Several authors have suggested that k is likely to vary from ecosystem to ecosystem, and that the value must therefore be empirically determined for each study site, particularly for shallow estuarine sites (Kremer et al. 2003; Vachon et al. 2010; Kemp and Testa 2011). Kremer et al. (2003) reported a far lower slope to the relationship between k and wind speed for another shallow estuary on Cape Cod (Waquoit Bay) than the regression we use here, developed from a compilation of freshwater and marine system measurements (Marino and Howarth 1993). Consequently, we made oxygen gas exchange measurements and determined the relationship of k with wind for West Falmouth Harbor as well as for Waquoit Bay using the exact equipment and approach originally employed in the Hudson River estuary (Marino and Howarth 1993). Briefly, the partial pressure of oxygen in the gas space of a free-floating dome was lowered by adding N_2 gas, and the rate of increase in oxygen was then measured

over time. The temperature of the dome was maintained within 1 °C through evaporative cooling. We made several deployments in July and August of 2006 in both basins of West Falmouth Harbor (Outer Harbor and Snug Harbor) and in the open waters of Waquoit Bay to the northeast of Washburn Island for periods of 10–30 min under winds that ranged between 3.8 and 8 $m s^{-1}$, measuring the wind concurrently at the site of the dome. The dome was allowed to drift with the wind and currents.

For each day the sondes were deployed, we estimated mean values for the change in DO attributable to metabolism (Eq. 2) during the daylight hours ($\Delta O_{x_{met-light}}$) and during the hours of darkness ($\Delta O_{x_{met-dark}}$). We then estimated R and GPP as follows:

$$R = -(24 \times \Delta O_{x_{met-dark}}) \quad (4)$$

$$GPP = D \times (\Delta O_{x_{met-light}} - \Delta O_{x_{met-dark}}) \quad (5)$$

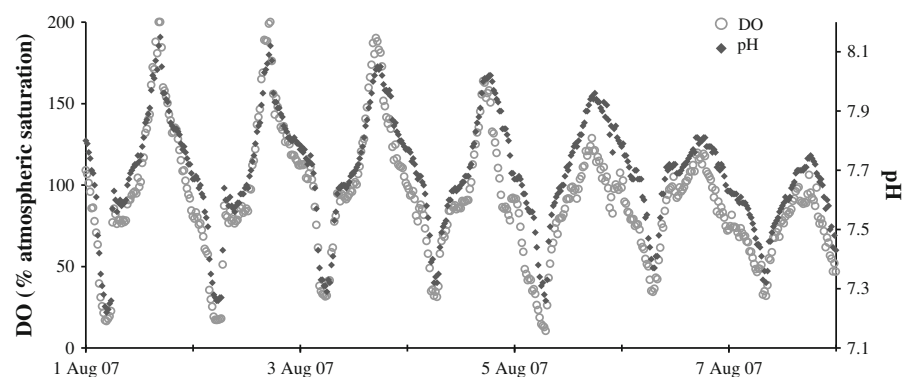
where D is the number of daylight hours on the particular observation day. NEP is calculated from R and GPP:

$$NEP = GPP - R \quad (6)$$

Functionally, Eq. 6 is equivalent to integrating Eq. 2 over 24 h. GPP, R, and NEP all have units of moles $O_2 m^{-2} day^{-1}$.

Our methodology assumes that R is the same in the dark and in the light. In fact, a variety of factors can increase R during daylight, including increased release of dissolved organic matter by primary producers in the light (with increased consumption by bacteria) and photorespiration and related processes such as the Mehler reaction (Howarth and Michaels 2000; Chapin et al. 2006; Roberts et al. in press). As a result, we are

Fig. 4 Twenty minute measurements of DO, expressed as percentage of atmospheric saturation, and pH in Snug Harbor over a 7-day deployment in early August 2007



likely underestimating R and overestimating GPP. This is true with almost all free-water oxygen metabolism measurements as well as with light–dark bottle measurements, yet these methods still have several advantages over the ^{14}C method for measuring productivity (Howarth and Michaels 2000). Note that the assumption of constant light–dark R has no influence on the estimate for NEP, as the errors associated with under-estimating R in the light and over-estimating GPP cancel out.

Our approach also does not fully account for anaerobic processes in sediments, such as sulfate reduction. Sulfate reduction typically dominates the respiration in organic-rich coastal marine sediments such as those in West Falmouth Harbor (see review by Howarth 1984), and would be included in our estimation of R only to the extent that the reduced products of sulfate reduction are re-oxidized during the summertime period of our measurements. On an annual scale, much of the reduced sulfur produced by sulfate reduction is re-oxidized, but a net storage of reduced sulfur in the sediments typically occurs during the summer (Howarth 1984). As a result, we are underestimating R and so overestimating NEP (Eq. 6). Our estimation of GPP is not affected by this assumption.

Daily light data were acquired from the Woods Hole Oceanographic Institution (<http://cis.whoi.edu/science/PO/climate>; Richard Payne, personal communication), located approximately 8 km south of West Falmouth Harbor. Data were collected using an Eppley Precision Spectral Pyranometer which measures total shortwave radiation (W h m^{-2}) in the range of 0.285–2.8 μm . Data were provided as mean hourly total radiation, which we summed over each deployment day to calculate total daily radiation.

Results and discussion

Patterns of DO and pH

Dissolved oxygen and pH both showed a large diel cycle, with DO and pH rising during daylight hours and falling at night in both Snug Harbor and the Outer Harbor. Figure 4 illustrates data for one deployment in Snug Harbor over 7 days in early August of 2007. The patterns in DO and pH are driven by the stoichiometric relationship between DO and dissolved carbon dioxide. As DO decreases with respiration overnight,

carbon dioxide increases, leading to lower pH. Conversely, the increase in DO in daylight hours due to photosynthesis is coupled to a decrease in carbon dioxide, resulting in a higher pH. Note that the mean daily DO values shown in Fig. 4 are near atmospheric saturation, while the mean pH is well below that of seawater in equilibrium with atmospheric carbon dioxide. Thus, while the changes in DO and pH track closely over the days, DO is oscillating around the atmospheric saturation level, while on these days, the pH indicates consistent super-saturation of dissolved carbon dioxide. We suggest that at least in part this reflects the slower atmospheric exchange of carbon dioxide compared to oxygen (Sirignano et al. 2010).

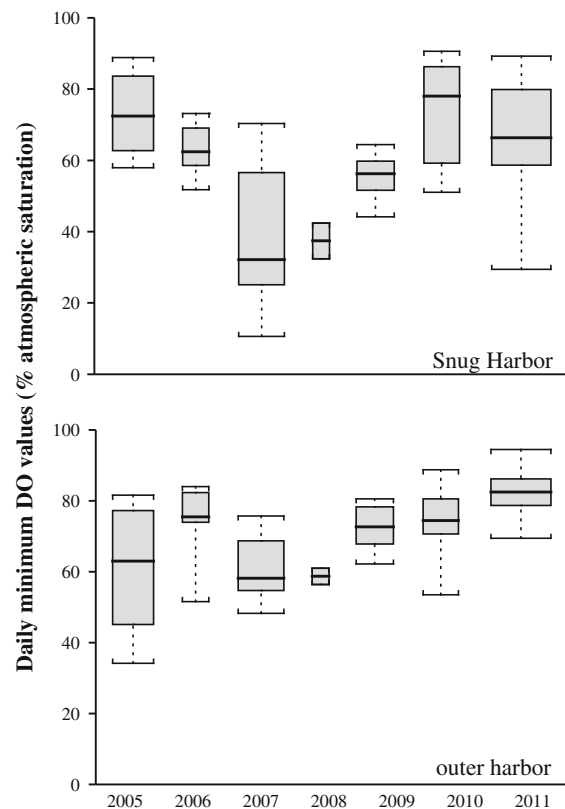


Fig. 5 Minimum observed DO values, expressed as a percentage of atmospheric saturation, for all days studied in July and August from 2005 to 2011 in Snug Harbor (*top*) and the Outer Harbor (*bottom*) for which both basins were sampled. The *whiskers* show the full range of observations. *Boxes* indicate the median 50 % of values of all measured days for each year, and the *horizontal lines* show the median for the observed values for each year. The widths of the *boxes* are proportional to the number of daily observations in each year. For 2008, data collection was limited, and thus the *boxes* show the full range of observations as well as the median 50 %

Figure 5 presents the minimum observed DO level observed for each day during July and August over the 7 years of our study, for both Snug Harbor and the Outer Harbor. On some days in some years, DO only fell to levels of 90 % of saturation. The median of the daily minimum DO levels we observed were in the range of 60–70 % saturation in both Snug Harbor and the Outer Harbor during most years of our study, although the median low DO values in the Outer Harbor in 2010 and 2011 were 75 and 80 % and for Snug Harbor in 2007 through 2009 ranged from 30 to 55 % saturation (Fig. 5). Ecological effects on sensitive species in estuaries have been demonstrated at DO levels below 50 %, although most studies have only examined the consequences of sustained hypoxia over periods of several days (Breitburg 2002). Given the

highly dynamic DO cycle in shallow lagoons, we stress the need to examine the consequences of repeated but short-lived hypoxic events in shallow estuarine systems. The comparison between Snug Harbor and the Outer Harbor suggest that periodic hypoxia may be associated with the higher N load.

Figure 6 presents the minimum pH values observed during each day over our July and August deployments for the 7-year study. These were almost always lower than 8.0, particularly in Snug Harbor. The pH fell below 7.5 on many days in both Snug Harbor and the Outer Harbor in 2005, 2006, 2007, and 2008, and below 7.0 on occasion in 2006. The depression in pH from the accumulation of respiratory carbon dioxide is far greater than the long-term ocean acidification from human-caused increase in atmospheric carbon dioxide, which has decreased the average pH of seawater by only 0.1 units since the start of the industrial revolution (Jacobson 2005). Ocean “acidification,” or depressed pH associated with hypoxia, is common in eutrophic coastal waters, with pH values often as low as we report here (Doney et al. 2009; Borges and Gypens 2010; Howarth et al. 2011). However, most previous studies have focused on waters that remain hypoxic over weeks to months, and not on systems exhibiting the diel hypoxia observed in West Falmouth Harbor. To date the ecological consequences of this dynamic, hypoxia-driven acidification (and how this may interact with the effects of the low DO) have received little if any study.

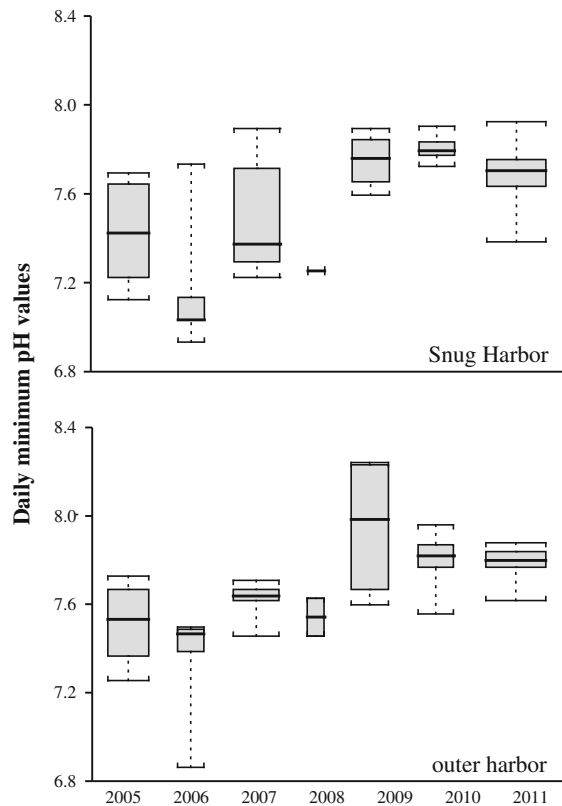


Fig. 6 Minimum observed pH values for all days studied in July and August from 2005 to 2011 in Snug Harbor (*top*) and the Outer Harbor (*bottom*) for which both basins were sampled. The *whiskers* show the full range of observations. *Boxes* show the median 50 % of values of days for each year, and the *horizontal lines* show the median for the observed values for each year. The widths of the *boxes* are proportional to the number of daily observation in each year

Atmospheric exchange of oxygen

Our measurements in both West Falmouth Harbor and in Waquoit Bay for the oxygen gas transfer coefficient, k , as a function of wind velocity are comparable to those reported for the Hudson River estuary (Marino and Howarth 1993), measured using the same equipment and approach (Fig. 7). All of the measurements in this study fall well within the 95 % confidence limits for the regression of k as a function of wind speed previously developed in Marino and Howarth (1993), except for one particularly high value in Waquoit Bay. More recent measurements in several other estuaries (Borges et al. 2004) and lakes (Vachon et al. 2010) also tend to fall within the 95 % confidence limit shown in Fig. 7 (when converted to values of k for oxygen at 20 °C, as in Marino and Howarth 1993 and Borges et al. 2004), although the

estimates of k reported by Kremer et al. (2003) for Waquoit Bay tend to fall outside these confidence limits at wind speeds greater than 5 m s^{-1} . Our estimates of k in Waquoit Bay are higher at any given wind velocity than those reported by Kremer et al. (2003), perhaps in part because they made their measurements in an area of the Bay that was more narrow and protected from the wind by trees (Kremer, personal communication).

Overall, we are confident in using the regression from Marino and Howarth (1993) in our estimation of atmospheric oxygen exchange in West Falmouth Harbor for the purposes of this study (see “Methods” section). We further note any error in our estimation of atmospheric exchange is small in the overall calculation of metabolism rates in West Falmouth Harbor; for example, inclusion of the atmospheric oxygen exchange increases our estimate for GPP by 12 % on average compared to a calculation that assumes absolutely no atmospheric exchange (i.e., F_{atm} set to zero; data not shown). The influence of k on estimation

of NEP at our study sites is even less. The relative insensitivity of the metabolism estimates to the atmospheric exchange term in West Falmouth Harbor resulted because on most days, DO excursions were symmetrical around the atmospheric saturation during both daylight and night-time hours: despite the large diel oscillation, DO values tended to be equally above and below 100 % saturation both during the daylight hours (when they were increasing from low to high values) and during the dark hours (when they were falling from high to low values). In ecosystems where DO is more consistently below or above saturation on average over the day, the atmospheric exchange term becomes a larger part of the calculation of metabolism rates. For example, the relative insensitivity to a correction for atmospheric oxygen diffusion in WFH contrasts strongly with work in the Hudson River estuary (Marino and Howarth 1993) and in some shallow lagoons in Virginia (Giordano et al. 2012), where the estimation of metabolism rates was found to be moderately to strongly sensitive to the atmospheric exchange terms.

It is important to consider the time scale of interest in applying k when choosing the best approach for estimation of gas transfer, as the relationship of k with wind speed is non-linear (Fig. 7). In this study, we estimated system metabolism using measured changes in oxygen every 20 min (Eq. 2), the same time scale we used to measure O_2 flux and k with our floating dome. Often gas transfer is measured over longer time scales of days to weeks using in situ tracers, such as added SF_6 . This is appropriate if the interest is in estimating gas exchange integrated over longer time scales, but note that the values of k so obtained are not equivalent and cannot be compared without consideration of the non-linear relationship to wind speed (Marino and Howarth 1993; Vachon et al. 2010).

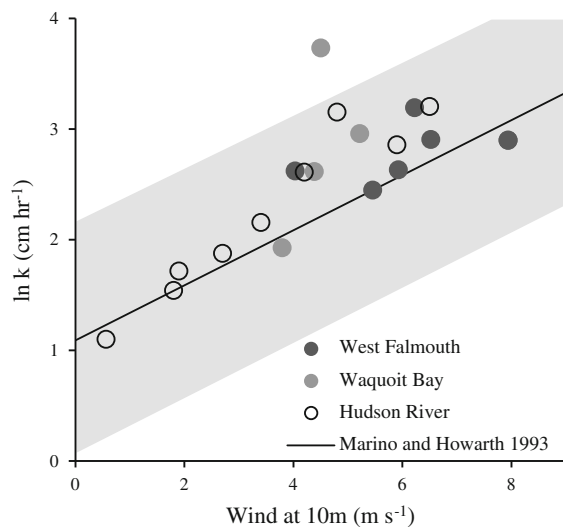


Fig. 7 The influence of wind velocity on the natural log of the gas transfer coefficient, k , determined for oxygen exchange at 20°C . The solid line represents the best linear fit of observations taken by many methods in many different aquatic ecosystems as presented in Marino and Howarth (1993), while the gray-shaded area represents the 95 % confidence limits around the regression. Open circles represent observations made with a floating dome technique in the Hudson River estuary (Marino and Howarth 1993). The solid black and gray circles represent observations made with the same equipment and approach as used by Marino and Howarth (1993), for this study in West Falmouth Harbor and Waquoit Bay respectively

Does advection influence the metabolism estimates?

As we discussed in the “Methods” section, we assumed that advection does not affect our calculation of metabolism rates since the sondes were deployed in relatively uniform habitats with similar bathymetry within 150 m or so, the average distance a water mass moved during the 20 min between DO readings (Fig. 2a, b). We tested this assumption in two ways. First, in 2006, we simultaneously deployed two sondes

in Snug Harbor for 7 days, spaced 200 m apart; rates of GPP, R, and NEP were not statistically different (data not shown).

Second, we separately analyzed data for flooding and for ebbing tides across the entire 7 years of our study, examining the rate of change in oxygen levels during the four mid-day hours at both the Snug Harbor and the Outer Harbor sites. To our surprise, we found that in fact the rate of increase in oxygen levels was approximately twice as great during ebbing tides than on flooding tides at both sites. The difference in the means of hourly oxygen flux on incoming versus outgoing tides was significantly greater than zero for both the Outer Harbor and Snug Harbor (student's *t* test, $p = 4.0 \times 10^{-6}$ and $p = 1.6 \times 10^{-5}$, respectively). We cannot fully explain this result, other than to suggest that GPP was in fact greater on one side of our sonde-deployment sites than on the other. The frequency of our sampling was equal on flooding and ebbing tides over the 7 years of our study, however, and so the average results for metabolism we present below should be robust representations for the study sites. Nonetheless, this result indicates that some of the day-to-day variability we observed may well reflect the difference between flooding and ebbing tides.

Temporal patterns in metabolism

In Fig. 8 we present data from one 7-day deployment to illustrate some typical patterns in rates of metabolism in West Falmouth Harbor. On these days in August 2011, GPP was always greater than R in the Outer Harbor, and so NEP was always positive, reflecting net autotrophy. In Snug Harbor during this deployment, GPP was greater than R on most days, but on 16 August R was somewhat greater than GPP, and on 19 August R equaled GPP, resulting in a negative and a zero value of NEP respectively on these two dates. During this particular deployment, the difference between GPP and R tended to be greater in the Outer Harbor than in Snug Harbor, leading to higher values of NEP, but this was by no means universally true across all deployments, as we discuss further below.

We observed significant day-to-day variation in rates of GPP (Fig. 8). As discussed below, we suspect much of this variation is related to variation in light. Whole-system R also varied from day to day and rates tended to track the rate of GPP (Fig. 8). Figure 9 compares the rate of GPP and R for individual 24-h periods observed across all of our deployments during

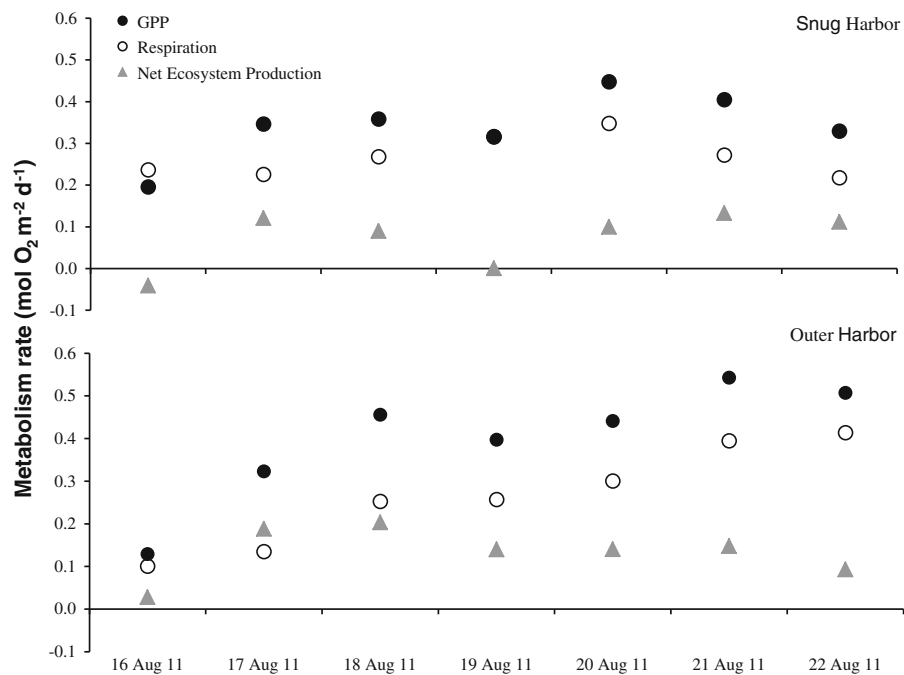


Fig. 8 Rates of GPP, R, and NEP over 7 days in August 2011 in Snug Harbor (*top*) and the Outer Harbor (*bottom*)

July and August over the 7 years. In both Snug Harbor and the Outer Harbor, most of the data tend to be scattered around the 1:1 line for the GPP-R plot. One explanation for this pattern is that much of total ecosystem R is driven by respiration of recently fixed photosynthate by the primary producers themselves. If so, accumulation of biomass by primary producers over the peak July to August summer season would seem to be low, at least in comparison to whole-ecosystem GPP. That is, net primary production (NPP) would be low. However, as we discuss below in the section on “Contribution of seagrasses and phytoplankton to GPP,” our available data indicate that NPP by seagrasses in the Outer Harbor (but not Snug Harbor) may be a major part of whole-system GPP.

Role of light and temperature

A significant amount of the variation in GPP was controlled by differences in surface light (Fig. 10). For both Snug Harbor and the Outer Harbor, GPP tended

to be higher on sunnier days (slopes are significantly greater than 0 for linear fits in Fig. 10; for Snug Harbor, F -statistic = 17.32, $p = 8.1 \times 10^{-5}$, 77 degrees of freedom; for Outer Harbor, F -statistic = 9.32, $p = 0.0031$, 77 degrees of freedom). In Fig. 10, we only present data for the dates we simultaneously deployed sondes in both Snug Harbor and the Outer Harbor, to facilitate comparison between the sites, but data from the other dates look very similar. Note that the very highest rates of GPP on individual days observed in Snug Harbor occurred on several days in 2007 (when the light was not unusually high compared to many other years), while rates of GPP in the Outer Harbor on those same days were not unusually high and in fact tended to be less than in other years on days with similar light levels (Fig. 10). We also observed relatively high rates of GPP in Snug Harbor but not the Outer Harbor for 2008, although due to deployment problems, we only have data for GPP on 2 days in common for the two sites in 2008.

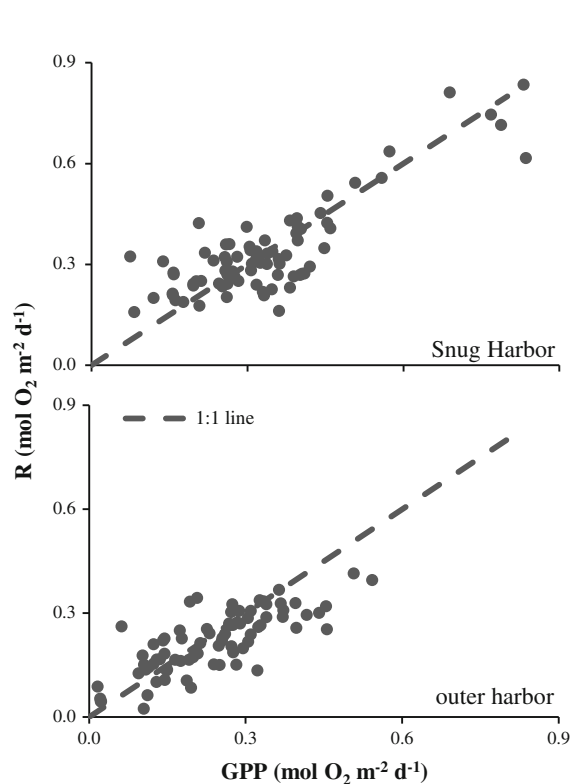


Fig. 9 Relationship between GPP and R measured on individual days in Snug Harbor (top) and the Outer Harbor (bottom). Only days when metabolism was measured simultaneously in both locations are included in this figure

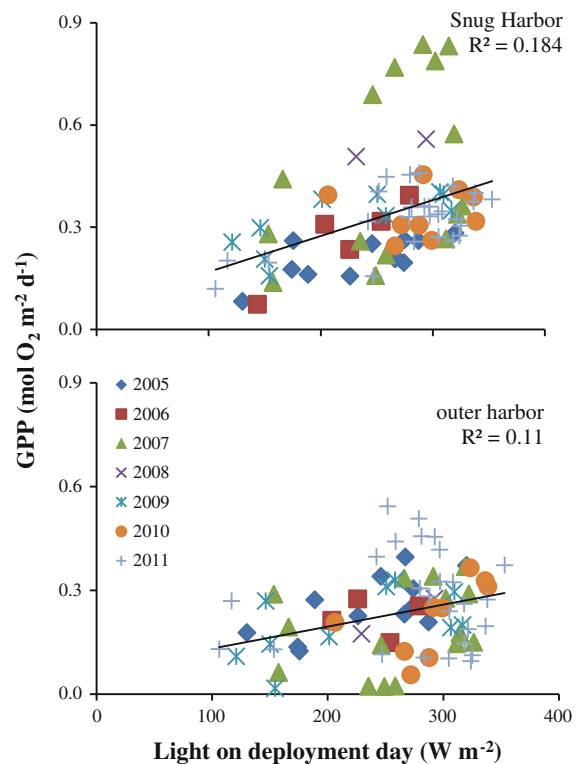


Fig. 10 Gross primary production measured on individual days as a function of light on that day across all years for Snug Harbor (top) and the Outer Harbor (bottom). Only days when metabolism was measured simultaneously in both locations are included in this figure

Possible reasons for the unusually high rates of GPP in Snug Harbor in 2007 and 2008 are discussed below.

Respiration rates are known to be sensitive to temperature, and in many other coastal marine ecosystems, temporal variation in R has been shown to be due in part to variation in temperature (Kemp and Testa 2011). This was not the case for West Falmouth Harbor during our study period (Fig. 11), quite likely because the range in temperature we observed was small. There was no significant relationship between R and water temperature (for Snug Harbor, F -statistic = 2.67, $p = 0.11$; 76 degrees of freedom; $R^2 = 0.03$; for Outer Harbor, F -statistic = 0.23, $p = 0.64$, 76 degrees of freedom; $R^2 = 0.003$). Note further that water temperatures in Snug Harbor and in the Outer Harbor were very similar (Fig. 11), and temperature is not significantly related to surface light in West Falmouth Harbor in the summer (data not shown; for Snug Harbor, F -statistic = 1.87, $p = 0.18$;

76 degrees of freedom; $R^2 = 0.02$; for Outer Harbor, F -statistic = 0.93, $p = 0.34$, 76 degrees of freedom; $R^2 = 0.01$), perhaps because of the large influence of water exchange with Buzzards Bay on harbor water temperature. As discussed below, we believe the major factor controlling the day-to-day variation in R in West Falmouth Harbor during the mid-summer months was the day-to-day variation in GPP.

Mean rates of GPP and R

Figure 12 shows the mean rates of GPP, R and NEP during the July–August period for each year across the 7 years of our study, for both Snug and the Outer Harbor. Both GPP and R tended to be greater in Snug Harbor than in the Outer Harbor across the years (a one-tailed t test indicates that the mean of the difference for rates in Snug Harbor and the Outer Harbor on individual days is greater than 0; for GPP, $p = 8.4 \times 10^{-8}$; for R , $p = 1.9 \times 10^{-9}$). The greatest differences in rates of GPP between the two sites were clearly in 2007 and 2008 (Fig. 12). However, even if we exclude those 2 years, rates were still significantly greater in Snug Harbor (one-tailed t test for GPP, $p = 1.1 \times 10^{-4}$). We suspect that the higher rates of GPP in Snug Harbor were primarily the result of the higher N load there, as is discussed further below in the section on “Role of N.” That the rates of GPP remained high in Snug Harbor in 2010 and 2011 after the loss of seagrasses there suggests that other primary producers—probably benthic macro-algae, or benthic micro-algae and benthic cyanobacteria—either increased their rate of production or were dominant there throughout our study, as we discuss below. Borum and Sand-Jensen (1996) found that eutrophication in shallow lagoons can lead to a loss of seagrasses and a switch in dominant primary producers with little if any change in GPP.

The inter-annual variability in mean summertime rates for both GPP and R was relatively small in both Snug Harbor and the Outer Harbor, except for the unusually high rates observed in Snug Harbor in 2007 and 2008 (Fig. 12). The inter-annual variation that did occur was not correlated with year-to-year variation in light or temperature. Figure 13 shows average daily rates of GPP for each year for July and August as a function of the average light and water temperature during the times of deployment. GPP was higher in Snug Harbor than the Outer Harbor for six of the

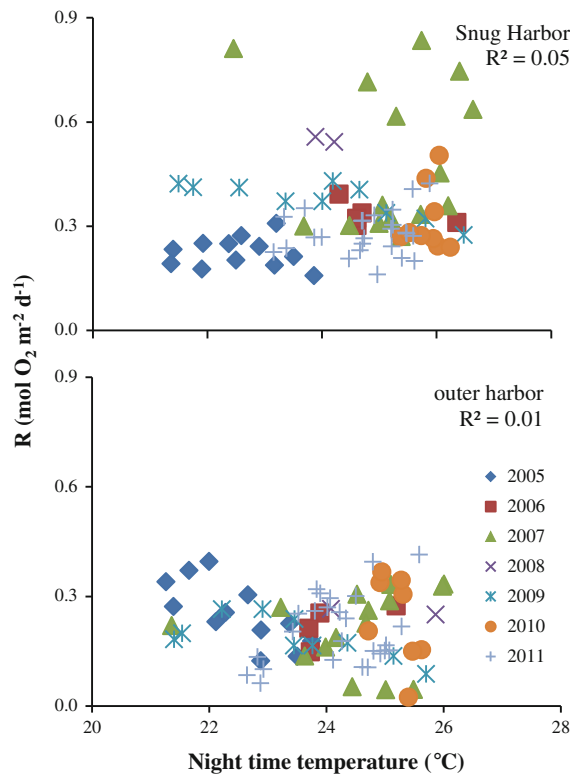


Fig. 11 Respiration measured on individual days as a function of temperature on that night across all years for Snug Harbor (top) and the Outer Harbor (bottom). Only days when metabolism was measured simultaneously in both locations are included in this figure

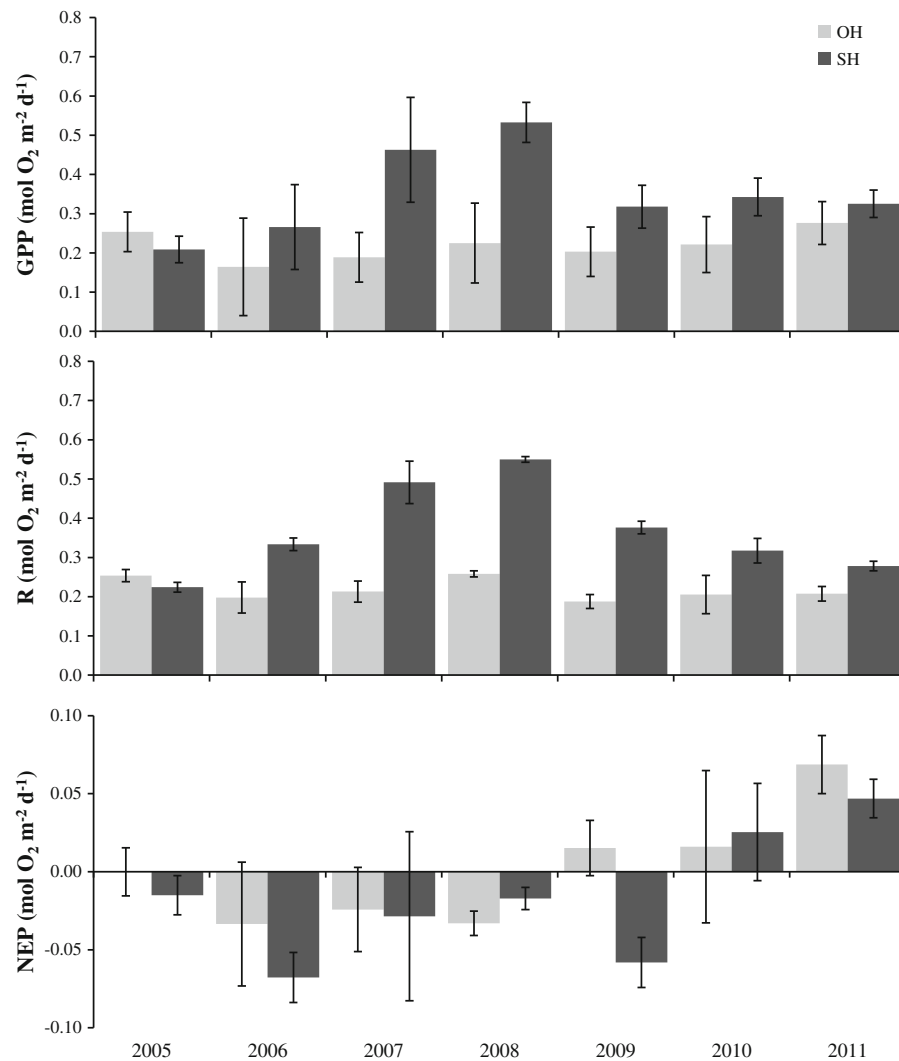


Fig. 12 Mean and 95 % confidence limits for rates of summertime metabolism in Snug Harbor and in the Outer Harbor for each year from 2005 to 2011, using only data when

metabolism was simultaneously measured at both sites. *Top panel* shows GPP, *middle panel* R, and *bottom panel* NEP

7 years, at the same light levels. But the very highest average rates of GPP in Snug Harbor were in 2007 and in 2008, years that only had intermediate levels of average surface sunlight (261 and 262 W m^{-2} respectively).

Contribution of seagrasses and phytoplankton to GPP

We have separately estimated above-ground NPP by seagrasses in West Falmouth Harbor for the summers of 2006 to 2009 as $0.84 \text{ g C m}^{-2} \text{ day}^{-1}$ in Snug Harbor and $1.6 \text{ g C m}^{-2} \text{ day}^{-1}$ in the Outer Harbor,

on average, within the seagrass beds (McGlathery et al. ms. in prep.). If we assume a 1:1 stoichiometry between C fixed and O_2 released, further assume that NPP is 50 % of GPP for seagrasses, and apply our measured estimates of 20 % coverage of seagrasses in Snug Harbor and 63 % in the Outer Harbor, we can very roughly estimate that average seagrass GPP rates were 0.027 and $0.17 \text{ mol O}_2 \text{ m}^{-2} \text{ day}^{-1}$ respectively in Snug Harbor and the Outer Harbor when averaged over the area of the whole basins. These rates correspond to somewhat less than 10 % of total ecosystem GPP in Snug Harbor and ~ 75 % in the Outer Harbor. Belowground seagrass NPP production

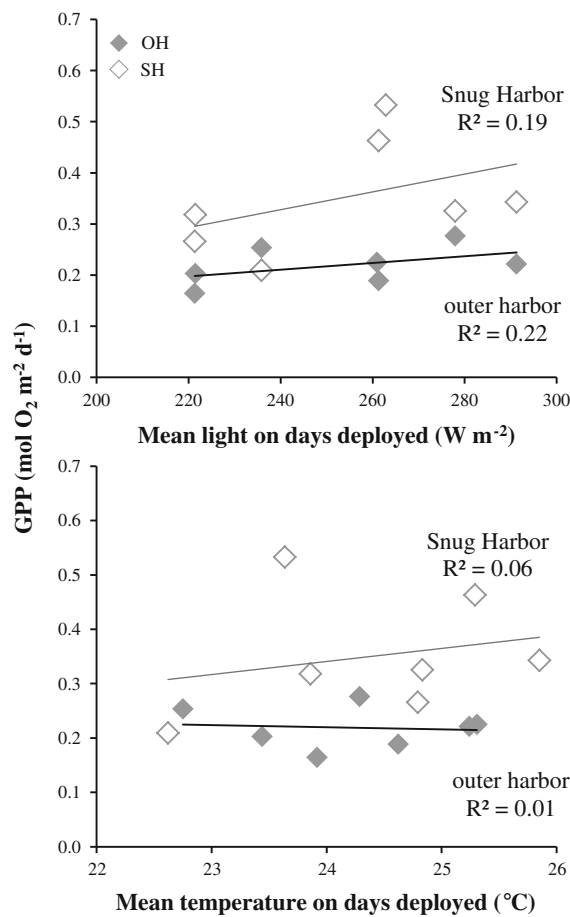


Fig. 13 Mean values of GPP as a function of mean surface light (*top*) and water temperature (*bottom*) on the days of deployment during July and August for Snug Harbor and the Outer Harbor for each year from 2005 through 2011

is not included in these estimates, and so the seagrass contribution to GPP may be even higher than these values indicate, particularly in the Outer Harbor; in Snug Harbor, the grasses had almost no roots and much less extensive rhizomes than in the Outer Harbor.

Between 2006 and 2011, we measured water-column chlorophyll concentrations more than 200 times in West Falmouth Harbor, representing hourly sampling over 24 h on 9–10 different days. The mean values were 2.0 $\mu\text{g l}^{-1}$ in the Outer Harbor and 7.0 $\mu\text{g l}^{-1}$ in Snug Harbor (unpublished data). Assuming 15 h of daylight per day and well-established estimates of GPP per chlorophyll concentration (Ryther and Yentsch 1957), we conclude that phytoplankton probably contributed an average of 0.04 and

0.01 mol O₂ m⁻² day⁻¹ to GPP in Snug Harbor and the Outer Harbor respectively, or on average ~10 and ~5 %, respectively, of whole-ecosystem GPP in the two basins. The relatively short water residence times limit the ability of phytoplankton to respond to the high N load (Swaney et al. 2008).

Our analysis of the relative contribution of the different primary producer organisms to peak summertime GPP is far from complete, but we conclude thus far that benthic producers dominate and that phytoplankton play a small role in both the Outer Harbor and Snug Harbor, probably because of the short water residence times. In the Outer Harbor, seagrasses are the major contributor to GPP, but other primary producers must dominate GPP in Snug Harbor (likely macro-algae and benthic and epiphytic micro-algae and cyanobacteria). Given the low contribution to GPP by seagrasses in Snug Harbor, it is not surprising that we observed no major change in GPP there after the 2010 die-off of the grasses.

Role of N

Despite the high N load to West Falmouth Harbor, primary productivity remained limited by N, as indicated by ratios of dissolved inorganic N (DIN) to soluble reactive phosphorus (SRP) that averaged ~1:1 (molar) and very seldom exceeded 3:1 in both the Outer Harbor and Snug Harbor (Hayn et al. 2013; Marino et al. ms. in prep.). DIN concentrations remained low, on average less than 1 μM throughout the harbor, except for an increase to 1–2 μM in Snug Harbor in 2010 following the seagrass die-off (Marino et al. ms. in prep.). One mechanism for the continued N limitation despite the high load from the contaminated aquifer and terrestrial watersheds was a relatively large import of phosphorus (P) relative to N from the tidal exchange of coastal waters with Buzzards Bay (Hayn et al. 2013). A greater contribution of P than N (compared to the N:P ratio in primary producers) from coastal water exchange occurs in many other estuaries, and often contributes to the maintenance of N limitation (Howarth et al. 2011).

We hypothesize that the higher rates of GPP in Snug Harbor relative to the Outer Harbor were due to the higher effective N load to that sub-basin. Two-thirds of the entire N load to West Falmouth Harbor

entered Snug Harbor from the contaminated ground-water plume from the wastewater treatment facility (Hayn et al. 2013). This N load was obviously less if distributed over the entire harbor, rather than just Snug Harbor where it originally entered. Further, some of the N was probably retained in Snug Harbor, particularly during the summer due both to retention in biomass and loss through denitrification (McGlathery et al. ms. in prep.); note that West Falmouth as a whole retained all of its external N input during summer months, and exported N to Buzzards Bay only during other seasons (Hayn et al. 2013). The average N load to Snug Harbor was estimated to be $17 \text{ mmol N m}^{-2} \text{ day}^{-1}$, while the average load to all of West Falmouth Harbor was $4.2 \text{ mmol N m}^{-2} \text{ day}^{-1}$ (see “Methods” section). The external N load to the Outer Harbor must be lower, by some unknown amount, than the average load to all of West Falmouth Harbor, due to seasonal retention and denitrification in Snug Harbor.

In contrast to deeper, phytoplankton-dominated estuaries where GPP tends to increase in a linear fashion with greater N loads, GPP in shallow marine lagoons may increase with increasing N load to a threshold level and then remain flat as the N load further increases (Borum and Sand-Jensen 1996; Nixon et al. 2001; McGlathery et al. 2007). Do the differences between Snug Harbor and the Outer Harbor fit this pattern, with the N load to Snug Harbor above this threshold and that to the Outer Harbor being below it? Nixon et al. (2001) suggested a threshold response to N loading at $2 \text{ mmol N m}^{-2} \text{ day}^{-1}$ based on results from a seagrass mesocosm experiment. Below this threshold, rates of primary production increased as the N load increased, but production saturated with no further increase in production at higher N loads. Note that Nixon et al. (2001) expressed their data as rates of “apparent daytime production,” which is equivalent to $\Delta O_{x_{\text{met-light}}}$ (Eq. 5) in our analysis. Our rates of $\Delta O_{x_{\text{met-light}}}$ (data not shown) in Snug Harbor are comparable to the rates reported by Nixon et al. (2001) in their mesocosms above this threshold with the exception of our measured rates in 2007 and 2008, which were much higher. Our rates in the Outer Harbor were comparable to those reported by Nixon et al. (2001) for an N load of $1 \text{ mmol N m}^{-2} \text{ day}^{-1}$. Of course, the precise threshold loading level may vary some across lagoon ecosystems, due to differences in hydrology, depth,

sediments, and other characteristics. Further, in the Nixon et al. (2001) mesocosms, all of the N was added directly to the water column, while the N load to West Falmouth Harbor (and many other lagoons) entered largely through groundwater, probably resulting in some loss of N through denitrification before reaching the water column of the estuary. We note that rates of GPP in shallow lagoons on the Delmarva Peninsula were substantially less than in West Falmouth Harbor, at N loads between 0.27 and $4.9 \text{ mmol N m}^{-2} \text{ day}^{-1}$ (Giordano et al. 2012), suggesting a higher threshold loading than shown in the Nixon et al. (2001) mesocosms. Our results are broadly consistent with those of D’Avanzo et al. (1996) who measured GPP in three portions of the nearby Waquoit Bay estuary on Cape Cod at N loading up to $12 \text{ mmol N m}^{-2} \text{ day}^{-1}$. We tentatively conclude that our data on GPP in West Falmouth Harbor are consistent with a threshold N load concept (with the possible exception of the data for Snug Harbor for 2007 and 2008, discussed further below), but we cannot estimate the magnitude of the threshold with any precision.

The inter-annual variation in GPP in Snug Harbor (that is, the very high rates in 2007 and 2008) cannot be explained by variation in external N loads. This should not be surprising, even if the threshold-response model for lagoons is incorrect, as the external load to Snug Harbor varied by less than 15 % from year to year, from 15 to $17 \text{ mmol N m}^{-2} \text{ day}^{-1}$ (see “Methods” section). Note that within this narrow range, the highest rates of GPP occurred in 2007 and 2008, when the N loads were at the lower end, 16 and $15 \text{ mmol N m}^{-2} \text{ day}^{-1}$, respectively.

Why were rates of GPP so high in Snug Harbor (but not the Outer Harbor) in 2007 and 2008 compared to the other years of our study? Snug Harbor (but not the Outer Harbor) in these two summers was characterized by unusually high biomass of epiphytes on the seagrasses and unusually high rates of N fixation by the epiphytes (Marino et al. in prep.). The epiphytes themselves included algae and cyanobacteria that probably contributed to the higher GPP in 2007 and 2008, and the N fixation contributed significantly to the total N inputs to Snug Harbor in those 2 years which may have also stimulated other primary producers. We believe that the high epiphyte biomass in Snug Harbor in 2007 and 2008 was favored by low abundances of organisms such as *Bittium* snails and amphipods that graze on epiphytes; these animals

were significantly less numerous in Snug Harbor than in the Outer Harbor (Reynolds et al. submitted), perhaps because of the lower DO and pH values there (Fig. 5). Our detailed data on epiphytic N fixation and the potential significance to the West Falmouth Harbor ecosystem will be presented in a separate paper (Marino et al. in prep.).

Net ecosystem production

In contrast to GPP and R, the summertime mean rates of NEP were much lower and were also highly variable from year to year (Fig. 12). For many years during July and August, NEP was not significantly different from zero in either Snug Harbor or the Outer Harbor, as indicated by the 95 % confidence limits containing zero. NEP was negative during the summer months in Snug Harbor in 2006, 2008, and 2009 as well as in the Outer Harbor in 2008, reflecting net heterotrophy and indicating a net loss of organic carbon. In 2011, NEP was positive (reflecting net autotrophy and storage or export of organic carbon) in both Snug Harbor and the Outer Harbor. We do not yet have a strong explanation for what factors may drive these inter-annual switches between net heterotrophy and autotrophy, but note that they were due to small changes in the closely coupled relationship between GPP and R. Perhaps the import of organic matter from Buzzards Bay during some major storm event in the past had contributed to R, with this contribution slowly decreasing over time. Since seagrasses contributed relatively little to total ecosystem GPP in Snug Harbor before 2010 and GPP there changed little after the die-off, it should not be surprising that the loss of seagrasses also caused no major change in rates of NEP.

Many previous studies have presented rates of NEP in shallow lagoons, with both positive rates (Santos et al. 2004; Stutes et al. 2007; Giordano et al. 2012) and negative rates (Barron et al. 2004; Gazeau et al. 2006; Eyre et al. 2011) reported. However, few other studies have presented data on the inter-annual variability in rates of NEP. A notable exception is the work of Barron et al. (2004) who demonstrated a steady increase in R and a steady decrease in NEP for a tropical seagrass bed over 6 years following the establishment of the bed as a result of trapping of detrital organic matter.

Kemp and Testa (2011) characterized NEP across many deeper estuaries as a function of the loading ratio of DIN to total organic carbon (TOC), with negative NEP values (net heterotrophy) when the ratio was less than ~ 0.2 (mol:mol) and positive values (net autotrophy) at ratios greater than ~ 0.5 . That is, greater N loads favor autotrophy, while greater TOC loads favor heterotrophy. We do not have a loading estimate for TOC to West Falmouth Harbor, and we are not aware of any studies that have evaluated NEP in shallow lagoon ecosystems in terms of the ratio of the DIN:TOC load. However, Caffrey (2004) demonstrated a positive relationship between N loading and NEP at the annual scale across several of the National Estuarine Research Reserves, which include shallow lagoons. At N loads less than $7 \text{ mmol m}^{-2} \text{ day}^{-1}$, NEP rates were negative (the ecosystems were heterotrophic). At higher N loads of $8\text{--}20 \text{ mmol m}^{-2} \text{ day}^{-1}$, NEP rates were near zero (roughly balanced between heterotrophy and autotrophy). Our rates of NEP for Snug Harbor during the summer were consistent with this model based on annual data, but we might expect to have observed more negative rates for NEP in the Outer Harbor (where the N load is lower) than in Snug Harbor, which is not the case (Fig. 11). In contrast to the pattern from Caffrey (2004), Giordano et al. (2012) reported positive rates of NEP (net autotrophy) for four lagoons on the Delmarva Peninsula at relatively low N loads ($0.27\text{--}4.9 \text{ mmol m}^{-2} \text{ day}^{-1}$), with the lowest rate of NEP in their most N-loaded ecosystem. Stutes et al. (2007) also reported relatively high, positive rates of NEP in lagoons with low N loads ($0.1\text{--}0.5 \text{ mmol m}^{-2} \text{ day}^{-1}$). Perhaps patterns of NEP in shallow estuaries may be more interpretable in the context of the ratio of the DIN load to TOC load, as more data on the TOC loads to these systems become available. The ability of lagoons to trap particles from adjacent coastal waters and retain detritus from seagrasses and other producers may also influence NEP rates, as demonstrated by Barron et al. (2004) for a tropical lagoon. We urge more emphasis on variation in the seasonal and inter-annual rates of NEP in shallow estuaries.

Whatever the cause of the change in net ecosystem production, the trend towards increased autotrophy may have contributed to the seagrass die-off in Snug Harbor in 2010. Seagrasses have a high light requirement (Orth et al. 2006), but can tolerate substantial shading as long as the concentration of dissolved

carbon dioxide is high enough. Because seagrasses are quite inefficient at using dissolved carbon dioxide, they are less tolerant of shading when the carbon dioxide concentration is low (Zimmerman et al. 1997; Greve and Binzer 2004; Björk et al. 2008). The shift to net autotrophy (positive NEP) in Snug Harbor in 2010 and 2011 (Fig. 12) resulted in lower concentrations of dissolved carbon dioxide, reflected in higher pH values (Fig. 6). We hypothesize that the N-induced shading by epiphytes may have been the ultimate cause of seagrass dieback in Snug Harbor, but the change in net ecosystem metabolism that led to higher pH's and lower dissolved carbon dioxide may have been the proximate trigger for the sudden die-off in 2010. Other stressors such as chronically high nitrate inputs, such as those to Snug Harbor, can weaken seagrasses by a direct physiological effect (Burkholder et al. 1992) and perhaps combined with pH and other environmental stressors exacerbate seagrass decline.

West Falmouth Harbor—what will the future bring?

The wastewater treatment plant that is the source of the N-contaminated groundwater entering Snug Harbor began N-removal technology in late 2005, and given the 7–10 year travel time of the groundwater from the sewage treatment plant to the harbor (Kroeger et al. 2006), the N load should start to show a large decrease some time between 2013 and 2016. The decrease was not observable as of early 2013 (unpublished data). This reduction of N input may lead to lower GPP and R in Snug Harbor, if the decrease in N load is sufficiently great relative to the saturating threshold (if any) for the response of GPP to N load in this system. If the load from the sewage-contaminated groundwater were completely eliminated (which seems unlikely, as N-removal technology at the wastewater plant is not completely effective), the estimated background loads to all of West Falmouth Harbor and to just Snug Harbor would be 1.4 and 2.7 mmol N m⁻² day⁻¹, respectively (based on the information presented in the “Methods” section). We suspect such a decrease would be sufficient to lead to a noticeable decrease in GPP.

Our finding of continued high GPP in Snug Harbor in 2010 and 2011 after the loss of seagrasses confirms that other primary producers in the system—probably benthic macro- and micro-algae—dominated GPP.

This pattern may change with decreased N loading into Snug Harbor in the future, and the possible recovery of seagrasses there. Continued measurement of metabolism rates as the N load decreases, and the system starts to recover from eutrophication and perhaps even as seagrasses eventually recover, and analysis of the partitioning of GPP and R among the various primary producers should prove instructive. Shallow coastal ecosystems such as West Falmouth Harbor are important habitats and filters for anthropogenic nutrients, and adequate management and protection of these systems requires a better understanding of the responses to reductions in nutrient load and associated biological stressors such as periods of lower DO and pH.

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