Oxygen and Triple Oxygen Isotope Measurements Provide Different Insights into Gross Oxygen Production in a Shallow Salt Marsh Pond

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Abstract
The metabolism of estuarine environments is often estimated by measuring changes in dissolved oxygen concentrations. A central assumption of common oxygen-based approaches is that oxygen consumption rates (primarily respiration) are similar under light and dark conditions. Evaluating this assumption is critical, especially in benthic-dominated systems, because differences between daytime and nighttime respiration could result in underestimation or overestimation of ecosystem productivity. We evaluated rates of gross oxygen production over hourly to seasonal time scales in a shallow, temperate salt marsh pond. To assess whether a dissolved oxygen diel mass balance underestimated gross oxygen productivity, we compared rates using this traditional approach and using the triple oxygen isotope tracer of photosynthesis. This is a powerful combination because the triple oxygen isotope approach is theoretically insensitive to respiration. The methods agreed well over daily to seasonal time scales. However, during midday periods of peak light and productivity, the triple oxygen isotope approach resulted in higher hourly scale gross oxygen production rates. The timing and magnitude of this short-term difference is consistent with light-dependent oxygen uptake fluxes including photoreduction and/or light-stimulated community respiration. Finally, aquatic vegetation was associated with variability in productivity across the pond. Such small-scale environmental heterogeneity is evidence that this shallow pond was not laterally well mixed, and likely contributes to the dynamism of these common estuarine environments.

Keywords Metabolism · Light-dependent respiration · Oxygen · Triple oxygen isotopes · Salt marsh · Pond

Introduction
Dissolved oxygen (O2) fluxes are widely used to estimate aquatic ecosystem metabolism rates, including in lakes (Staehr et al. 2010), streams (Demars et al. 2015), estuaries (Caffrey 2004), and the ocean (Yang et al. 2017). However, attribution of these fluxes to photosynthesis and respiration is complicated because the physical and biological processes that affect net oxygen fluxes vary over time and space and may be difficult to disentangle without additional tracers. In

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particular, deriving photosynthesis rates from a dissolved O$_2$ mass balance typically requires either assuming that nighttime respiration is representative of daytime respiration (e.g., Odum 1956; Stæhr et al. 2010) or using submodels of photosynthesis as a function of irradiance and respiration as a function of temperature (Holtgrieve et al. 2010; Winslow et al. 2016). Neither approach accounts for light-dependent increases in ecosystem respiration or non-respiratory O$_2$ uptake. Yet, O$_2$ consumption in aquatic ecosystems including sediments and pelagic environments in lakes, estuaries, and the open ocean may be two to ten times greater in the light than in the dark (Falkowski and Owens 1978; Bender et al. 1987; Kana 1990; Epping and Jørgensen 1996; Parkhill and Gulliver 1998; Pringault et al. 2009). The same studies found that if light-dependent O$_2$ uptake is not explicitly accounted for, photosynthetic production may be underestimated by 23–62%.

Thus, ecosystem rates of photosynthesis and respiration based on dissolved O$_2$ fluxes may be systematically too low, complicating assessment of O$_2$-driven biogeochemistry and attribution of changes in ecosystem metabolism rates to environmental drivers.

Observations of light-dependent O$_2$ consumption are generally derived from concurrent comparisons between net O$_2$ fluxes and either production or respiration, separately evaluated using other methods. Some studies measure either short-term responses to light, including methods based on fluorometry (Suggett et al. 2009) and hysteresis of dissolved O$_2$ responses to irradiance changes (Falkowski and Owens 1978; Epping and Jørgensen 1996). Others compare net O$_2$ or carbon fluxes to photosynthetic production evaluated with carbon or oxygen isotope labeling of photosynthetic substrates (Bender et al. 1987; Laws et al. 2000). Laboratory studies may inhibit specific cellular pathways in order to isolate the particular light-dependent O$_2$ process of interest (e.g., Helman et al. 2005). Each method has different sensitivities to different mechanisms of O$_2$ uptake. This diversity of tracers and methods used can complicate the attribution of measured O$_2$ fluxes to specific light-dependent processes as opposed to methodological biases. It is therefore challenging to generalize the wide range of light-dependent effects on respiration and productivity reported in the literature.

One promising approach for estimating in situ photosynthesis in aquatic environments is the triple oxygen isotope (TOI) method (Luz and Barkan 2000), which involves the simultaneous measurement of natural abundance $^{16}$O, $^{17}$O, and $^{18}$O of O$_2$ dissolved in water. The oxygen isotope ratios can be combined in a respiration-independent manner in order to calculate the fraction of dissolved O$_2$ derived from splitting of water in photosystem II during photosynthesis compared to the fraction of O$_2$ entering the water through air-water gas exchange. Thus the evolution of the oxygen isotope ratios with time provides an unambiguous estimate of gross oxygen production (GOP), similar to the H$_2^{18}$O isotopic spike method (Bender et al. 1987). However, a crucial difference between the TOI method and H$_2^{18}$O or other incubation methods is that the natural abundance triple oxygen isotopes can be used to evaluate photosynthesis in situ, in intact ecosystems, whereas incubation methods require removing organisms from their natural system (e.g., into bottles). Used in this way, the TOI method for estimating GOP shares a major source of systematic uncertainty with the dissolved O$_2$-derived production: air-water gas exchange. This facilitates a direct comparison with dissolved O$_2$ fluxes derived from in situ sensors in a common O$_2$ “currency,” and allows evaluation of O$_2$ uptake in the light under ambient environmental conditions. The shared uncertainties and sensitivity to in situ conditions of these two methods contrasts with the primarily incubation-based approaches outlined above, in which results may diverge from whole ecosystem production and respiration rates because of altered growth environments (“bottle effects”) or subsampling of the heterogeneous autotrophic and heterotrophic community of organisms.

Differences between TOI and dissolved O$_2$-derived rates of gross O$_2$ production should directly reflect the importance of light-dependent O$_2$ uptake processes (see “Light-Dependent Oxygen Uptake Processes” section). Yet, despite this potential utility and increasing adoption of this approach (e.g., Juranek and Quay 2013), the TOI method has rarely been directly compared to GOP from dissolved O$_2$ fluxes. Sarma et al. (2005) reported GOP from in situ TOI measurements to be nearly twice that derived from O$_2$ in light-dark bottle incubations for the surface mixed-layer of a coastal setting, though that ratio varied seasonally. In a Lagrangian study in the surface mixed layer of the pelagic ocean, Hamme et al. (2012) found that in situ GOP rates from the TOI method ranged from half to double the GOP from an O$_2$ diel mass balance, though the two rates were not significantly different after a sufficiently long period elapsed. In a shallow estuary, Stanley and Howard (2013) found that the GOP derived from either method agreed when both the oxygen isotopes and dissolved O$_2$ were measured in benthic chambers at hourly frequencies. To the best of our knowledge, no previously published work has compared in situ GOP fluxes from the two methods across the range of time scales (hourly to seasonal) that O$_2$ data are commonly collected for studies of freshwater and estuarine metabolism.

In this work, we compare in situ photosynthetic rates derived from a standard dissolved O$_2$ diel mass balance to those from the TOI method in a salt marsh pond. These shallow, continuously submerged environments are well-lit, highly productive, have high rates of aerobic and anaerobic sedimentary respiration producing reduced compounds, and undergo large diel changes in O$_2$ concentrations (Spivak et al. 2017, 2018). These characteristics have been identified as likely to stimulate light-dependent O$_2$ uptake in other environments (Falkowski and Raven 1997; Fenchel and Glud 2000;
Buapet et al. 2013). Because we apply both the TOI and dissolved O₂ mass balance methods to in situ data collected at the same time from the same salt marsh pond, sources of systematic error between approaches are limited and incubation effects are eliminated; any differences in O₂ production rates between the two approaches are more confidently assigned to light-dependent O₂ uptake. Our goals are to: (1) evaluate whether GOP rates from the TOI and dissolved O₂ diel mass balance are in good agreement or show systematic biases over seasonal, daily, or hourly time scales; (2) determine the magnitude and significance of light-dependent O₂ uptake in this setting; and (3) discuss the relationship of TOI and dissolved O₂-derived ecosystem metabolism fluxes to variations in environmental properties.

**Methods**

**Theory**

**Dissolved O₂ Diel Method**

The dissolved oxygen mass balance for a parcel of water depends on production, respiration, air-water gas exchange, light-dependent processes that consume O₂, entrainment and mixing with adjacent water parcels, and bubble processes including wave driven bubble injection and partial bubble exchange, and ebullition from underlying sediments. We do not quantify mixing or bubble processes, as neither could be adequately constrained over the entire study period, but consider the effects of these processes in the discussion. The resulting simplified O₂ mass balance for a well-mixed water parcel is expressed as:

\[ \frac{\partial}{\partial t} ([O_2]) = \text{GOP}_{O_2} - R + k_{O_2} ([O_2]_{sat} - [O_2]) - LD \]  

(1)

Here, \( h \) is the depth of the well-mixed water parcel being considered, \([O_2]\) and \([O_2]_{sat}\) are the measured and air-water saturation (at equilibrium) concentrations of dissolved O₂, \( \text{GOP}_{O_2} \) is the areal gross oxygen production rate, \( R \) is the areal community respiration rate, \( k_{O_2} \) is the air-water gas transfer velocity, and \( LD \) is the areal rate of a light-dependent process that results in net consumption of O₂. \( k_{O_2} \) is calculated from wind speed and pond area using the parameterization of Vachon and Prairie (2013).

Only the sum of the oxygen-producing and oxygen-consuming processes can be directly evaluated from dissolved O₂ data. If light-dependent processes are minor contributors then the net biological O₂ flux is equivalent to net ecosystem metabolism (NEM = GOP\(_{O_2} - R\), sometimes alternatively referred to as net community production). In order to calculate \( \text{GOP}_{O_2} \), \( R \) is assumed to equal net oxygen uptake measured during nighttime periods (GOP\(_{O_2}\) and PD equal zero) and further assumed to be identical in the day (Odum 1956). We use this simple approach and note that it yields similar results to more nuanced calculations (Spivak et al. 2017) informed by temperature dependence of respiration and production (Yvon-Durocher et al. 2012) and light-dependent parameterizations of photosynthesis (Winslow et al. 2016). To the degree this assumption is incorrect, \( \text{GOP}_{O_2} \) and GOP derived from the triple oxygen isotopes (\( \text{GOP}_{TOI} \)) would diverge in a manner which provides additional information about environmental drivers of respiration.

**Triple Oxygen Isotope Method**

Ratios of the three stable oxygen isotope ratios (\( ^{18}O/^ {17}O/^ {16}O \)) can be used to define the TOI tracer \( 17\Delta \) (defined after Angert et al. 2003):

\[ 17\Delta = [\ln(^{17}X) - \ln(^{18}X)] \times 10^6 \text{ per meg} \]  

(2)

\( ^{1}X \) relates the isotopic ratio of dissolved oxygen (\( ^{1} \) denotes the heavier isotope) to that in the atmospheric air standard, e.g., \( ^{1}X = (^{18}O/^ {16}O)_{\text{sample}} / (^{18}O/^ {16}O)_{\text{air}} \). Per meg notation is used to denote part per million level variation in gas ratios (Keeling et al. 1998). \( \lambda \) is the ratio of the mass-dependent isotope enrichment factors for \( ^{17}O/^ {16}O \) and \( ^{18}O/^ {16}O \). \( \lambda \) is constant within uncertainties for mitochondrial respiration (and photorespiration via RuBisCo) in the photosynthesizers cultured and measured to date (\( \lambda = 0.518 \); Helman et al. 2005; Luz and Barkan 2005; Eisenstadt et al. 2010); thus, \( 17\Delta \) is defined to be respiration independent with \( \lambda \). We use this conventional value to represent the pond community, however, recent work suggests that a higher value (\( \lambda = 0.522 \)) is better supported by theory and recent dark respiration experiments in a freshwater reservoir (Ash et al. 2020); substituting this higher value results in qualitatively similar results in this work and does not alter our conclusions (ESM S1).

Photosynthetic O₂ has a high value of \( 17\Delta \) similar to the isotopic composition of the water from which it is derived (Luz and Barkan 2000), while atmospheric oxygen has low \( 17\Delta \) resulting from mass-independent fractionation of ozone in the stratosphere (Thiemens 2001). Therefore, greater values of \( 17\Delta \) in dissolved O₂ indicate increased photosynthetic production relative to gas exchange with the atmosphere.

Gross primary production-independent of normal, mitochondrial respiration can then be calculated from an isotopic mass balance of dissolved oxygen (Kaiser 2011; Prokopenko et al. 2011). We provide full derivations and equations for the triple oxygen isotopic mass balance in ESM S2, including mixing and bubble processes not quantified in this work. The resulting abbreviated isotopic mass balance in terms of the measured isotopic ratios and \( 17\Delta \):

\[ \text{NEM} = \text{GOP}_{O_2} - R \]
\[
\frac{\partial[O_2]}{\partial t} = \frac{\alpha}{\alpha_p} (17\Delta) \quad \text{Change in tracer with time}
\]

\[
= \text{Gross oxygen production} + k_2 \text{O}_2 \text{O}_2 - k_2 \text{O}_2 \text{O}_2 \quad \text{Air–water gas exchange}
\]

\[
- \frac{\partial}{\partial t} \left( \frac{17\Delta}{\lambda} \right) \quad \text{Light–dependent process}
\]

\[X_w \text{ and } X_c \text{ refer to the isotopic endmembers for air (1 when air is the reference) and water (calculated as a mixture of seawater and meteoric water; Manning et al. 2017). } X \text{ without a subscript refers to the measured ratios of dissolved } O_2. \alpha \text{ represents the isotopic fractionation factors associated with production (} \alpha_p, \text{ kinetic; Eisenstadt et al. 2010; Luz and Bakan} 2011), \text{ air–water gas exchange (} \alpha_e, \text{ equilibrium; Benson and Krause Jr. 1980, 1984; Reuer et al. 2007; } \alpha_k, \text{ kinetic; Li et al. 2019), and the light-dependent process of interest (} \alpha_{pd}, \text{ kinetic; Helman et al. 2005)—Eq. 3d assumes that the light-dependent process removes } O_2 \text{ isotopically similar to that in the surrounding water rather than directly consuming } O_2 \text{ from photosystem II (Kana } 1990; \text{ Bender et al. } 1999). \text{ Constants are chosen or calculated based on the preceding references (and summarized in ESM S2); however, other choices may be appropriate for alternative definitions of } 17\Delta \text{ (Kaiser } 2011; \text{ Nicholson } 2011; \text{ Kaiser and Abe } 2012). \text{ The rate of bulk } O_2 \text{ change is explicitly included in the derivation of Eqs. } 3a–3d \text{ (Kaiser } 2011; \text{ Prokopenko et al. } 2011). \text{ ESM S2 includes an example calculation. The MATLAB toolbox “calcGOP” also may be used to calculate resulting GOP\textsubscript{TOI} using Eqs. } 3a–3c \text{ (with the simplifying assumptions that } \alpha_k = 1 \text{ and } \alpha_p \text{ is the average value for marine phytoplankton; Manning and Howard } 2017). \]

### Light-Dependent Oxygen Uptake Processes

Light-dependent O\textsubscript{2} consumption is variously attributed to five major processes: photoreduction (Falkowski and Raven 1997), photosynthesis (Buapet et al. 2013), light stimulation of mitochondrial (“dark”) respiration of autotrophs (Grande et al. 1989), indirect stimulation of heterotroph respiration via release of labile dissolved organic carbon by photosynthesizers (Laws et al. 2000; Pringault et al. 2009), and, in benthic environments, oxidation of reduced compounds stored in sediments (Fenchel and Glud 2000). Each of these processes is expected to lead to larger GOP\textsubscript{TOI} than GOP\textsubscript{O2}. Photoreduction can cause higher GOP\textsubscript{TOI} but does not affect GOP\textsubscript{O2}, while the other processes all decrease GOP\textsubscript{O2} but are not expected to significantly affect GOP\textsubscript{TOI}. These effects are summarized in Table 1 and described further in ESM S1.

### Data Collection and Analysis

#### Setting

The study site was a salt marsh pond, located at the Plum Island Ecosystems Long-Term Ecological Research site in Massachusetts, USA (42.7411° N, 70.8309° W). The pond was approximately 7000 m\textsuperscript{2} in area with a 25 cm mean depth. The pond was situated in the high marsh, which is predominantly vegetated by Spartina patens, and proximal to a tidal creek. The pond flooded with water from the surrounding tidal creek during the highest spring tides, roughly once daily over a few successive days every two weeks. Ecosystem metabolism and environmental heterogeneity (Spivak et al. 2017, 2018), diel cycling of microbial processes (Keams et al. 2017), and air–water gas exchange and ebullition (Howard et al. 2018) have been previously examined in this pond.

#### Sampling Methods

Temperature, electrical conductivity (and resulting salinity), and O\textsubscript{2} saturation data were collected at 15 min frequency from May 7 to 28 October 2014. Sensor data were recorded at a single location over sediment without macrophytes, far from the pond banks (Fig. 1). Sensors were deployed approximately 10 cm above the sediment–water interface. The sensors were cleaned and calibrated (pre- and post-deployment) approximately every 2 weeks. Calibrations included 1-point O\textsubscript{2} calibration to water-saturated air (with initial zero-O\textsubscript{2} calibration in May 2014), and 2-point conductivity calibrations (1×10\textsuperscript{4} and 5×10\textsuperscript{4} μS cm\textsuperscript{−1} YSI standards). Additional details of sensor deployment, cross-calibration, and post hoc correction of salinity are in the supporting information (ESM S2)—no sensor drift or offsets between different sensor deployments were observed for temperature and O\textsubscript{2}.

Photosynthetically active radiation flux (PAR, 400–700 nm wavelengths) and meteorological data used to calculate air–water gas exchange were collected at a meteorological tower 200 m northeast from the study site (Forbrich and Giblin 2015). Air–water gas exchange was calculated from meteorological data as described in Howard et al. (2018) using the wind speed based parameterization of Vachon and Prairie (2013). In situ and air–water equilibrium concentrations of O\textsubscript{2}, [O\textsubscript{2}], and [O\textsubscript{2}]\textsubscript{eq} (Garcia and Gordon 1992, 1993) were smoothed using a 30 min (n = 3) moving mean to limit instrument signal noise.

Samples for TOI analysis were collected approximately weekly, during 20 daytime periods when the pond was tidally isolated from the adjacent tidal creek. Pond water was collected in pre-poisoned, 500 mL evacuated glass flasks, which were filled with roughly 300 mL of water while submerged at 10 cm depth. Care was taken to exclude bubbles and debris, and samples were collected 2 m from the pond edge using an...
inner-tube to avoid suspending sediments during sampling. Samples were collected over bare sediments at three or more timepoints between 10:00 and 14:00, with a few days including early morning and evening periods. Additionally, concurrent time series over macroalgae (Ulva intestinalis) or rooted vascular plants (Ruppia maritima) were collected on several days. In order to evaluate replicate uncertainty in the TOI samples, two to five replicate samples were collected at 19 different times over the course of the study.

Additional O₂ saturation state, temperature, and salinity data were collected simultaneously with each TOI bottle sample using a handheld YSI Pro-ODO sensor (accuracy and precision 0.1 ± 0.2 °C and 2 ± 0.2 % of oxygen saturation) and handheld refractometer (2± on PSS-78). Both instruments were calibrated daily. Along the western edge of the pond where most daily time series were conducted, these measurements were similar to conditions at the sensor location. However, conditions were more varied around the pond perimeter, particularly on the eastern side of the pond where submerged grasses and macroalgae were more abundant. O₂ saturation state and temperature were surveyed in the morning and midday on May 29th, July 17th, July 23rd; August 7th, September 23rd, and October 13th.

Total sediment cover of submerged Ruppia and Ulva was visually estimated over 11 weeks between June 25th and August 13th, as well as between 11th and November 25th (Spivak et al. 2017). On each occasion, macrophyte cover was assessed from three 1 m² quadrats randomly sampled along each of two crossing transects (different transects for each sample period) for a total of six sample locations. All percent cover data were pooled to map the average conditions over the sampling season and binned and averaged over a 5×5 m grid. To fill missing data, we used an image interpolation and extrapolation approach (MATLAB function “inpaint_nans,” method 4; D’Errico 2012). This method generates equivalent results to linear interpolation, but behaves conservatively during spatial extrapolation to fill missing data
within the limits of (no higher than) adjacent sampled data (ESM S1).

Triple Oxygen Isotope Analysis

Water and gas headspace in the TOI samples were equilibrated at room temperature, and the headspace was processed on an automated cryogenic line which collected O2 and Argon (Ar) while separating and discarding water vapor and dinitrogen gas (Stanley and Howard 2013). Oxygen isotope ratios were measured on a Thermo Scientific MAT 253 iso ratio mass spectrometer. Every sample was compared to a gas secondary standard with similar O2/Ar to seawater (Scott Specialty Gases); sample and standard voltages were balanced, resulting in similar pressure within the mass spectrometer. Samples were additionally referenced to both a gas primary standard (atmospheric air from Woods Hole, MA, USA) and air-equilibrated de-ionized water (blank solutions with no biological signature), which were run every nine samples. Samples were corrected for ion source interactions with Ar (Abe and Yoshida 2003) when O2/Ar ratios were sufficiently high that Ar matrix corrections were less than roughly 10% of the magnitude of measured isotope ratios, which was generally true at >70% of O2 saturation. At lower O2/Ar ratios (e.g., early morning samples), Ar and any trace methane was additionally stripped from the gas sample prior to measurement (ESM S1). Using either method, the oxygen isotope ratios were additionally corrected for sample size (Stanley et al. 2010) and small differences between 17\Delta calculated from calibrated 18O/16O and 17O/16O versus those on 17\Delta directly (Howard 2017) in order to determine precise isotope ratios over the entire range of O2 concentrations in the pond. Each calibration was well described as a linear function of isotopic composition (a few percent relative error in the slopes). There was no indication that pressure baseline errors were important sources of uncertainty following calibrations, in either the O2/Ar or pure O2 samples (ESM S1).

Water standards run concurrently with our samples were precise to $3 \times 10^{-2}$ per mil in $^{17}$O/$^{16}$O, $5 \times 10^{-2}$ per mil in $^{18}$O/$^{16}$O, and 6 per meg in $^{17}$\Delta (6×10^{-3} per mil; standard deviations for $n = 51$ water standards). Sample replicate precision was $7 \times 10^{-2}$ per mil in $^{17}$O/$^{16}$O, $13 \times 10^{-2}$ per mil in $^{18}$O/$^{16}$O, and 5 per meg in $^{17}$\Delta (4% relative error in all three measures). Water standards were not significantly different using either the high or low O2/Ar ratio methods ($p > 0.9$ for Welch’s $t$-test with null hypothesis of different population means for all isotopic variables).

Ecosystem Metabolism Rate Calculations

Equations 1 and 3 were discretized and rearranged to determine particular rates of interest. Changes over the period spanning two sampled times were calculated using midpoint values of the continuous variables (e.g., concentrations, air-water gas transfer velocity, isotopic ratios). For direct comparison of hourly GOP$_{TOI}$ and GOP$_{O2}$, GOP$_{O2}$ was averaged over a 90 min window centered on the time of GOP$_{TOI}$, similar to the TOI sampling frequency.

In order to compare full day rates of GOP$_{TOI}$ and GOP$_{O2}$, integrated GOP$_{TOI}$ during the midday observational period was multiplied by the ratio of the integrated dawn-dusk PAR over the integrated PAR during the TOI sampling period. We took this simple scaling approach because a single photosynthesis-irradiance (P-I) curve could not fit all the GOP results over the six month time series, and there were generally insufficient data to fit daily P-I curves. However, unsampled periods were generally at low PAR, where GOP and PAR should have been linearly related. Indeed, even without excluding samples from periods likely beyond the saturating irradiance, integrated GOP$_{TOI}$ and PAR over each hour-scale measurement period were significantly linearly correlated ($r = 0.53, p = 3 \times 10^{-7}$ for a null hypothesis of no correlation, 35% uncertainty in correlation slope). Further, the unsampled morning and evening periods generally contributed less than a quarter of integrated PAR. Thus the theoretical errors associated with this approach ($\leq 20\%$, relative standard deviation) were of similar size to other uncertainties. For the three daily time series in which TOI was sampled in mornings and evenings, daily GOP$_{TOI}$ agreed well with the PAR-scaled daily GOP$_{TOI}$ derived from the 10:00–14:00 samples—the ratio of measured to scaled GOP$_{TOI}$ was 1.0(0.1; standard deviation; no bias between rates).

Both hourly and daily average rates are reported in terms of areal production per hour, for comparability of the magnitude and variability of rates over different time scales.

Statistics

In order to examine environmental variability, the effect of the variability of O2 changes was calculated by taking the standard deviation of all measured rates of change at each sample location over the study and dividing by the average of standard deviations at all sample locations. This normalized effect size highlights where in the pond temporal variability in oxygen changes is highest or lowest—e.g., an effect size of 2 means that on average, O2 saturation state at a location increased twice as much as the mean across the pond.

GOP, $R$, and NEM errors were propagated from each input variable’s standard probability distribution via a Monte Carlo simulation with 10,000 iterations, with the standard deviation across all iterations reported as the rates’ uncertainties. Shared sources of systematic uncertainty between both TOI and dissolved O2-derived metabolic rates were not included in uncertainty estimates (e.g., uncertainties in the parameterizations of the gas transfer velocity and O2 solubility), but random errors expected to vary between sample locations and times were included (e.g., short-term variability in wind, instrumental precision of measured O2 saturation state, and changes in solubility driven by temperature heterogeneity within the pond).
Uncertainties for subsequent comparisons of metabolic rates were calculated in quadrature.

In order to determine whether short, daily to weekly changes of environmental parameters in time contributed to changes in daily GOP\textsubscript{O2} and \( R \), the time series of each environmental property considered (temperature, PAR, windspeed, wind direction, and tidal flooding) were detrended to remove autocorrelation (prewhitened) using an Autoregressive Integrated Moving Average (ARIMA) procedure with the “arima.m” function in MATLAB. Differencing, autoregressive (lag), and moving average (smoothing) terms were assigned based on analysis of the autocorrelation and partial autocorrelation functions of the variables of interest, with the goal of reducing the residuals of the observations versus the ARIMA model to white noise. An additional periodic term was used in the tidal stage ARIMA. The cross-correlation coefficients (\( r \)) between the residuals of the environmental variable and metabolic rates relative to the ARIMA model for that environmental variable were then calculated.

Correlations of GOP\textsubscript{TOI} with environmental variables were calculated based on only the subset of data from days when GOP\textsubscript{TOI} was sampled. Data were not prewhitened for any variables in this reduced subset because of the small number of samples and discontinuous time series—autocorrelations and partial-autocorrelations were already near zero and not reduced by an ARIMA procedure.

Throughout, \( p \) values are presented for the following statistical tests, unless otherwise specified: Significance of linear correlations are evaluated for the null hypotheses of no correlation or a regression differing in sign (a one-tailed distribution), using Fisher’s z-transformation on the linear correlation coefficients, \( r \); and evaluating resulting tails of the normal cumulative distribution functions. Alternatively, significance of bias (mean rate difference of one method relative to the other) is evaluated with the null hypothesis of zero difference using a paired sample Student’s t-test. Standard deviations or relative standard deviations are noted in parentheses following mean values (e.g., mean (standard deviation)). Linear correlations use Model II regressions, in which root mean square errors are calculated normal to the regression slope (neither variable is assumed to be independent and error free); \( r \) are reported for the linearity of regressions, and, where data is normally distributed, \( r^2 \) is used to calculate the fraction of total variance shared by regressed variables.

Results

Metabolic Rate Comparison

On hourly time scales, GOP\textsubscript{O2} and GOP\textsubscript{TOI} (Fig. 2a–c) were significantly correlated (\( r = 0.45, p = 1 \times 10^{-5} \)). Both GOP rates generally peaked concurrently with daily PAR (Fig. S1 in ESM S1). However, the magnitude of hourly GOP\textsubscript{TOI} tracked hourly fluctuations in PAR more closely than GOP\textsubscript{O2} did (Fig. 2a–c). This resulted in greater divergence between methods (GOP\textsubscript{TOI}-GOP\textsubscript{O2}) with larger changes in PAR within a day (\( r = 0.24, p = 4 \times 10^{-2} \); correlation of \( z \) scores standardized by day). In part because of this differing sensitivity, the two GOP rates exhibited coarse agreement overall (Fig. 3a; limits of agreement—95% confidence intervals surrounding the mean rate difference—were 15 mmol O\textsubscript{2} m\textsuperscript{-2} h\textsuperscript{-1}, similar to peak midday rates), and GOP\textsubscript{TOI} was on average slightly greater than GOP\textsubscript{O2} (GOP\textsubscript{TOI}-GOP\textsubscript{O2} = 1.6 mmol O\textsubscript{2} m\textsuperscript{-2} h\textsuperscript{-1}, \( p = 0.05 \)). This mean difference (bias) was not significant when normalized to the magnitude of production (Fig. 3b; [GOP\textsubscript{TOI}-GOP\textsubscript{O2}] / mean [GOP\textsubscript{TOI}, GOP\textsubscript{O2}] = 0.1, \( p = 3 \times 10^{-1} \)). Despite the lack of major biases in the mean, the rate differences were correlated to the magnitude of GOP in both absolute (\( r = 0.35, p = 1 \times 10^{-3} \)) and relative terms (\( r = 0.23, p = 4 \times 10^{-2} \)).

Hourly NEM was autotrophic at midday, but heterotrophic in the morning and evening. Overnight \( R \) was relatively constant, despite hourly variability and of similar magnitude to daytime GOP.

Daily rates of GOP\textsubscript{O2} and GOP\textsubscript{TOI} (scaled to PAR, “Ecosystem metabolism rate calculations” section; Fig. 2d) were similarly significantly correlated (\( r = 0.56, p = 1 \times 10^{-2} \)) and in broad agreement (Fig. 3c, d; limits of agreement were 6 mmol O\textsubscript{2} m\textsuperscript{-2} h\textsuperscript{-1}). There was no significant bias between rates (absolute difference 0.2 mmol O\textsubscript{2} m\textsuperscript{-2} h\textsuperscript{-1}, \( p = 8 \times 10^{-1} \); relative difference 0.0, \( p = 7 \times 10^{-3} \)) or rate divergence as a function of production (correlation of absolute rate difference to mean GOP: \( r = 0.38, p = 1 \times 10^{-1} \); correlation of relative difference: \( r = 0.41, p = 8 \times 10^{-2} \)). Both GOP\textsubscript{TOI} and GOP\textsubscript{O2} followed similar seasonal patterns, with generally increasing rates in May through August and lower rates in mid-September through October.

Daily respiration rates similarly decreased from summer into fall, while daily NEM was relatively constant and heterotrophic over the time series. Large, synchronous decreases in GOP\textsubscript{O2}, NEM, and \( R \) lasting several days were associated with periods of spring tide flooding of the pond. It is unclear whether these rate decreases reflect homogenization of metabolic tracers across the marsh environment during periods of tidal interconnectivity or limitations of the mass balance in the presence of potential lateral fluxes; in either case, GOP\textsubscript{TOI} was not evaluated during periods of tidal flooding.

Spatial Environmental Heterogeneity

Temperature, O\textsubscript{2} saturation state, the TOI ratios (\(^{17}\Delta\)), and GOP\textsubscript{TOI} varied across the pond (Table S1 in ESM S3), particularly along the eastern edge where plant and macroalgal abundance was high. The southernmost portion of the pond also had macroalgal cover (e.g., sample location 4, Fig. 1) but was omitted from weekly surveys to minimize interference with concurrent experiments. The spatial surveys on May 29
were broadly representative of variability observed across the time series (Fig. 4): In the morning, temperature, O₂ saturation state, and $^{17}\Delta$ were similar around the pond. However, by midday the areas with more vegetation were generally warmer and had higher O₂ saturation state and $^{17}\Delta$. The same areas had greater and more variable rates of dissolved O₂ increases across the time series (Fig. 5; Table S2 in ESM S3). Compared to unvegetated areas, these observations were consistent with increased accumulation of photosynthetic O₂ relative to gas exchange with the atmosphere (Fig. 4), but not necessarily higher production rates (Fig. 2d). While wind speed was generally low, wind direction changed throughout the day, which may have led to temporal and spatial differences in wind-driven gas transfer and water transport that modified the effect of vegetation. In contrast to lateral variability, no vertical gradients in water column properties were detected.

**Daily to Seasonal Environmental Variability**

Oxygen production covaried with PAR, temperature, tidal stage, and winds over the seasonal time series. In particular, GOP and $R$ tracked both short- and long-term variations in PAR and were suppressed by biweekly periods of spring-tide flooding (Fig. S2 in ESM S1) and potential connectivity to the broader marsh (Spivak et al. 2017). The response of GOP, NEM, and $R$ to daily to weekly scale environmental variability was evaluated using an ARIMA procedure (Table S3 in ESM S3; the following summary notes significant correlations, $p < 0.05$). GOP$_{O2}$ and $R$ were significantly, positively correlated with PAR, and negatively correlated with windspeed and recent tidal flooding. GOP$_{O2}$ was also significantly correlated with wind direction; onshore, westerly winds were associated with greater GOP$_{O2}$. Onshore winds tend to correspond to fewer clouds and thus higher PAR ($r = 0.31$ for correlation between wind direction and PAR, $p = 4 \times 10^{-5}$). Neither $R$ nor GOP$_{O2}$ was correlated with daily to weekly variability in temperature. Correlations with PAR, winds, and flooding only accounted for 27% of the variance in $R$ and 51% of the variance in GOP$_{O2}$.

In contrast to GOP$_{O2}$, GOP$_{TOI}$ was not generally correlated with daily to weekly variability in PAR, despite tracking PAR closely at hourly scales, nor was it correlated with the other environmental variables. GOP$_{O2}$ was calculated from $R$ and thus these rates were highly cross-correlated ($r = 0.79$, $p = 3 \times 10^{-26}$), but independently measured GOP$_{TOI}$ was also significantly correlated with $R$ ($r = 0.63$, $p = 6 \times 10^{-3}$). These cross-correlations between GOP and $R$ accounted for a greater share of the total variance than accounted for by the measured environmental variables. Thus as yet untested factors may underpin the daily to weekly variability in rates from each
method—ebullition is one likely driver of differences between the two methods over daily time scales (Howard et al. 2018). However, an important caveat is that daily GOP TOI rates were evaluated over only 10% of the overall time series (17 of 174 days), limiting our statistical power.

Discussion

Convergent Rates of Daily to Seasonal GOP

Mean daily rates of GOP TOI and GOP O2 broadly agreed over the time series, with similar seasonal trends (Fig. 2d) and no significant bias (Fig. 3c). The mean ratio of GOP TOI/GOP O2 = 1.0(0.4). This is similar to the mean and range of ratios calculated in pelagic ocean Lagrangian experiments (Hamme et al. 2012) and estuarine benthic chambers (Stanley and Howard 2013). This agreement implies that even in a setting expected to favor light-dependent O2 uptake, the contributions of such processes at daily to seasonal time scales are not large compared to the relative methodological uncertainties (on average, 10% of GOP).

There were exceptions to this broad agreement. Eight of the daily GOP TOI rates (Fig. 2d) differed from GOP O2 by a larger degree than could be explained by methodological uncertainties (> 2 standard deviations). However, these differences were not consistent with a major role for light-dependent O2 uptake; larger GOP differences were not systematically distributed over the time series with respect to seasonal trends or daily changes in PAR. Instead, environmental heterogeneity associated with vegetation likely contributed to periods with larger than expected rate differences between GOP TOI at the sample locations and GOP O2 at the sensor location.

Temperature and O2 varied by tens of percent around the pond margins, suggesting that this setting was not always well-mixed despite the lack of vertical gradients. Submerged aquatic vegetation reduces turbulence and increases mixing time scales (Koch and Gust 1999; Romano et al. 2003; Nepf and Ghisalberti 2008). In addition, U. intestinalis mats likely limited air-water gas exchange (e.g., Wollenberg and Peters 2009; Attermeyer et al. 2016) and enhanced accumulation of photosynthetic oxygen compared to unvegetated areas. Vegetation likely also contributed to variability in important O2 sinks in this pond such as ebullition from photosynthetic surfaces (Howard et al. 2018) and the sedimentary uptake dominating the net metabolism of the pond (e.g., sulfide oxidation; Spivak et al. 2018). Thus we infer that the heterogeneity in vegetation cover, and resulting biological and
physical impacts on O$_2$ dynamics, contributed to variability in production rates around the pond. In larger lakes, spatial heterogeneity in temperature and oxygen can lead to highly variable estimates of gross productivity and respiration (Van de Bogert et al. 2012), and submerged aquatic vegetation strongly influences these environmental drivers (Vilas et al. 2015).
2017). This is also consistent with the important role of vegetation cover in explaining variability in metabolism rates between salt marsh ponds (Spivak et al. 2017).

Light-Dependent Effects on Rates of Hourly GOP

In contrast to the daily rates, there were systematic discrepancies in hourly rates of GOP_TOI and GOP_O2 during midday periods which could reflect light-dependent processes. There was a small but significant bias between GOP_TOI and GOP_O2 (Figs. 2a–c and 3a). This resulted in a ratio of hourly GOP_TOI/ GOP_O2 equal to 1.4 (1.7). The variability in this ratio was increased compared to daily rates in part because of the large relative uncertainty associated with near-zero dawn and dusk GOP rates; the ratio derived from only the highest production rate on each day was 1.5 (0.6). This poorer agreement during periods of peak production and PAR is likely due to light-dependent O2 uptake. The greater GOP_TOI relative to GOP_O2 was consistent with the expected effects of plausible light-dependent processes (Table 1), and within the range of the 23–62% difference expected if light-dependent O2 uptake were two to ten times greater than in the dark (e.g., Bender et al. 1987; Epping and Jørgensen 1996; Pringault et al. 2009). This ratio was greater than could be explained by the expected uncertainties in the difference between hourly rates (on average, 16% of GOP).

Daytime oxidation of reduced compounds produced overnight in the sediments (Fenchel and Glud 2000) is likely in shallow pond sediments, but would be expected to cause GOP rates to diverge most in the morning. Photorespiration would cause GOP rates to diverge most in the afternoon when the ratio of O2 to carbon dioxide is highest in this pond (Howard 2017) and nearby shallower pools (Koop-Jakobsen and Gutbrod 2019). Instead, the GOP_TOI-GOP_O2 difference is greatest at peak production and PAR. Light-stimulation of mitochondrial respiration can cause GOP_O2 to underestimate productivity, and contributes to both autotrophic and heterotrophic carbon metabolism at ecosystem scales (Grande et al. 1989; Pringault et al. 2009). In contrast, photoreduction, or the Mehler reaction, is largely decoupled from carbon metabolism (Williams and del Giorgio 2005), and may primarily serve to remove excess electrons at the cellular level (Raven and Beardall 2005). Photoreduction reduces O2 to water at photosystem I (PSI), and can be a major oxygen uptake flux for autotrophs in the light, consuming the equivalent of 10–75% of photosystem II (PSII) O2 output (Milligan et al. 2007; Halsey et al. 2010; Roberty et al. 2014) and causing GOP_TOI to overestimate productivity. Both processes could lead to the observed midday divergence between GOP_TOI and GOP_O2 (ESM S1).

However, as with the daily GOP rates, environmental heterogeneity at hourly scales may play a large role in this setting, and the limited spatial resolution across the pond makes it difficult to confirm that the observed differences at short time scales are mainly due to light-dependent processes. Ebullition in particular, where active, may lead to divergent GOP_O2 and GOP_TOI in the midday and afternoon when most bubbles escape (Howard et al. 2018).

Daytime Production and Net Ecosystem Metabolism

The pond in this study was shallow and heterotrophic on daily to seasonal time scales, but autotrophic during the daytime. This metabolic dynamism may contribute to our seemingly contradictory findings of a potential role of light-dependent O2 uptake over short periods during autotrophic daytime periods, but no effect over daily to seasonal periods; large, light-insensitive respiration rates could mask smaller light-dependent fluxes when integrated over longer time periods. Midday (~ 3 h) chamber experiments found lower rates of respiration and a more autotrophic balance of production and respiration in surface waters than in chambers overlying sediments (Howard 2017). GOP_TOI and GOP_O2 agreed in chambers over microalgae and macroalgae covered sediments, and the metabolism of suspended microalgae was minor compared to sedimentary fluxes. Thus, potential light-
Dependent differences may arise from portions of the pond with *R. maritima*.

Prior work in this and other salt marsh ponds showed that organic-rich sediments support high rates of ecosystem respiration (Spivak et al. 2017), through both aerobic and anaerobic pathways including microbial sulfur cycling (Wilbanks et al. 2014; Rao et al. 2016; Spivak et al. 2018). Thus, reduced compounds in pond sediments have the potential to consume much of the O2 produced during daytime periods of water column autotrophy. This point is illustrated by comparing ratios of NEM/GOP (Fig. 6); during daylight periods ratios were ~ 0 (using GOP from either method), indicating that as much O2 was consumed as was produced. Over 24 h, nighttime O2 uptake pushed the system to net heterotrophy (NEM/GOP ~ −0.4, i.e., respiration exceeded production by 40%).

The net result that NEM varied little over the six month study period (Fig. 2d) is underlain by a steady background of sedimentary O2 uptake. Concurrent assessments of microbial activity in this pond also point to more stable sediment conditions compared to the overlying water column; microbial activity in the water column was strongly associated with diel changes in environmental conditions, but microbial communities in surficial sediments were insensitive to changes in overlying temperature and O2 (Kearns et al. 2017).

Conclusions

The TOI method was expected to highlight light-dependent processes that could affect GOP estimates from dissolved O2 mass balances. On daily to seasonal time scales, we found good overall agreement between daily to seasonal rates GOPTOI and GOMP2, despite a number of environmental factors expected to cause light-dependent O2 uptake. This agreement may reflect the strong heterotrophy and dominance of sedimentary respiration in this shallow pond, which consumed more O2 than photosynthetically produced.

Hourly GOP rates within individual days did exhibit discrepancies between the methods that were consistent with light-dependent processes. Given the ambiguous importance of light-dependent O2 uptake in this setting, we could not disentangle the potential light-dependent processes affecting our results. However, photoreduction and light-stimulated mitochondrial respiration are likely processes in this setting that are consistent with the observed O2 dynamics.

Ultimately, the importance of daily to seasonal agreement (or hourly disagreement) between the TOI and dissolved O2 mass balance methods depends upon the research question. The hourly time series in this study point to isotopic method having sufficient resolution to study light-dependent O2 uptake processes in a common O2 currency with a dissolved mass balance. In a setting with smaller respiratory fluxes these differences would be proportionally larger, which could contribute to the high ratios of light versus dark respiration reported for other environments (e.g., Bender et al. 1987). However, the typical use of dissolved O2 mass balances is to study ecosystem metabolism fluxes over daily to yearly time scales. In this salt marsh pond, the daily production rates derived from the TOI method agreed with those from the dissolved O2 mass balance. Our results support the typical assumption that daytime and nighttime rates of O2 consumption rates are similar, at least in environments where light-independent sediment respiration dominates ecosystem metabolism. Thus we view the TOI method, with additional analytical requirements, as being best suited for targeted process studies rather than routine monitoring in aquatic environments in which dissolved O2 sensors can be readily deployed and maintained. For pelagic locations where instrumentation is not practical (e.g., infrequently occupied hydrographic stations), this work suggests that the TOI method can provide a good alternative for evaluating in situ oxygen production.
The heterogeneity of production over small spatial scales around this small pond is an important additional finding. This contributes to the growing understanding that even very shallow aquatic environments may not be well-mixed (e.g., Holgerson et al. 2016), which can complicate interpretation of biogeochemical tracers and drive substantial spatial heterogeneity in metabolic rates (Van de Bogert et al. 2012).

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