

# The Whole Ecosystem Metabolism of a Shallow Temperate Estuary

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**Abstract:**

The rates of respiration, gross primary production, and net ecosystem production, referred to collectively as the whole ecosystem metabolism, were estimated for a shallow temperate estuary, West Falmouth Harbor on Cape Cod, MA, using the open-water diel oxygen method. We took continuous in situ measurements of dissolved oxygen levels at two sites within the estuary over five separate 5-7 day periods from July 2005 through November 2005. We developed a simple model to estimate the metabolic rates based on the changes in dissolved oxygen after correcting for the diffusion of oxygen at the air-water interface. We found no significant difference in the metabolic rates between the two sites even though they are believed to differ in the composition of their primary producer communities and in the rates of flushing. The rate of respiration averaged between the sites decreased from  $4.4 \text{ g C m}^{-2} \text{ d}^{-1}$  in mid-July to  $1.6 \text{ g C m}^{-2} \text{ d}^{-1}$  in late-November. The average rate of gross primary production also decreased from  $4.1 \text{ g C m}^{-2} \text{ d}^{-1}$  to  $1.0 \text{ g C m}^{-2} \text{ d}^{-1}$  over the same period. Net ecosystem production was less than zero indicating net heterotrophic conditions throughout the study period and ranged from  $-0.2 \text{ g C m}^{-2} \text{ d}^{-1}$  to  $-0.6 \text{ g C m}^{-2} \text{ d}^{-1}$ . We conducted a sensitivity analysis using the model and found that this method is somewhat sensitive to the atmospheric exchange flux calculation during late fall when the metabolic rates were low and wind speeds were high. The results are comparable to other shallow estuaries where similar studies to estimate the whole ecosystem metabolism have been conducted. The method and model developed for this project will be useful for quantifying changes in the whole ecosystem metabolism of West Falmouth Harbor as nitrogen loading rates increase rapidly over the next few years.

**Introduction:**

Anthropogenic nutrient enrichment from coastal watersheds is having severe impacts on the health of estuarine ecosystems worldwide (Howarth et al., 2003). The high nutrient content of septic system leachate and discharge from wastewater treatment facilities can cause oxygen depletion and shifts in the composition of primary producer communities (Valiela et al., 2000). Nitrogen is typically the limiting nutrient in estuarine ecosystems, and excess nitrogen inputs can stimulate growth rates of primary producers to extremely high levels, reaching a state of eutrophication (Howarth and Marino, 2006). In shallow temperate estuaries, stimulated growth of suspended primary producers such as phytoplankton and algae can decrease light penetration of the water column causing declines in ecologically-valuable benthic primary producers such as seagrasses (Short et al., 1993; Duarte, 1995; Nixon et al., 2001).

A shift from a seagrass-dominated to a phytoplankton- and algae-dominated primary producer community can lead to shifts in the composition of higher trophic levels (Heck et al., 2000; Deegan et al., 2002). Since seagrass beds provide good habitat for many fish and other macro-faunal species, a shift to a phytoplankton-dominated system would result in less suitable habitat available for these larger organisms. Quantifying the response of the primary producer community to increased nitrogen loading is critical for making management decisions regarding acceptable nitrogen loading rates to coastal systems in order to maintain valuable marine habitat.

The rates of primary production and respiration, referred to collectively as the whole ecosystem metabolism, are widely-used indicators for the degree of nutrient enrichment in aquatic ecosystems (Hopkinson and Smith, 2004). High nutrient loading rates generally lead to high rates of primary production, which are stimulated by the

increased availability of limiting nutrients. In turn, the accumulation of dead organic material increases respiration by microbes. However, recent studies on shallow seagrass-dominated estuaries suggest that perhaps these systems are able to mediate excess nutrient loading unlike deeper estuarine and freshwater systems (Nixon et al., 2001). The metabolic rates of an estuary can be measured by a variety of methods; two of the most popular methods being the light/dark bottle method and the open-water diel oxygen method (Hopkinson and Smith, 2004; Howarth and Michaels, 2000).

The light/dark bottle method entails incubating water samples in transparent bottles under varying light conditions and measuring the changes in dissolved oxygen concentration over time to estimate the rates of primary production and respiration (Kenney et al., 1988). While this method has been successfully employed for a number of aquatic systems, it requires substantial effort and suffers from so-called bottle effects that result in biased estimates of primary productivity and respiration (Howarth and Michaels, 2000). One major effect is the artificial selection of certain primary producers, such as phytoplankton, that are well-adapted for growing in bottles. Benthic producers, such as seagrasses, are excluded from this method due to their larger size, even though they can be a significant component of the primary producer community especially in shallow estuaries. Other effects such as reduced turbulence, shifts in the composition of grazers, and trace metal contamination can also have significant impacts on the measurements of the ecosystem metabolism by this method (Howarth and Michaels, 2000).

The open-water diel oxygen method is similar to the light/dark bottle method in that changes in dissolved oxygen levels are measured over time to estimate the metabolic rates. Unlike the light/dark bottle method, however, measurements are taken in situ and are therefore more representative of the actual whole system metabolism. By measuring the rate of oxygen production during daytime and the rate of oxygen consumption during nighttime the rates of respiration, gross primary production, and net ecosystem production can be estimated. This method also has some issues to consider, particularly the diffusion of oxygen at the air-water interface and the effect of advection due to tidal flooding (Kemp and Boynton, 1980; Marino and Howarth, 1993; Swaney et al., 1999).

The purpose of this project is to test whether the open-water diel oxygen method is a valid approach for estimating the rates of production and respiration in the shallow seagrass-dominated estuary West Falmouth Harbor. Within the watershed of West Falmouth Harbor, the Falmouth Wastewater Treatment Plant (FWTP) has been spraying secondary-treated wastewater effluent onto a neighboring forest for the past 15 years in hopes of naturally removing nitrogen by immobilization in soil stocks and plant uptake. However, much of the nitrogen sprayed on the forest floor has seeped into the groundwater resulting in a large plume of nitrate that has been moving from the FWTP forest towards West Falmouth Harbor with the groundwater. This plume has recently begun entering the harbor and is expected to yield a roughly two-fold increase in nitrogen loading over the next five years. This rapid increase in nitrogen loading is expected to stimulate phytoplankton and algae growth resulting in the decline of seagrass beds due to light limitation. However, recent studies have suggested that shallow seagrass-dominated estuaries are able to mediate the effects of increased nitrogen loading maintaining production and respiration rates below eutrophic levels. More research is needed to investigate the response of these systems to increased nitrogen loading.

The immediate goals of this project are to compare the metabolic rates spatially between two locations within the estuary and temporally over seasonal time scales from

mid-summer to early-winter. We expect the metabolic rates to differ spatially as the two locations are believed to differ in flushing rates, vegetative communities and nitrogen loading rates. We also expect the rates to change temporally, decreasing in magnitude from mid-summer to early-winter due to decreases in temperature and the length of daylight. In addition, we will compare the metabolic rates of West Falmouth Harbor to those estimated in a similar system by another study that used the same open-water diel oxygen method. The long-term goal of this project is to provide a method and model that will be useful for quantifying the effects of increasing nitrogen loading on the whole ecosystem metabolism of a shallow seagrass-dominated estuary.

## **Methods:**

### *Description of Study Site:*

West Falmouth Harbor is located on the coast of Buzzard's Bay along the western shore of Cape Cod, MA (Figure 1). It is a relatively shallow estuary with maximum and mean depths at mean lower low tide of about 3 m and 1.1 m, respectively (Figure 2). The harbor can be divided geometrically into four separate lobe-shaped regions: the Outer Harbor, Middle Harbor, Snug Harbor and South Harbor (Figure 3). We chose to focus on the two regions that appeared to differ the most: the Outer Harbor and Snug Harbor. Snug Harbor has an average depth of 1.2 m at mean lower low tide with an area of 21 ha and directly receives the majority of the nutrient and freshwater inputs for the entire harbor. Since Snug Harbor is further from the outlet to Buzzards Bay it is expected to have a longer residence time relative to the Outer Harbor, which has a similar average depth of 1.2 m and a smaller area of 15 ha. We visually concluded that the vegetative communities of the two harbors appear to differ with Snug Harbor having a greater abundance of macroalgae and phytoplankton in the water column than in the Outer Harbor, which contains more seagrass beds and less turbid water. West Falmouth Harbor is unique to the region because seagrass beds have persisted over the past century whereas many other estuaries along the coast of Cape Cod, such as Waquoit Bay, have lost much or all of their seagrass due to nitrogen pollution or disease (Short et al., 1993).

### *Data Collection:*

We measured dissolved oxygen levels in the water column in both the Outer Harbor and Snug Harbor simultaneously using two Hydrolab Data Sonde 4 and 4a instruments (Figure 3). We secured the Hydrolabs to a mooring system that kept them at a constant height above the sediment by a sub-surface float: about 0.5 m in the Outer Harbor and 1.2 m in Snug Harbor. The Hydrolabs recorded temperature [°C], salinity [ppt], dissolved oxygen (in percent saturation and absolute concentration [mg O<sub>2</sub>/L]), pH, photosynthetically active radiation (PAR) [ $\mu\text{mol m}^{-2} \text{sec}^{-1}$ ], and depth below the water surface [m] at 20 minute intervals for deployments lasting for periods of 5-7 days. We conducted five deployments at each site once a month from July 2005 through November 2005 yielding a total of ten deployments.

We calibrated the dissolved oxygen, pH, and conductivity sensors on the Hydrolabs prior to each deployment according to the Hydrolab Sonde 4a manual (Hydrolab Corporation, 1998). The oxygen sensor was calibrated to 100% saturation by equilibrating it with the atmosphere. The pH sensor was calibrated using two buffer

solutions of pH 7.0 and 10.0. The conductivity sensors were calibrated using two conductivity standards with specific conductivities of 1,000 and 50,000  $\mu\text{S}$ .

We acquired wind speed data collected at the Buzzard Bay, MA station (BUZM3), which is located about 40 km southwest of West Falmouth Harbor in the middle of Buzzards Bay, by the National Oceanic and Atmospheric Administration's National Data Buoy Center. The wind measurements were taken at a height of 24.8 m above sea level at 10 minute intervals.

*Model Description:*

To facilitate data analysis and computation of the collected data sets, we developed a model using Microsoft Excel 2003 named the Whole Ecosystem Metabolism from Dissolved Oxygen (WEMDO). For the sake of brevity, only a conceptual description of the model as applied to West Falmouth Harbor is provided in this paper; the complete description and user's manual of the generalized version will be available elsewhere. The principle purpose of the model is to use continuous measurements of temperature, salinity, dissolved oxygen, PAR and wind speed to estimate the rates of respiration (R), apparent daytime production (ADP), gross primary production (GPP), and net ecosystem production (NEP).

The rate of respiration includes all autotrophic and heterotrophic respiration in the ecosystem and is assumed to be the same during the daytime as it is during the nighttime. ADP is the net amount of carbon fixed from the atmosphere by primary producers during daytime only. GPP is the gross amount of carbon fixed from the atmosphere during the daytime prior to autotrophic respiration. NEP is the net amount of carbon fixed from the atmosphere during an entire 24-hour day. NEP is similar to ADP in that it represents net primary production, but ADP only accounts for net production during the daytime while NEP accounts for the additional loss of organic carbon by respiration that occurs during the nighttime.

The data collected for each deployment, which refers to a single 5-7 day period of continuous measurements at a single location, were downloaded from the Hydrolab Data Sondes and imported to WEMDO. The mean length of daytime during each deployment,  $T_{day}$  [hr], was first calculated by taking the mean of the total time that PAR measurements were above  $5 \mu\text{mol m}^{-2} \text{sec}^{-1}$  during each day of the deployment. The mean length of nighttime,  $T_{night}$  [hr], was then simply calculated as:  $T_{night} = 24 \text{ hrs} - T_{day}$ .

The change in dissolved oxygen concentration at each time point,  $\frac{dDO(t)}{dt}$  [ $\text{g O}_2 \text{ m}^{-3} \text{ hr}^{-1}$ ], is first calculated by:

$$\frac{dDO(t)}{dt} = \frac{DO(t+dt) - DO(t)}{dt}$$

where  $DO(t)$  is the concentration of dissolved oxygen at time  $t$  [ $\text{g O}_2 \text{ m}^{-3}$ ] and  $dt$  is the time interval between each measurement [hr], in this case 20 minutes or 1/3 hour.

We used a simple mass balance of dissolved oxygen to estimate the biological rates of oxygen consumption and production:

$$\frac{dDO(t)}{dt} \cdot V(t) = \frac{dDO_{bio}(t)}{dt} \cdot V(t) + \frac{dDO_{adv}(t)}{dt} \cdot V(t) - F_{am}(t) \cdot A$$

where  $dDO_{bio}(t)/dt$  is the change in oxygen concentration over time due to biological processes [ $\text{g O}_2 \text{ m}^{-3} \text{ hr}^{-1}$ ],  $V(t)$  is the volume of the site at time  $t$  [ $\text{m}^3$ ],  $dDO_{adv}(t)/dt$  is the change in oxygen concentration due to advection [ $\text{g O}_2 \text{ m}^{-3} \text{ hr}^{-1}$ ],  $F_{atm}(t)$  is the atmospheric flux [ $\text{g O}_2 \text{ m}^{-3} \text{ hr}^{-1}$ ], and  $A$  is the surface area of the site [ $\text{m}^2$ ]. We assumed that the role of advection on the oxygen dynamics is negligible since the dissolved oxygen levels were generally similar throughout the entire harbor at any given time. The validity of this assumption will be considered in the discussion section.

By setting the advective term to zero, dividing both sides by  $V(t)$  and rearranging this mass balance equation, the changes in oxygen due to biological production and consumption can be determined from the calculated changes in dissolved oxygen and the estimated atmospheric flux:

$$\frac{dDO_{bio}(t)}{dt} = \frac{dDO(t)}{dt} + F_{atm}(t)/h(t)$$

where  $h(t)$  is the depth of the water column [ $\text{m}$ ] at time  $t$  and is equal to the volume of water in the site divided by the surface area:  $h(t) = V(t)/A$ .

To estimate the flux of oxygen at the air-water interface, the saturation concentration, which is the concentration of dissolved oxygen when water is in equilibrium with the atmosphere, is calculated as a function of temperature and salinity at each time point using the algorithm presented in Chapra (1997). The flux of oxygen at the air-water interface,  $F_{atm}$  [ $\text{g O}_2 \text{ m}^{-2} \text{ hr}^{-1}$ ], is estimated using a first order approximation:

$$F_{atm} = k(DO - DO_{sat})$$

where  $k$  is the piston velocity [ $\text{m hr}^{-1}$ ],  $DO$  is the concentration of dissolved oxygen [ $\text{g O}_2 \text{ m}^{-3}$ ], and  $DO_{sat}$  is the saturation concentration of dissolved oxygen [ $\text{g O}_2 \text{ m}^{-3}$ ]. If the water is supersaturated with respect to oxygen then  $DO > DO_{sat}$  and  $F_{atm} > 0$ .

Therefore,  $F_{atm}$  represents the flux of oxygen out of the water into the air since oxygen would diffuse out of the water if it is supersaturated. A negative atmospheric flux would represent undersaturated conditions with oxygen diffusing into the water from the air.

The piston velocity,  $k$ , is estimated at each time point as a function of wind speed using one of two regressions by Kremer et al. (2003) or Marino and Howarth (1993). These regressions were designed for measurements taken at a height of 10 m above the water surface. Since the wind speeds obtained from the National Data Buoy Center were measured at a height of 24.8 m, these measurements had to be normalized using the logarithmic transformation from Kremer et al. (2003):

$$U_{10} = \frac{U_z}{0.097 \cdot \ln(z/10) + 1}$$

where  $U_{10}$  is the estimated wind speed at a height of 10 m [ $\text{m/s}$ ], and  $U_z$  is the measured wind speed [ $\text{m/s}$ ] at a height  $z$  [ $\text{m}$ ]. Marino and Howarth (1993) used a different method to normalize wind speeds to a height of 10 m that was specific to their measurements made at a height of 1 m and thus could not be used to adjust wind speeds for this project.

The Kremer et al. (2003) piston velocity regression is based on measurements taken at another Cape Cod estuary, Sage Lot Pond near Waquoit Bay, which is similar to West Falmouth Harbor, and is described by the equation:

$$k = 1.65 \exp(0.15 U_{10}) / 100$$

The regression by Marino and Howarth (1993) is more generalized and is based on measurements from a wide array of estuaries varying in size and geographic location:

$$k = \exp(1.09 + 0.249 U_{10}) / 100$$

For this study I chose to primarily use the Kremer et al. regression since it is based on a system with characteristics similar to West Falmouth Harbor including geographic location, vegetation and climate. However, both regressions are used for comparison in the discussion regarding the sensitivity of this method to atmospheric flux calculations.

The hourly rate of respiration,  $R_{hour}$ , is calculated for each nighttime during the deployment by integrating  $dDO_{bio}(t)/dt$  over time from sunset to sunrise, and then dividing by the length of nighttime,  $T_{night}$  [hr]:

$$R_{hour} = \frac{\int_{sunset}^{sunrise} \frac{dDO_{bio}(t)}{dt} \cdot dt}{T_{night}}$$

As a matter of convention, respiration rates are then multiplied by -1 to convert them from negative to positive values. However, note that in all figures respiration rates are plotted as negative rates for the sake of clarity.

The hourly rate of apparent daytime production,  $ADP_{hour}$ , which represents the net primary production during the daytime, is calculated by integrating  $dDO_{bio}(t)/dt$  over time from sunrise to sunset and dividing by the length of daytime,  $T_{day}$  [hr]:

$$ADP_{hour} = \frac{\int_{sunrise}^{sunset} \frac{dDO_{bio}(t)}{dt} \cdot dt}{T_{day}}$$

The rates of respiration and apparent daytime production are then converted from units of  $[g O_2 m^{-3} hr^{-1}]$  to units of  $[g C m^{-3} hr^{-1}]$  assuming a molar ratio of 1:1 between dissolved oxygen consumed/produced and organic carbon produced/consumed.

For each day, the average rates of respiration and apparent daytime production per day,  $R_{day}$  and  $ADP_{day}$ , respectively, are calculated from the average hourly rates by:

$$R_{day} = R_{hour} \times 24 \text{ hrs}$$

$$ADP_{day} = ADP_{hour} \times T_{day}$$

For each 5-7 day deployment, the overall average rates of  $R_{day}$  and  $ADP_{day}$  were calculated by taking the mean of all days in that deployment for which wind speeds were not excessively high. The piston velocity regressions used to estimate the atmospheric flux of oxygen are only valid for wind speeds less than 10 m/s and so days or nights during which speeds exceeded this maximum had to be excluded from further analysis (Kremer et al., 2003; Marino and Howarth, 1993). We specifically excluded all day or night periods for which there were more than five measurements in excess of 10 m/s.

The average daily rate of gross primary production,  $GPP_{day}$ , for each deployment is then calculated by adding the hourly rate of R to the hourly rate of ADP, resulting in  $GPP > ADP$  since  $R > 0$ , and multiplying by the length of daytime since production only occurs during the day:

$$GPP_{day} = (ADP_{hour} + R_{hour}) \times T_{day}$$

Finally, the daily rate of net ecosystem production,  $NEP_{day}$ , is calculated by subtracting the daily rate of respiration from the daily rate of gross primary production, resulting in  $NEP_{day} < GPP_{day}$  since  $R > 0$ :

$$NEP_{day} = GPP_{day} - R_{day}$$

All rates are then multiplied by the average depth of the site to convert from a per-volume basis to a per-area basis with units of  $[g C m^{-2} d^{-1}]$ .

### Results:

For all deployments, the levels of dissolved oxygen oscillated according to the expected diel pattern: increasing during the daytime as primary producers produce oxygen by photosynthesis and decreasing during the nighttime as oxygen is consumed by respiration (Figure 4). All dissolved oxygen data sets showed some degree of day-to-day variability especially during the later seasons. This variability can be attributed to differences in cloud cover during each day which would affect total incident radiation on the system in addition to temperature. Due to excessively high wind speeds, 18 of the nighttime periods and 14 of the daytime periods were excluded from the results. The total numbers of days or nights used to calculate each deployment-averaged rate are listed in Tables 1 and 2.

The rates of respiration and apparent daytime production were not significantly different between the two sites ( $p > 0.01$  using a two-tailed t-test for independent samples with unequal variance; Tables 1, 2). The rates generally decreased in magnitude from mid-July to the end of November, except for net ecosystem production which increased in magnitude becoming more negative over this period (Figures 5, 6). In the Outer Harbor, respiration decreased from 4.6 to 1.6  $g C m^{-2} d^{-1}$ , gross primary production decreased from 4.2 to 1.0  $g C m^{-2} d^{-1}$  and net ecosystem production increased in magnitude becoming more negative from -0.4 to -0.6  $g C m^{-2} d^{-1}$  (Figure 5). In Snug Harbor, respiration decreased from 4.2 to 1.5  $g C m^{-2} d^{-1}$ , gross primary production decreased from 4.0 to 0.9  $g C m^{-2} d^{-1}$  and net ecosystem production increased in magnitude becoming more negative from -0.2 to -0.6  $g C m^{-2} d^{-1}$  (Figure 6). Net ecosystem production was consistently less than zero suggesting that both sites experience net heterotrophic conditions throughout the second half of the year. The amount of day-to-day variability decreased from summer through fall as indicated by the standard deviations for each deployment, which were calculated from the set of daily rates for each day within each deployment.

When the piston velocity regression by Marino and Howarth (1993) was used to calculate the atmospheric flux, the metabolic rates were greater and the system was more heterotrophic particularly during late fall, as compared to the results using the Kremer et al. regression (Figures 7, 8). In the Outer Harbor, respiration decreased from 4.9 to 2.4  $g C m^{-2} d^{-1}$ , gross primary production decreased from 4.5 to 1.3  $g C m^{-2} d^{-1}$ , and net ecosystem production became more negative from -0.4 to -1.2  $g C m^{-2} d^{-1}$  reaching an

overall maximum in early November at  $-1.8 \text{ g C m}^{-2} \text{ d}^{-1}$  (Figure 7). In Snug Harbor, respiration decreased from  $4.2$  to  $2.3 \text{ g C m}^{-2} \text{ d}^{-1}$ , gross primary production decreased from  $4.1$  to  $1.1 \text{ g C m}^{-2} \text{ d}^{-1}$ , and net ecosystem production became more negative from  $-0.1$  to  $-1.1 \text{ g C m}^{-2} \text{ d}^{-1}$  (Figure 8). These results are similar to those using the regression by Kremer et al. (2003) but suggest slightly more heterotrophic conditions particularly during late fall. The amount of day-to-day variability during each deployment was again greater during the summer season than during the fall.

### **Discussion:**

The metabolic rates decreased from mid-summer to late-fall as expected due to decreases in temperature and the length of daylight. Surprisingly, the rates were not significantly different between the two sites despite differences in the observed vegetative communities and expected residence times. We anticipated greater metabolic rates in Snug Harbor since it is further from the outlet to Buzzard's Bay and would therefore have a longer residence time. A greater residence time gives phytoplankton and algae more time to grow before being flushed out of the harbor and indeed we visually observed more algae and phytoplankton in Snug Harbor than in the Outer Harbor. However, the similarities between the two sites suggests that either the harbor is very well mixed such that changes in oxygen levels are averaged out spatially or that the rates of production and respiration are in fact similar in both regions.

The rate of net ecosystem production was consistently negative suggesting that the harbor is net heterotrophic meaning more organic carbon is respired than is produced. This may occur if there is a large flux of organic matter that enters the harbor during tidal flooding from Buzzard's Bay. Alternatively, the more negative NEP (greater system heterotrophy) during late fall may be due to seagrass blades which are produced early in the year and are later decomposed after senescence in the fall.

Sulfate reduction and sulfide oxidation in the sediments may also explain the greater rates of respiration over those of gross primary production. When sediments are oxygen depleted, which is typical for estuarine sediments, anoxic bacteria produce hydrogen sulfide as they employ sulfate reduction pathways to decompose organic carbon anaerobically. This hydrogen sulfide builds up in the sediments during the spring and summer and begins to diffuse up towards the oxygen rich waters above where it is oxidized by biological and abiological processes that consume dissolved oxygen (Howarth, 1984). The consumption of oxygen due to sulfide oxidization may be a significant sink causing oxygen levels to drop lower than if they were only affected by aerobic respiration resulting in overestimation of biological respiration in the water column during the later seasons. Additionally, biological respiration rates would be underestimated during the spring and summer when reduced sulfur in the form of hydrogen sulfide is being stored in the sediment. This would in turn suggest that NEP is even more negative and the system is more heterotrophic during summer. More research must be conducted to determine the main driving force of this net heterotrophy.

The calculation of the atmospheric flux of oxygen at the air-water interface appears to be somewhat sensitive depending on which piston velocity regression is used. The regression by Kremer et al. (2003) yielded slightly lower rates throughout the year than that by Marino and Howarth (1993), which resulted in greater rates especially during late fall when wind speeds were high and biological processes were slow. Developing these regressions is a difficult task; the measurements of oxygen diffusion

are highly sensitive to temperature changes and other factors such as turbulence at the water surface or bottom morphology making it difficult to apply a regression made for one system to another system. At high wind speeds ( $> 10$  m/s) these regressions no longer hold since surface turbulence may result in breaking waves and bubble formation which can drastically alter atmospheric exchange rates (Marino and Howarth, 1993; Kremer et al., 2003).

One of the key simplifying assumptions of this model is that advection has a negligible effect on the oxygen dynamics. In shallow estuaries, the volume of water that is exchanged during a tidal cycle can be significant. For West Falmouth Harbor, the average tidal height is about the same as the average depth at low tide ( $\sim 1$ - $1.25$  m) and thus the volume of water in the estuary roughly doubles from low to high tide, which presumably causes significant mixing between the water from Buzzards Bay and the water already in the harbor. If the incoming water has a dissolved oxygen level that is different from that within the harbor then the dissolved oxygen level in the harbor will change. Estimating the effect of advection requires measurement of the dissolved oxygen level of the incoming water and the degree of mixing within the estuary. In shallow estuaries with little salinity gradients, this can prove difficult and may require the aid of complex hydrodynamic models.

The results for West Falmouth Harbor are comparable to other estuaries where similar studies have been conducted. D'Avanzo et al. (1996) also used the open-water diel oxygen method to estimate the metabolic rates of the Childs River estuary, located about 5 km east of West Falmouth Harbor in East Falmouth, MA. They found similar trends with metabolic rates generally decreasing in magnitude from mid-summer to late fall (Figure 9). They also observed higher day-to-day variability during the summer than during the fall. The magnitudes of their rates were fairly similar to those for West Falmouth Harbor after converting to their units of  $\text{g O}_2$  instead of  $\text{g C}$  (Figure 10).

We also compared the rates of apparent daytime production in West Falmouth Harbor to those measured by Nixon et al. (2001) for varying nitrogen loading rates. The current nitrogen loading rate in West Falmouth Harbor is believed to be about  $3.5 \text{ mmol m}^{-2} \text{ d}^{-1}$  (Ken Foreman, personal communication). We added the apparent daytime production rate for mid-July averaged between the two sites, which was  $3.6 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$ , to a plot by Nixon et al. (2001) of apparent daytime production as a function of nitrogen loading rates and found that it agreed well with their results (Figure 11). Nixon et al. (2001) found that apparent daytime production rates tended to leveled off as nitrogen loading rates increased from the current nitrogen loading rate of West Falmouth Harbor. Therefore, if West Falmouth Harbor follows this same trend then we would expect the metabolic rates to not increase substantially. This result would suggest that seagrass-dominated estuaries are somehow able to buffer the effects of increased nutrient loading on the ecosystem metabolic rates.

### **Conclusion:**

The open-water diel oxygen method appears to be a valid approach for estimating the whole ecosystem metabolism of West Falmouth Harbor. The metabolic rates decreased from summer through fall as expected due to seasonal changes in temperature and incident radiation. The similarity of the results for the two sites suggest that West Falmouth Harbor is either well-mixed or that the rates of respiration and primary production are relatively homogenous throughout the harbor. Further investigation into the gradients in nutrients, chlorophyll and flushing rates may provide

insight into the spatial differences in production, respiration and the composition of the primary production communities. Better estimates of the atmospheric flux may be achieved with more accurate wind speed measurements taken directly on site, and construction of a piston velocity regression specific to West Falmouth Harbor. More research into the role of advection is also critical for applying the open-water diel oxygen method to estuarine ecosystems where tidal flooding drives circulation. The model and method developed for this project will be useful for quantifying the response of this ecosystem as the rate of nitrogen loading increases over the next few years.

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**Figures:**



Figure 1. Location of West Falmouth Harbor (red star) in the state of Massachusetts.

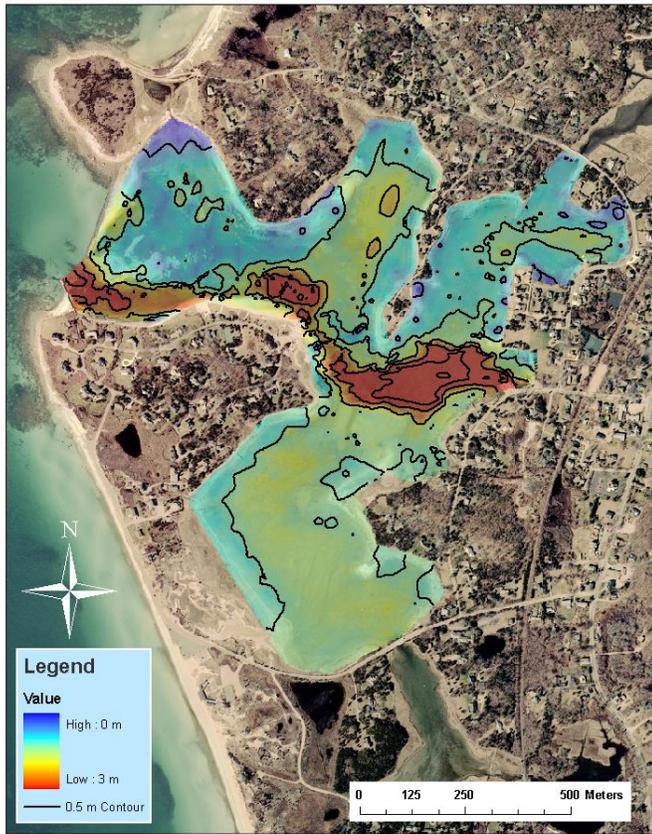


Figure 2. Bathymetric map of West Falmouth Harbor with 0.5 m contours.



Figure 3. Divisions of West Falmouth Harbor and locations of Hydrolab measurements in Snug Harbor and the Outer Harbor.

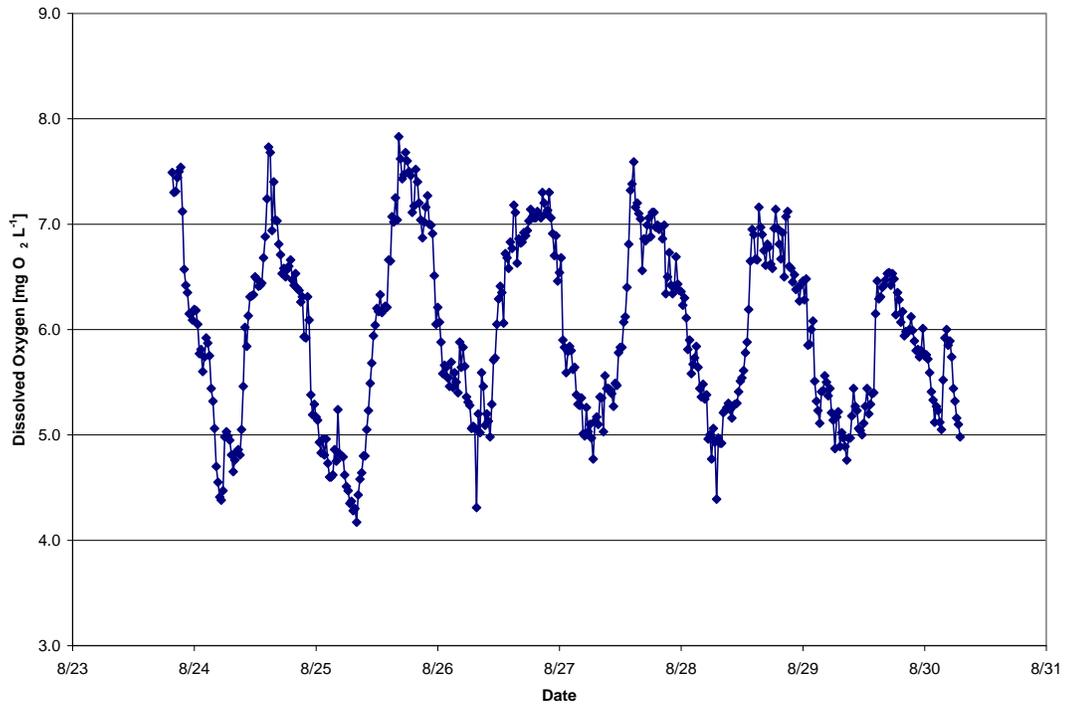


Figure 4. Example of the diel oxygen cycle from Snug Harbor during the end of August showing oxygen production due to photosynthesis during the day and oxygen consumption due to respiration during the night.

Deployment	Outer Harbor			Snug Harbor			t-stat	p-value
	mean	st. dev.	n	mean	st. dev.	n		
7/11/2005	-4.55	1.49	7	-4.23	1.13	7	0.449	0.662
8/23/2005	-4.45	1.91	7	-4.46	1.22	7	-0.0118	0.991
9/29/2005	-2.74	0.660	5	-3.95	0.630	5	-2.97	0.021
11/1/2005	-1.89	0.000	1	-1.38	0.000	1	N/A	N/A
11/21/2005	-1.57	0.566	6	-1.50	0.533	6	0.225	0.827

Table 1. Means, standard deviations, sample sizes, t-statistics and p-values for respiration rates in both harbors for each deployment. P-values were computed using an approximate two-tailed t-test for independent samples with unequal variance. Note that a t-statistic could not be computed for the 11/1/2005 deployment since each sample only contained one value (all other nights on the deployment were removed due to high wind speeds).

Deployment	Outer Harbor			Snug Harbor			t-stat	p-value
	mean	st. dev.	n	mean	st. dev.	n		
7/11/2005	1.31	1.15	7	1.38	0.999	7	0.114	0.911
8/23/2005	1.27	1.32	7	1.26	0.778	7	-0.0135	0.990
9/29/2005	0.636	0.381	6	1.37	0.865	6	1.90	0.106
11/1/2005	0.425	0.334	5	0.790	0.625	5	1.15	0.293
11/21/2005	0.347	0.347	4	0.313	0.457	4	-0.119	0.910

Table 2. Means, standard deviations, sample sizes, t-statistics and p-values for the rates of apparent daytime production in both harbors for each deployment. P-values were computed using an approximate two-tailed t-test for independent samples with unequal variance.

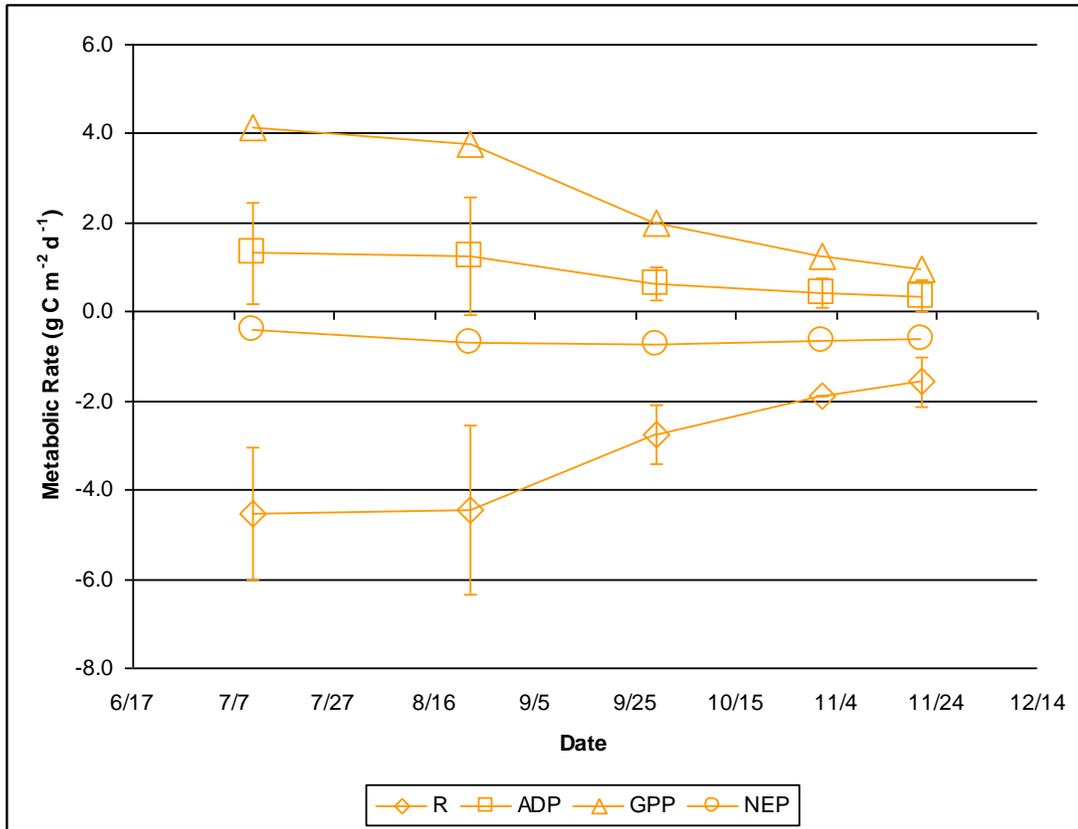


Figure 5. Rates of respiration (diamonds), apparent daytime production (squares), gross primary production (triangles) and net ecosystem production (circles) for the Outer Harbor using the piston velocity regression by Kremer et al. (2003). Error bars on R and ADP data points represent  $\pm 1$  standard deviation as calculated from the mean daily rates during each deployment. For the sake of clarity, respiration rates are plotted as negative values since respiration is a carbon consuming process.

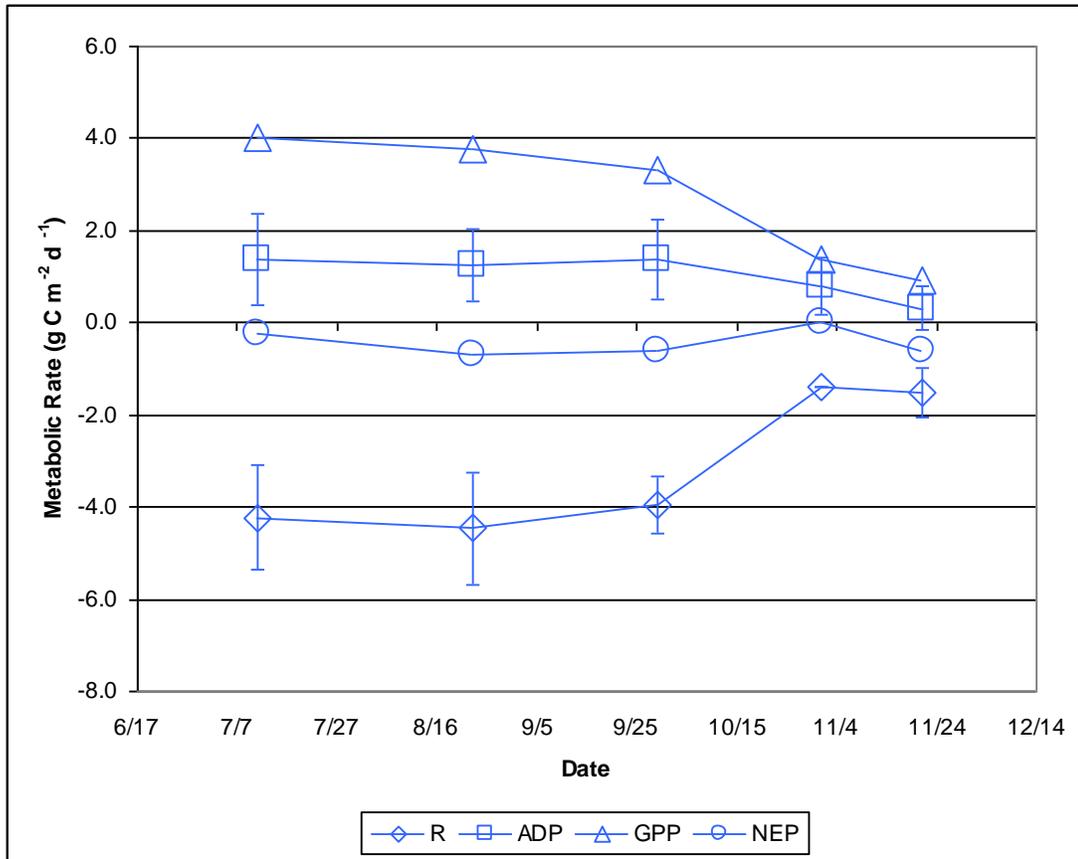


Figure 6. Rates of respiration (diamonds), apparent daytime production (squares), gross primary production (triangles) and net ecosystem production (circles) for Snug Harbor using the piston velocity regression by Kremer et al. (2003). Error bars on R and ADP data points represent  $\pm 1$  standard deviation calculated from the daily rates during each deployment. For the sake of clarity, respiration rates are plotted as negative values since respiration is a carbon consuming process.

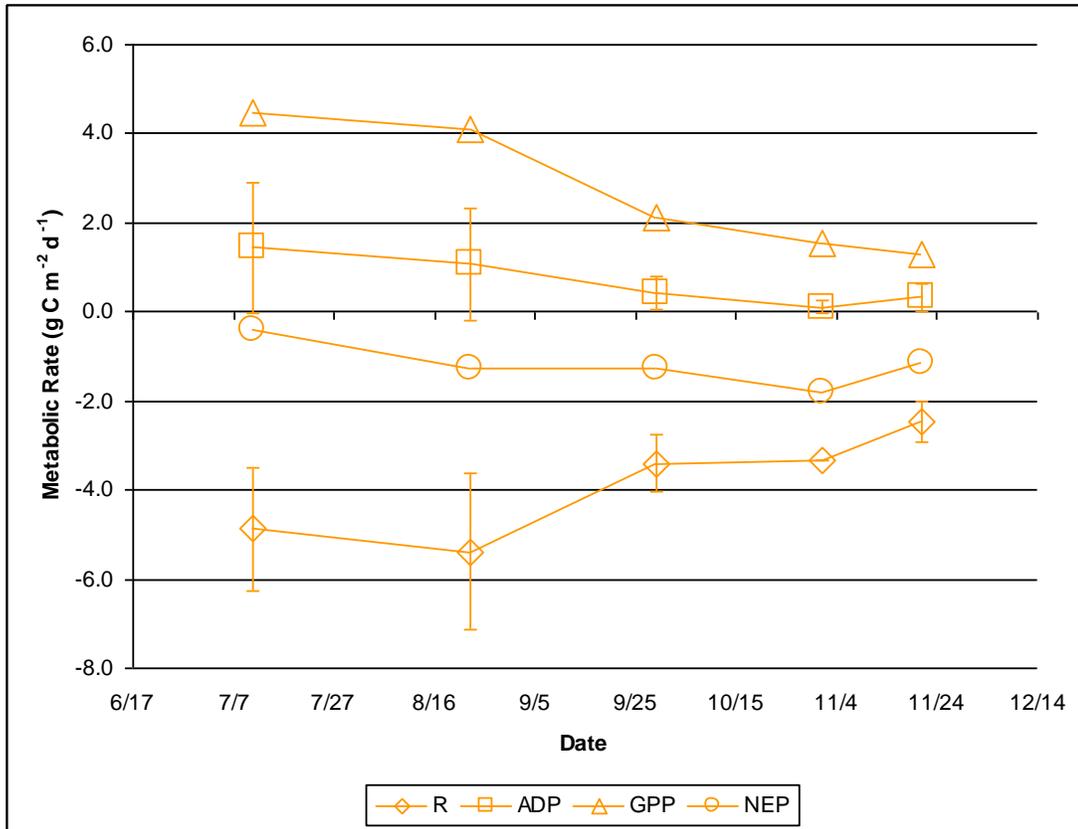


Figure 7. Rates of respiration (diamonds), apparent daytime production (squares), gross primary production (triangles) and net ecosystem production (circles) for the Outer Harbor using the piston velocity regression by Marino and Howarth (1993). Error bars on R and ADP data points represent  $\pm 1$  standard deviation calculated from the daily rates during each deployment. For the sake of clarity, respiration rates are plotted as negative values since respiration is a carbon consuming process.

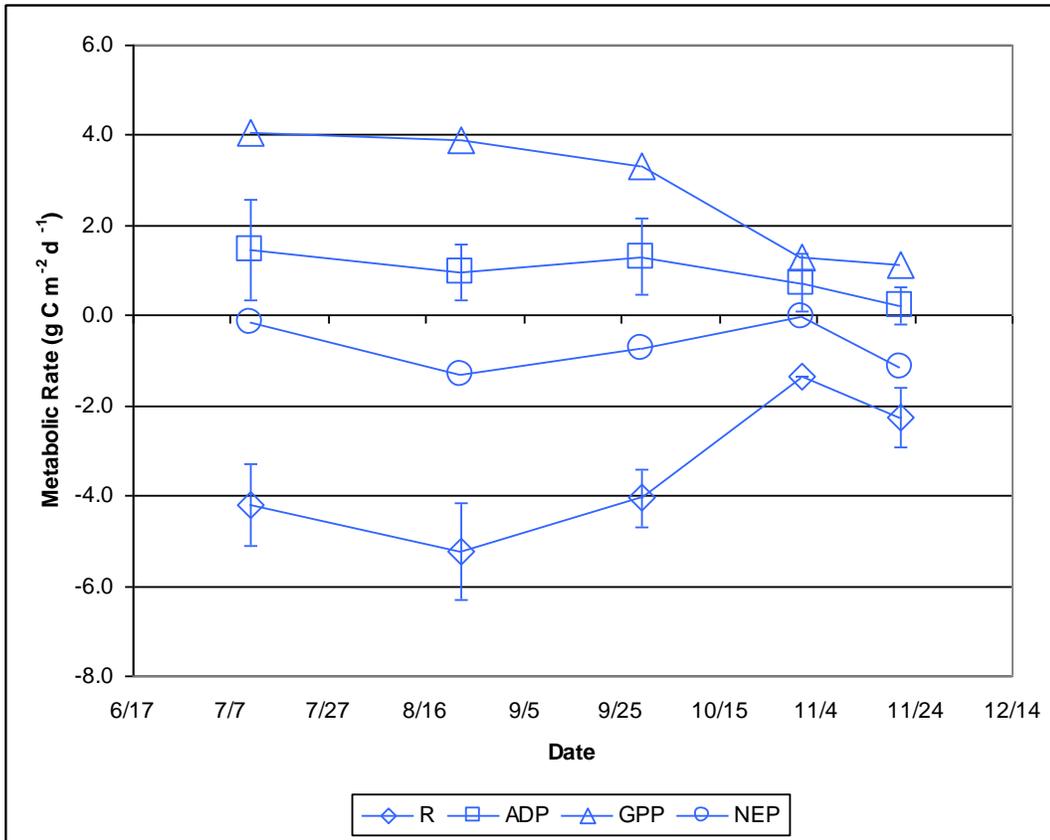


Figure 8. Rates of respiration (diamonds), apparent daytime production (squares), gross primary production (triangles) and net ecosystem production (circles) for Snug Harbor using the piston velocity regression by Marino and Howarth (1993). Error bars on R and ADP data points represent  $\pm 1$  standard deviation calculated from the daily rates during each deployment. For the sake of clarity, respiration rates are plotted as negative values since respiration is a carbon consuming process.

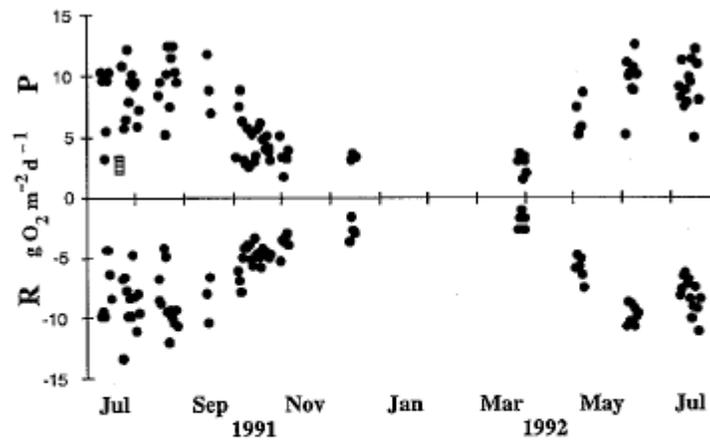


Fig. 1. Day-to-day variation in daily ecosystem production (P) and respiration (R;  $O_2$ ) over a year in 10 deployments of the automated conductivity-temperature- $O_2$  sensors in the Childs River, Waquoit Bay estuary, Cape Cod, MA, USA. (mm) Average SD of 3 measurements along the estuary on 4 d or night cycles in midsummer, an indication of the variability within an estuary

Figure 9. Adapted from Figure 1 of D'Avanzo et al. (1996) for the Childs River Estuary.

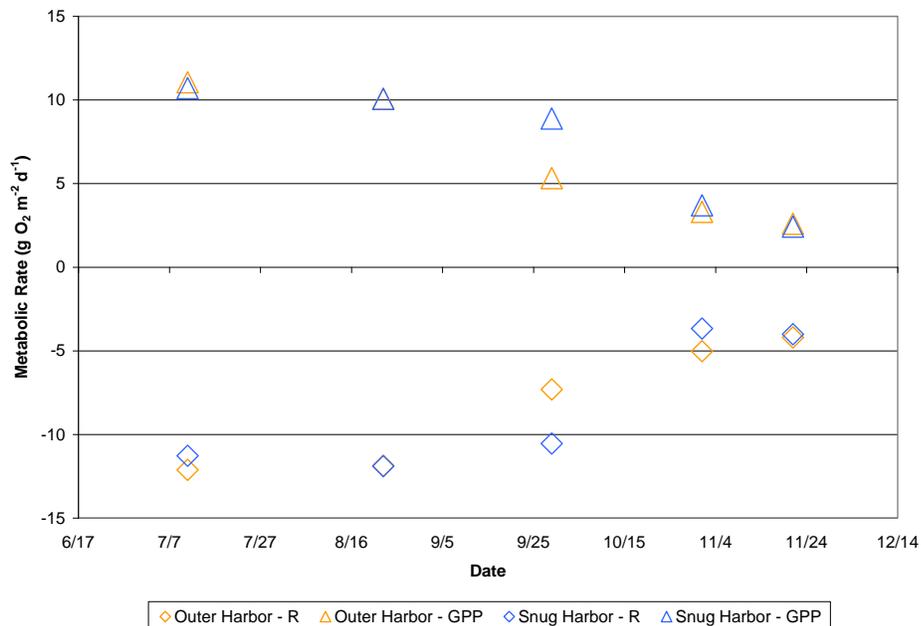
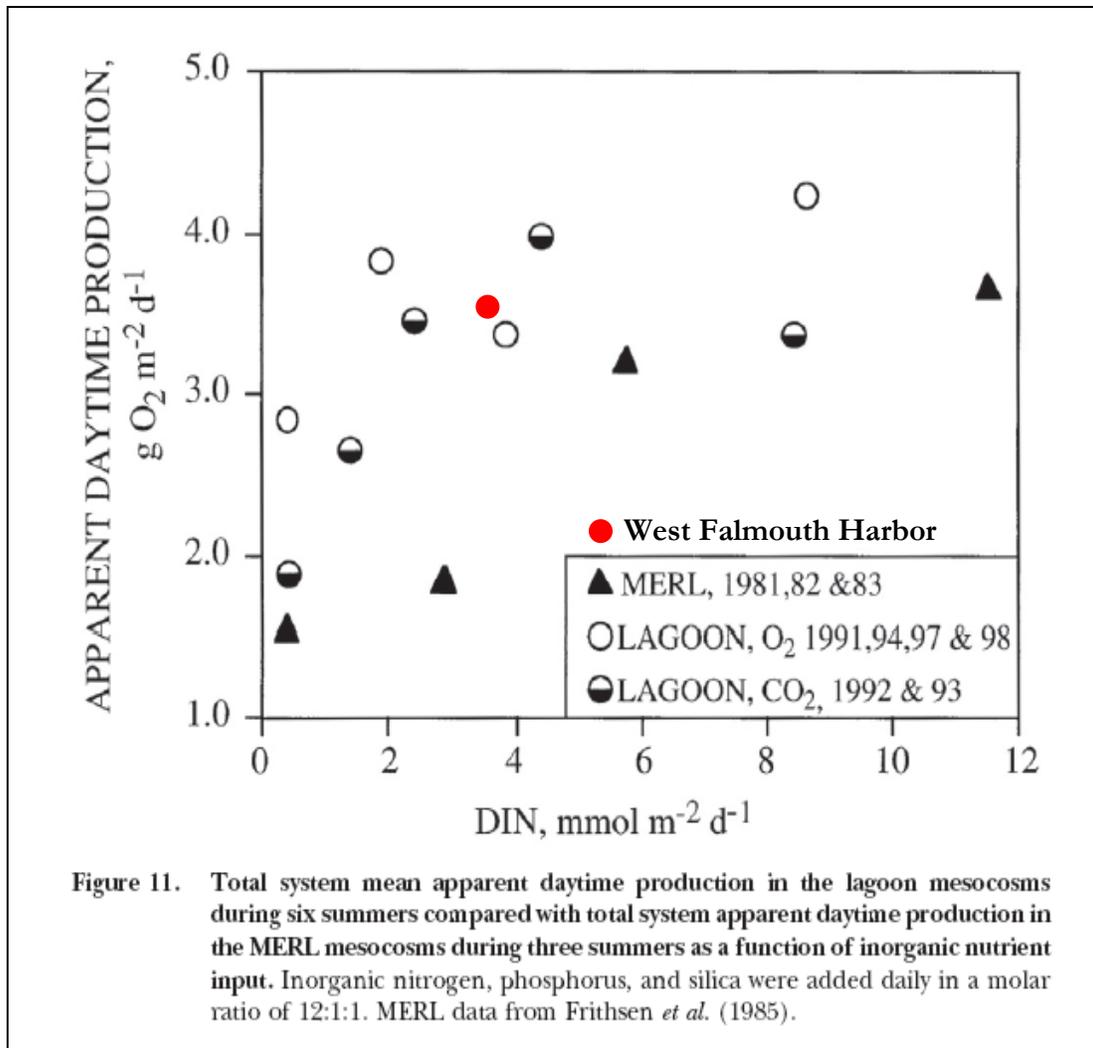


Figure 10. The rates of respiration and gross primary production for both sites in West Falmouth Harbor in units of  $\text{g O}_2$  for comparison to those of the Childs River estuary plotted in Figure 9. The rates for the Outer Harbor are in orange while those for Snug Harbor are in blue. For the sake of clarity, respiration rates are plotted as negative values since respiration is a carbon consuming process.



Adapted from Fig. 11 in Nixon et al. (2001)