

Evaluation and correction of noise related to physical processes in estimates of estuary metabolism

Marcus W. Beck¹, Michael C. Murrell², James D. Hagy III², Jane M. Caffrey³

¹*ORISE Research Participation Program*

*USEPA National Health and Environmental Effects Research Laboratory
Gulf Ecology Division, 1 Sabine Island Drive, Gulf Breeze, FL 32561
Phone: 850-934-2480, Fax: 850-934-2401, Email: beck.marcus@epa.gov*

²*USEPA National Health and Environmental Effects Research Laboratory
Gulf Ecology Division, 1 Sabine Island Drive, Gulf Breeze, FL 32561*

Phone: 850-934-2433, Fax: 850-934-2401, Email: murrell.michael@epa.gov

³*USEPA National Health and Environmental Effects Research Laboratory
Gulf Ecology Division, 1 Sabine Island Drive, Gulf Breeze, FL 32561*

Phone: 850-934-2455, Fax: 850-934-2401, Email: hagy.jim@epa.gov

⁴*University of West Florida*

*Center for Diagnostics and Bioremediation, 11000 University Parkway, Pensacola, FL 32514
Phone: 850-857-6089, Fax: 850-474-3130, Email: jcaffrey@uwf.edu*

Running head: Noise in Estuary Metabolism

Acknowledgments

Abstract

Reliable estimates of ecosystem metabolism depend on measures of dissolved oxygen (DO) flux that are dominated by biological processes. Long-term time series of DO measurements may include variation related to both biological and physical processes such that the use of observed data may be insufficient in many examples. Statistical modelling techniques that quantify variation in DO over time and tidal changes have the potential to isolate biological signals in DO variation to more accurately estimate metabolism. We used a simulation approach to create an observed DO time series as the summation of diel variation. A weighted regression method that estimates DO as a function of time and tidal height was used to normalize, or detide, the predicted DO signal. Comparisons of detided estimates with the known, simulated biological DO signal suggested the method accurately and precisely removed variation attributed to tidal advection. Extension of the method to four case studies provided a proof of concept illustrating the method could be useful for *in situ* data. We provide a detailed discussion on use of the method for improving certainty in evaluation of DO measurements from sites with strong tidal influences. Moreover, we propose that the method will greatly expand use of the open-water method for estimating ecosystem metabolism given that the approach can provide robust estimates of DO values that are independent of tidal advection. This could facilitate the use of shorter deployment periods for water quality monitors or incomplete time series given that known biases related to water movement could be removed with weighted regression.

{acro:DO}

Key words:

Introduction

{intro}

Ecosystem metabolism is broadly defined as the difference between primary production and aerobic respiration and provides a basis for evaluating trophic state (Kemp and Testa 2012, Needoba et al. 2012). Primary producers, such as phytoplankton, establish the means of energy transfer to upper trophic levels. Productive systems are characterized by more efficient transfer of organic matter between trophic levels, whereas less productive systems are sinks of organic matter that are supported by allochthonous sources of energy input. The balance between production and respiration is an integrated measure of metabolism that accounts for varying rates in processes that create and consume organic matter. Although metabolic rates vary naturally in different regions (Caffrey 2004), human activities and infrastructure development are contributing factors that increase rates of production (Diaz 2008). Inputs of limiting nutrients beyond background concentrations may decrease the resilience of an ecosystem such that higher rates of production are coupled with higher biological oxygen demand (Yin et al. 2004, Kemp et al. 2009). Cultural eutrophication is frequently linked to declines in water quality through lower levels of dissolved oxygen and increased frequency of noxious algal blooms. Reliable estimates of ecosystem metabolism are critical for measuring both background rates of production and potential impacts of human activities on ecosystem condition.

Ecosystem metabolism can be estimated using several techniques, each of which is appropriate under different conditions or assumptions. Bottle-based techniques rely on rate measurements from discrete water quality samples, whereas open-water techniques infer metabolic rates using *in situ* measurements from continuous monitoring data. Bottle-based techniques are useful for direct partitioning of metabolic contributions into discrete habitats, such

as planktonic production rates during specific time periods (Kemp and Testa 2012). However, such measurements may be inappropriate for evaluating whole ecosystem metabolism if significant production occurs in habitats that are not sampled, such as benthic or seagrass production. As such, the open-water technique provides an integrative measure of metabolism by inferring process rates from *in situ*, continuous monitoring data. Originally proposed for use in streams (Odum 1956), the method has been used with varying success in lakes (Staeher et al. 2010, Coloso et al. 2011, Batt and Carpenter 2012) and estuaries (Caffrey 2004, Hopkinson and Smith 2005, Caffrey et al. 2013). The ability of the open-water method to accurately estimate metabolism depends on whether the assumptions for its use are met, which are often only implicitly verified in practice.

The open-water method uses the diel fluctuation of dissolved oxygen to infer rates of ecosystem metabolism, after correcting for losses or gains through air-water exchange (Kemp and Testa 2012). Daily integrated measurements of metabolism are based on the balance between daytime estimates of gross production and nighttime estimates of respiration extrapolated to a 24 hour period. The fundamental assumption of the open-water method is that measurements come from a water mass that has the same recent history (Needoba et al. 2012). Estimates of metabolism from a single location may be inaccurate if substantial variation in water column mixing occurs throughout the period of observation. As such, the original technique designed for use in streams requires the comparison of data from an upstream and downstream station (Odum 1956). Application of the method to systems without continuous flow, such as lakes or estuaries, have often assumed that a single sampling station provides sufficient data for estimating metabolism (Staeher et al. 2010). While single stations may be valid under specific conditions, numerous studies have shown that the open-water method may be inappropriate given the effects

of physical mixing (Ziegler and Benner 1998, Caffrey 2003, Coloso et al. 2011, Batt and Carpenter 2012, Nidzieko et al. 2014).

The open-water method has recently been applied to coastal and oceanic ecosystems with mixed success. An exhaustive analysis by Caffrey (2003) applied the method to estimate metabolism at 28 continuous monitoring stations at 14 US estuaries. Data from two of the reserves were used to evaluate the assumption of homogeneity of water masses measured by each sensor. Although significant differences were not observed for metabolism estimates between adjacent stations, the analysis was based on a comparison of means using conventional significance tests rather than a systematic comparison of time series. Moreover, a portion of metabolism estimates from all stations were negative for production during the day and positive for respiration during the night. These values were opposite in sign than expected since production increases oxygen during the day (i.e., positive effect on metabolism) and respiration consumes oxygen at night (i.e., negative effect on metabolism). These ‘anomalous’ values were attributed to violations in the assumption of water-column heterogeneity. Specifically, tidal variation could have caused sampling of different water masses by individual water quality sondes as water moved inland or seaward with changing tide.

The effects of tidal advection on estimates of ecosystem metabolism have been a point of concern in numerous studies (Ziegler and Benner 1998, Caffrey 2003, Collins et al. 2013, Howarth et al. 2014), although systematic estimates of its effects and methods for accounting for physical variation in dissolved oxygen (DO) measurements have been minimal. An exception is presented by Nidzieko et al. (2014) through quantitative assessment of the effects of fortnightly tidal modulations on metabolism estimates. Using a control volume approach to measure fluxes into and out of a shallow tidal creek, significant biases in metabolism estimates were observed.

Net heterotrophy was observed during spring tides, whereas metabolism was balanced during neap tides. The timing of irradiance relative to the tidal cycle was a primary factor contributing to heterotrophy during summer months such that maximum tides occurred during the night, increasing total area for respiration. The results of the analysis, although specific to the study location, suggest that the effects of tidal advection on DO measurements are of primary concern when selecting locations and length of time for sonde deployment in estuaries. In many cases, the relative magnitude of these effects may be a significant source of bias without quantitative evaluation to determine the roles of biological and physical signals in DO measurements. Analytical techniques to evaluate and correct for tidal advection could improve certainty in metabolism estimates and also increase the use of data from shorter deployment periods if sources of bias are quantified and removed.

This article describes use of a novel method for quantifying and removing noise in estimates of ecosystem metabolism for estuaries. Specifically, we characterize the effects of tidal advection on DO observations to improve estimates of open-water metabolism with multi-year time series of high frequency ($< \text{one hour}$) water quality data. The focus of our analysis is the use of a weighted regression method previously developed for trend analysis of pollutant concentrations in streams and rivers ([Hirsch et al. 2010](#)). A weighted regression approach is applied to create dynamic predictions of DO as a function of time and tidal height change, which is then used to normalize, or detide, the DO signal. The analysis is presented in two steps. First, we apply a simulation approach to create time series of DO observations with known characteristics to evaluate ability of the weighted regression to predict the time series and remove the effects of tidal advection. Second, four case studies of multi-year time series are used to further explore use of the weighted regression approach to remove potential noise in DO signals

from tidal advection. Comparisons of observed and detided DO values are compared, in addition to estimates of open-water metabolism before and after detiding of the DO time series. Overall, the analysis provides a means to improve certainty in conclusions from observed DO for evaluating the relative roles of biological and physical processes in estuarine systems. Applications of the weighted regression approach are expected to have wide-ranging implications for management and ecosystem monitoring by outlining strategies for obtaining water quality estimates with more accuracy.

Materials and Procedures

Weighted regression for modelling and detiding DO time series

The weighted regression model for detiding DO time series was adapted from the weighted regression on time, discharge, and season (WRTDS) method developed by [Hirsch et al. \(2010\)](#). The WRTDS method was developed to model pollutant concentration in streams and normalize predictions to changes in discharge. The functional form of our model is as follows:

$$DO_{obs} = \beta_0 + \beta_1 t + \beta_2 H \quad (1) \quad \{\text{funform}\}$$

where observed DO is a linear function of decimal time t and astronomical tidal height H . Decimal time is a continuous variable for the day and time of each observation with time as a proportion of the number of total observations added to each day. The beginning of each day was considered the nearest thirty minute observation (i.e., on the hour and half hour) at which sunrise was expected for a given location and time of year. Days were centered on the diel cycle rather than conventional times given that the objective was to develop a predictive model relevant for

biological DO variation that follows solar and seasonal cycles. The functional form also differed from the original WRTDS method that included parameters to estimate variation of the response variable on a sinusoidal period. DO variation was not modeled using this approach because rates of change may be abrupt following diurnal variation in irradiance or daily DO variation may be muted given the weather, as on cloudy days.

Weighted regression is implemented as a moving window that allows for estimation of DO throughout the time series by adapting to variation through time as a function of tide. Regression models are estimated sequentially for each observation in the time series using dynamic weight vectors that change with the center of the window. Weight vectors quantify the relevance of observations to the center of the window in respect to decimal time, hour of the day, and tidal height. Specifically, weights are assigned using a tri-cube weighting function ([Hirsch et al. 2010](#)):

$$w = \begin{cases} \left(1 - (d/h)^3\right)^3 & \text{if } |d| \leq h \\ 0 & \text{if } |d| > h \end{cases} \quad (2)$$

where the weight w of each observation is inversely proportional to the distance d from the center of the window such that observations more similar to the point of reference are given higher importance in the regression. Weights exceeding the maximum width of the window h are equal to zero. The tri-cube weighting function is similar to a normal distribution such that weights decrease gradually from the center until the maximum window width is reached. Observations that are half the distance from the center of the window to the maximum window width are weighted 1/3 less than values at the center. Regressions that use simpler windows (e.g., boxcar approach) are more sensitive to influential observations as they enter or leave the window,

whereas the tri-cube function minimizes their effect through gradual weighting of observations (Hirsch et al. 2010). The weight vector for each observation is the product of three separate weight vectors for decimal time, hour, and tidal height. A low weight is given to an observation if any of the three weighting values were not similar to the center of the window since the final weight vector is the product of three weight vectors for each variable.

A nontrivial issue with weighted regression is the choice of window width for calculating weights. Excessively large or small window widths may respectively under- or over-fit the data. Additionally, optimal window widths may depend on the objective for using the model. The weighted regression approach can be used for both predicting DO and normalizing to remove the variance in the DO signal from tidal changes. Optimal window widths that minimize prediction error or fit to the observed data are typically smaller than the optimum window widths for normalizing the time series. Similarly, window widths that more effectively detide the DO signal may produce predictions for the observed data that are not optimal. Evaluations of the weighted regression method with simulated DO time series, described below, used different window widths to identify an approximate optimal window width for detiding the DO signal. As such, the ability of the models to predict observed DO was not a primary concern given that the optimal window width for detiding likely corresponds to a model that predicts DO as a function of tide rather than observed DO as a function of both tide and biological variation.

Detiding the DO signal using weighted regression

The primary objective of the analysis was to evaluate ability of the weighted regression method to detide a DO signal to obtain more accurate estimates of metabolism. Hirsch et al. (2010) developed the normalization approach for the WRTDS method using a two-dimensional

interpolation grid that contains predicted values of pollutant concentrations across the time series and the range of stream discharge values observed in the study system (Hirsch et al. 2010).

Normalized values for pollutant concentration are obtained by averaging the model predictions across the discharge values that are likely to occur on a given day to provide an estimate that is independent of flow variation.

Predicted values of DO concentration were normalized to remove variation from tidal height changes, although the approach herein differs slightly from Hirsch et al. (2010). Our approach uses weighted regression to isolate sources of variation in the observed DO signal that are related to unique effects of tidal height and biological process (Fig. 1). Two sets of values are predicted for the observed time series DO_{obs} , rather than creating an interpolation grid. The first set of values uses the tidal height of an observation and second set uses the mean tidal height across the time series, DO_{tid} and DO_{nrm} respectively. In other words, the first set of predictions represent DO as a function of time and tide, where the second set represents DO conditional on time and mean tidal height:

$$DO_{tid} = f(DO_{obs}|H, t) \quad (3) \quad \{do_tid\}$$

$$DO_{nrm} = f(DO_{obs}|\bar{H}, t) \quad (4) \quad \{do_nrm\}$$

Assessment

Simulation of DO time series

The ability of the weighted regression to detide the DO signal was evaluated first using a simulation approach. Observed DO time series were created to represent the sum of variation

from biological processes and physical effects related to tidal advection:

$$DO_{obs} = DO_{bio} + DO_{adv} \quad (5) \quad \{do_obs\}$$

Biological DO signals are inherently noisy ([Batt and Carpenter 2012](#)) and can be further described as:

$$DO_{bio} = DO_{die} + DO_{unc} \quad (6) \quad \{do_bio\}$$

$$DO_{unc} = \epsilon_{obs} + \epsilon_{proc} \quad (7) \quad \{do_unc\}$$

where the biological DO signal is the sum of diel variation on a 24 hour scale plus uncertainty or noise. Total uncertainty in the biological DO signal is described as variation from observation and process uncertainty ([Hilboron and Mangel 1997](#)). Multiple time series at 30 minute observations over 30 days were created following eqs. (5) to (7) such that observed DO is generalized as the additive combination of four time series (Fig. 2):

$$DO_{obs} = DO_{adv} + DO_{die} + \epsilon_{obs} + \epsilon_{pro} \quad (8) \quad \{do_obs_a\}$$

Time series were created by varying the relative magnitudes of each of the four components of observed DO to test the effectiveness of weighted regression under different scenarios. The effects of air-sea gas exchange were not considered in the simulation given that methods are available for *in situ* data to correct observed DO for diffusion (i.e., [Th  bault et al. 2008](#)).

Each parameter of the simulated time series was created as follows. First, biological DO time series in eq. (6) were created by adding noise or variance to a diel component (Fig. 2). The

diel component, DO_{die} , was estimated using a sine/cosine function (Cryer and Chan 2008):

$$DO_{die} = \alpha + \beta \cos(2\pi ft + \Phi) \quad (9) \quad \{\text{do_sin}\}$$

such that the mean DO α was 8, amplitude β was 1, f was 1/48 to repeat on a 24 hour period every 30 minutes, t was the time series vector and Φ was the x-axis origin set for an arbitrary sunrise at 630am. The diel signal was increasing during the day and decreasing during the night for each 24 hour period and ranged from 7 to 9 mg L⁻¹. Noise or uncertainty was added to the diel DO signal to simulate natural variation in DO throughout the time series (Fig. 2). Total uncertainty was the sum of observation and process uncertainty for $n = 1440$ (30 minutes by 30 days) observations (Hilboron and Mangel 1997), such that:

$$DO_{unc,n} = \epsilon_{obs,n} + \int_{t=1}^n \epsilon_{pro,t} \quad (10) \quad \{\text{do_unc_n}\}$$

where observation and process uncertainty (ϵ_{obs} , ϵ_{pro}) were simulated as normally distributed random variables with mean zero and standard deviation varying from zero to an upper limit, described below. To induce auto-correlation, process uncertainty was estimated as the cumulative sum of n observations where the noise at time $t + 1$ was equal to the noise at time t plus additional variation drawn from the normal distribution. The noise vector for process uncertainty was rescaled to constrain the variation within the bounds for standard deviation defined by the random variable. The total uncertainty, DO_{unc} , was added to the diel DO time series to create the biological DO time series (Fig. 2).

A tidal time series was simulated by adding sine waves (harmonics) with relevant solar

and lunar periods (Foreman and Henry 1989). Each sine wave was created using eq. (9) by varying f for periods that approximated common tidal components, e.g., 1/25 for a 12.5 hour principal lunar semi-diurnal wave. The amplitude of each tidal component was set constant to one meter. The combined tidal series was the additive time series of all sine waves, scaled to 1 meter and centered at 4 meters. The tidal time series was added to the biological DO series to simulate DO changes with advection, DO_{adv} (Fig. 2). Conceptually, this vector represents the rate of change in DO as a function of horizontal water movement from tidal advection such that:

$$\frac{\delta DO_{adv}}{\delta t} = \frac{\delta DO}{\delta x} \cdot \frac{\delta x}{\delta t} \quad (11) \quad \{\text{deltdo}\}$$

$$\frac{\delta x}{\delta t} = k \cdot \frac{\delta H}{\delta t} \quad (12) \quad \{\text{deltx}\}$$

where the first derivative of the tidal time series, as change in height over time $\delta H/\delta t$, is multiplied by a constant k , to estimate horizontal tidal excursion over time, $\delta x/\delta t$. The horizontal excursion is assumed to be associated with a horizontal DO change, $\delta DO/\delta x$, such that the product of the two estimates the DO change at each time step from advection, DO_{adv} . In practice, the simulated tidal signal was used to estimate DO_{adv} :

$$DO_{adv} \propto H \quad (13) \quad \{\text{do_adv}\}$$

$$DO_{adv} = 2 \cdot a + a \cdot \frac{H - \min H}{\max H - \min H} \quad (14) \quad \{\text{do_adv}\}$$

where a is analogous to k in eq. (12) and is chosen as the transformation parameter to standardize change in DO from tidal height change to desired units. For example, $a = 1$ will convert H to a

scale that simulates changes in DO from tidal advection that range from $\pm 1 \text{ mg L}^{-1}$. The final time series for observed DO was the sum of biological DO and advection DO (Fig. 2).

Evaluation of weighted regression with simulated DO time series

Multiple time series were simulated by varying the conditions in eqs. (5) to (14). Specifically, the simulated data varied in the relative amount of noise in the measurement, relative amplitude of the diel DO component, degree of association of the tide with the DO signal, and tidal type as diurnal, semidiurnal, and mixed semidiurnal. Three levels were evaluated for each variable: relative noise as 0, 1, and 2 standard deviations for both process and observation uncertainty, amplitude of diel biological DO as 0, 1, and 2 mg L^{-1} , and DO change from tidal advection as 0, 1, and 2 mg L^{-1} . Three tidal categories were created from eq. (9) using a period of 24.82 hours (principal lunar) for diurnal, 12.42 hours (principal lunar semidiurnal) for semidiurnal, and adding both diurnal and semidiurnal series for mixed semidiurnal. A total of 243 time series were created based on 81 unique combinations of parameters for each tidal category (Fig. 3). Three window widths for each variable used to estimate the total weight vector were evaluated (as half window widths): decimal time as 1, 3, and 8 days, time of day as 6, 12, and 24 hours, and tidal height as 0.25, 0.5, and 1 as a proportion of the observed value at the center of the window. In total, 27 window width combinations were evaluated for each of 243 simulated time series, producing results for 6561 weighted regressions.

The detided or normalized values for each regression were compared to the simulated data to evaluate the ability of weighted regression to reproduce the biological DO signals. Results were summarized using Pearson correlation coefficients and the root mean square error (RMSE) between the predicted and observed DO values and the detided and biological DO values.

{acro:RMSE}

Overall, the weighted regressions provided accurate results for the detided time series compared to the ‘true’ biological time series regardless of the simulation parameters (Table 1) or window widths (Table 2). Mean correlation for all time series and window widths between the detided and biological values was 0.56, with values ranging from -0.78 to 1.00. Mean error was 1.27, with values ranging from 0.00 to 2.47. Simulations with very poor performance (e.g., negative correlations) were those that had minimum widths for day windows and maximum widths for hour windows, or were those with the DO signal composed entirely of noise from observation uncertainty. Conversely, simulations with detided time series that were identical to the true time series (e.g., correlation of one, RMSE of zero) were those for which there was no biological or tidal influence. While the latter examples do not represent real-world scenarios, they were included in the simulations to provide verification that the weighted regressions provide reasonable results in extreme scenarios.

Characteristics of DO time series that contributed to improved model performance were increasing amplitude of the diel DO component (DO_{die}) and increasing process uncertainty (e_{pro}), whereas increasing observation uncertainty contributed to decreasing performance (Table 1). Model performance was minimally influenced by magnitude of the tidal advection component (DO_{adv}), although performance decreased slightly with increasing tidal effects. Increasing widths for day and tidal proportion windows contributed to increasing model performance, whereas the opposite was true for increasing hour windows (Table 2). Graphical summaries of model performance by simulation parameters (Fig. 4) and half window widths (Fig. 5) supports the general trends described by Tables 1 and 2. Scale differences between Fig. 4 and Fig. 5 emphasize that model performance was more affected by characteristics of the DO time series rather than the selected window widths. For example, the range of correlation values

comparing the effects of half window widths (averaged across all simulation parameters, Fig. 5) were approximately half the range of correlations for comparing the effects of simulation parameters (averaged across all half window widths, Fig. 4).

Validation of weighted regression with case studies

The National Estuarine Research Reserve System (NERRS) is a federally-funded network of 28 protected estuaries established for long-term research, water-quality monitoring, education, and coastal stewardship (Wenner et al. 2004). Continuous water quality data have been collected at NERRS sites since 1994 through the System Wide Monitoring Program (SWMP). In addition to providing a basis for trend evaluation, data from SWMP provides an ideal opportunity to evaluate long-term variation in water quality parameters attributed to both biological and physical processes. Continuous SWMP data can be used to describe DO variation at sites with different characteristics, including variation from ranges in tidal regime (Sanger et al. 2002) and rates of ecosystem production (Caffrey 2003, 2004).

Continuous DO time series and tidal height measurements at four sites from the SWMP database (CDMO 2014) were used to further validate the weighted regression model. Monitoring data from January 1st to December 31st 2012 were obtained from a range of geographic locations (Fig. 6 and Table 3). Astronomical tidal heights were predicted for each site using harmonic regression applied to the sonde depth data (oce package in R, Foreman and Henry 1989, RDCT 2014). Although, the depth data represent tidal height variation from both astronomical (i.e., gravitational effects) and meteorological (e.g., wind, precipitation inflows) sources, we isolated the former given that daily metabolism estimates were more likely to be affected by repeated diel cycling from normal tidal changes. Each station was also chosen based on high correlations

between DO and tidal changes. The four sites included the Vierra Mouth station at Elkhorn Slough (California, 36.81°N, 121.78°W), Bayview Channel at Padilla Bay (Washington, 48.50°N 122.50°W), Middle Blackwater River station at Rookery Bay (Florida, 25.93°N 81.60°W), and Dean Creek station at Sapelo Island (Georgia, 31.39°N 81.28°W). The stations are generally macrotidal semidiurnal or mixed semidiurnal and net heterotrophic on an annual basis. Net heterotrophy (i.e., respiration exceeding production) is typical for shallow water systems at temperate latitudes (Caffrey 2003), although values in Table 3 are from observed DO time series that are strongly influenced by tidal advection.

Estimates of ecosystem metabolism before and after detiding

The weighted regression method was applied to the time series for each station to obtain a detided DO time series for estimating metabolism. The half window widths that produced the most robust results for the simulations were used for the case studies: eight days, six hours, and a tidal proportion of one. Unlike the simulated data, the true biological DO signal was unknown for the case studies. Accordingly, results were evaluated using correlations of DO and metabolism estimates with tidal height before and after application of the model. Results were also evaluated based on the occurrence of ‘anomalous’ daily production or respiration estimates, where anomalous was defined as negative production during the day and positive respiration estimates during the night. Anomalous values have been previously attributed to the effects of physical processes on DO time series (Caffrey 2003). We hypothesized that metabolism estimates using the detided signal would contain less ‘anomalous’ values than those from the observed DO time series. Although anomalies could be caused by processes other than tidal advection, e.g., abiotic dark oxygen production (Pamatmat 1997), we assume that physical processes are the dominant

sources of these values.

Ecosystem metabolism was estimated from the DO time series using the open-water technique (Odum 1956) as described in Caffrey et al. (2013). The method is used to infer net ecosystem metabolism using the mass balance equation:

$$\frac{\delta DO}{\delta t} = P - R + D \quad (15)$$

where the change in DO concentration (δDO , g O₂ m⁻³) over time (δt , hours) is equal to photosynthetic rate (P , g O₂ m⁻³ hr⁻¹) minus respiration rate (R , g O₂ m⁻³ hr⁻¹), corrected for air-sea gas exchange at the interface (D , g O₂ m⁻³ hr⁻¹) (Caffrey et al. 2013). D is estimated as the difference between the DO saturation concentration and observed DO, multiplied by a volumetric reaeration coefficient, k_a (Thébault et al. 2008). The diffusion-corrected DO flux estimates were averaged during day and night for each 24 hour period in the time series, where flux is an hourly rate of DO change as the difference between observations at time t and $t + 1$. Areal respiration rates were assumed constant during the night and subtracted from daily gross production estimates to yield net ecosystem metabolism (Table 3).

Detiding had significant effects on the correlations between tidal height changes, DO time series, and metabolism estimates (Table 4). Correlations of observed DO time series with predicted tidal height were highly significant, with all sites indicating positive relationships, except Padilla Bay where tidal increases were associated with declines in DO concentration. This suggests that seaward water masses were less anoxic than landward masses, with the opposite being true for Padilla Bay. The detided DO time series had greatly reduced correlations with tidal height, although relationships were still significant after detiding likely because of the large

sample size for each site ($n \approx 17500$). Metabolism estimates before and after detiding were compared to the mean rate of tidal height change (i.e., first derivative of the predicted tidal height) for each day during separate solar periods. Production rates were compared to mean rates of tidal height change during the day, respiration rates were compared to mean rates of change during the night, and net metabolism rates were compared to mean rates of change for the total 24 hour period each day. Comparison of metabolic rates to tidal changes before and after detiding produced inconsistent results (Table 4). Correlations for Elkhorn Slough and Sapelo Island showed consistent reductions in all three metabolisms estimates after detiding. Correlations for Padilla Bay and Rookery Bay were of opposite sign and greater magnitude after detiding for production and respiration, although net metabolism estimates had reduced correlations.

The percent of daily integrated metabolism estimates that were anomalous (negative production, positive respiration) were significantly reduced for all sites after detiding (Table 5). Before detiding, anomalous values ranged from 0.09 (Rookery Bay) to 0.22 (Padilla Bay) for production and 0.08 (Rookery Bay) to 0.21 (Elkhorn Slough) for respiration as proportions of the mean annual values. Anomalous values were reduced to zero for Rookery Bay and Sapelo Island, close to zero for Padilla Bay (0.05 for production, 0.06 for respiration), and reduced to approximately half the original proportions for Elkhorn Slough (0.11 for production, 0.12 for respiration). Metabolism estimates using detided DO time series also had decreased mean production and respiration for Elkhorn Slough, increased mean production and respiration for Padilla Bay, and generally unchanged mean production and respiration for Rookery Bay and Sapelo Island (Table 5). Mean net ecosystem metabolism was unchanged for all sites. Decreases in the standard error for all metabolism estimates (production, respiration, and net) were observed for all case studies after detiding.

An example from Sapelo Island further highlights the effects of weighted regression on metabolism estimates (Fig. 7). Tidal predictions for Sapelo Island indicated that the site is strongly semidiurnal with approximately two tidal peaks per 24 hour period. Tidal effects on the observed DO time series were apparent such that semidiurnal variation is closely correlated to tidal height variation. Weighted regression was successful in removing the variation in the observed DO time series from changes in tidal height. The detided DO time series exhibited more consistent diel variation with photoperiod (i.e., one peak per 24 hours) as compared to the observed time series (i.e., two peaks per 24 hours). However, metabolism before and after detiding for the period of observation was similar, suggesting that detiding the DO signal does not have a large effect on mean daily integrated metabolism estimates.

Discussion

Comments and recommendations

References

- Batt RD, Carpenter SR. 2012. Free-water lake metabolism: Addressing noisy time series with a Kalman filter. *Limnology and Oceanography: Methods*, 10:20–30.
- Caffrey JM. 2003. Production, respiration and net ecosystem metabolism in U.S. estuaries. *Environmental Monitoring and Assessment*, 81(1-3):207–219.
- Caffrey JM. 2004. Factors controlling net ecosystem metabolism in U.S. estuaries. *Estuaries*, 27(1):90–101.
- Caffrey JM, Murrell MC, Amacker KS, Harper J, Phipps S, Woodrey M. 2013. Seasonal and inter-annual patterns in primary production, respiration and net ecosystem metabolism in 3 estuaries in the northeast Gulf of Mexico. *Estuaries and Coasts*.
- CDMO (Centralized Data Management Office). 2014. National Estuarine Research Reserve System. <http://cdmo.baruch.sc.edu/>. (Accessed January, 2014).
- Collins JR, Raymond PA, Bohlen WF, Howard-Strobel MM. 2013. Estimates of new and total

- productivity in Central Long Island Sound from in situ measurements of nitrate and dissolved oxygen. *Estuaries and Coasts*, 36(1):74–97.
- Coloso JJ, Cole JJ, Pace ML. 2011. Difficulty in discerning drivers of lake ecosystem metabolism with high-frequency data. *Ecosystems*, 14(6):935–948.
- Cryer JD, Chan KS. 2008. *Time Series Analysis with Applications in R*. Springer, New York, New York, second edition.
- Diaz RJ. 2008. Spreading dead zones and consequences for marine ecosystems. *Science*, 321:926–929.
- Foreman MGG, Henry RF. 1989. The harmonic analysis of tidal model time series. *Advances in Water Resources*, 12(3):109–120.
- Hilborn R, Mangel M. 1997. *The Ecological Detective: Confronting Models with Data*. Princeton University Press, Princeton, New Jersey.
- Hirsch RM, Moyer DL, Archfield SA. 2010. Weighted regressions on time, discharge, and season (WRTDS), with an application to Chesapeake Bay river inputs. *Journal of the American Water Resources Association*, 46(5):857–880.
- Hopkinson CS, Smith EM. 2005. Estuarine respiration: an overview of benthic, pelagic, and whole system respiration. In: Giorgio PAD, Williams P, editors, *Respiration in Aquatic Ecosystems*, pages 122–146. Oxford Press, Oxford, United Kingdom.
- Howarth RW, Hayn M, Marino RM, Ganju N, Foreman K, McGlathery K, Giblin AE, Berg P, Walker JD. 2014. Metabolism of a nitrogen-enriched coastal marine lagoon during the summertime. *Biogeochemistry*, 118(1-3):1–20.
- Kemp WM, Testa JM. 2012. Metabolic balance between ecosystem production and consumption. In: Wolanski E, McLusky DS, editors, *Treatise on Estuarine and Coastal Science*, pages 83–118. Academic Press, New York.
- Kemp WM, Testa JM, Conley DJ, Gilbert D, Hagy JD. 2009. Temporal responses of coastal hypoxia to nutrient loading and physical controls. *Biogeosciences*, 6(12):2985–3008.
- Needoba JA, Peterson TD, Johnson KS. 2012. Method for the quantification of aquatic primary production and net ecosystem metabolism using in situ dissolved oxygen sensors. In: Tiquia-Arashiro SM, editor, *Molecular Biological Technologies for Ocean Sensing*, pages 73–101. Springer, New York.
- Nidzieko NJ, Needoba JA, Monismith SG, Johnson KS. 2014. Fortnightly tidal modulations affect net community production in a mesotidal estuary. *Estuaries and Coasts*.
- Odum HT. 1956. Primary production in flowing waters. *Limnology and Oceanography*, 1(2):102–117.

- Pamatmat MM. 1997. Non-photosynthetic oxygen production and non-respiratory oxygen uptake in the dark: A theory of oxygen dynamics in plankton communities. *Marine Biology*, 129(4):735–746.
- RDCT (R Development Core Team). 2014. R: A language and environment for statistical computing, v3.1.0. R Foundation for Statistical Computing, Vienna, Austria.
<http://www.R-project.org>.
- Sanger DM, Arendt MD, Chen Y, Wenner EL, Holland AF, Edwards D, Caffrey J. 2002. A synthesis of water quality data: National estuarine research reserve system-wide monitoring program (1995-2000). Technical report, National Estuarine Research Reserve Technical Report Series 2002:3. South Carolina Department of Natural Resources, Marine Resources Division Contribution No. 500, Charleston, South Carolina.
- Staehr PA, Bade D, de Bogert MCV, Koch GR, Williamson C, Hanson P, Cole JJ, Kratz T. 2010. Lake metabolism and the diel oxygen technique: State of the science. *Limnology and Oceanography: Methods*, 8:628–644.
- Thébault J, Schraga TS, Cloern JE, Dunlavy EG. 2008. Primary production and carrying capacity of former salt ponds after reconnection to San Francisco Bay. *Wetlands*, 28(3):841–851.
- Wenner E, Sanger D, Arendt M, Holland AF, Chen Y. 2004. Variability in dissolved oxygen and other water-quality variables within the National Estuarine Research Reserve System. *Journal of Coastal Research*, 45(SI):17–38.
- Yin KD, Lin ZF, Ke ZY. 2004. Temporal and spatial distribution of dissolved oxygen in the Pearl River Estuary and adjacent coastal waters. *Continental Shelf Research*, 24(16):1935–1948.
- Ziegler S, Benner R. 1998. Ecosystem metabolism in a subtropical, seagrass-dominated lagoon. *Marine Ecology Progress Series*, 173:1–12.

Figures

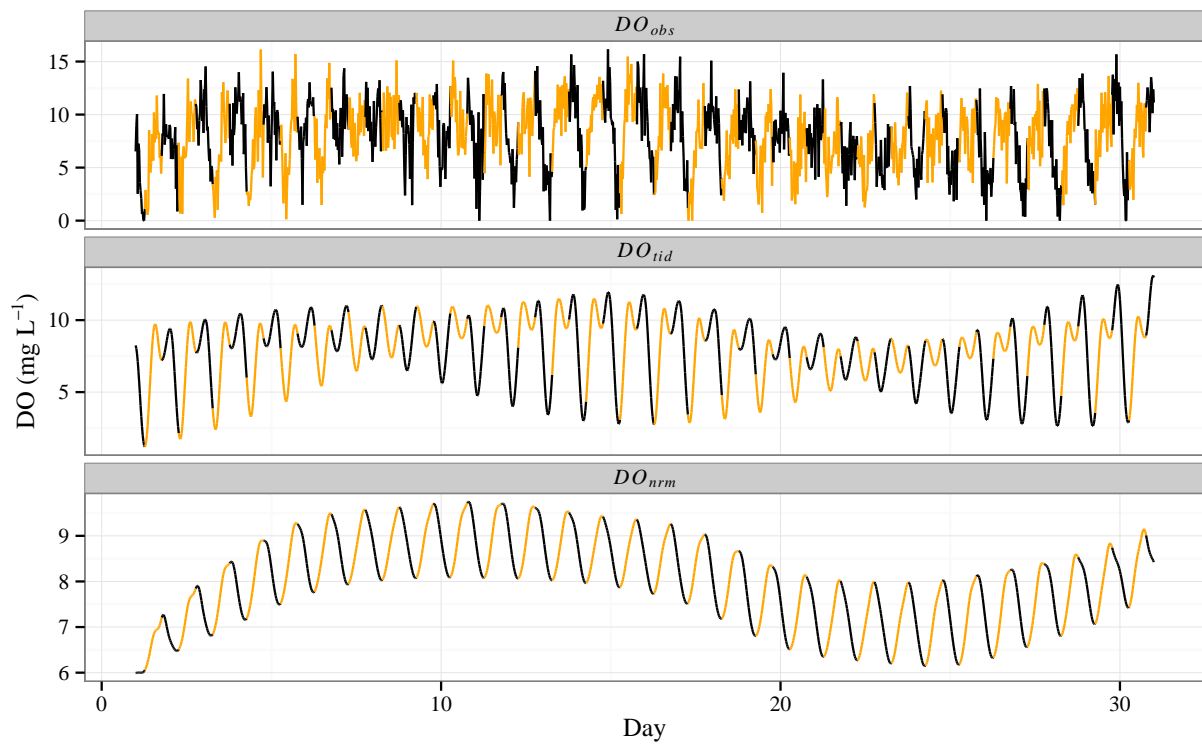


Fig. 1: Example of detiding a simulated DO time series. Simulated values are those in Fig. 2. Yellow indicates daylight periods.

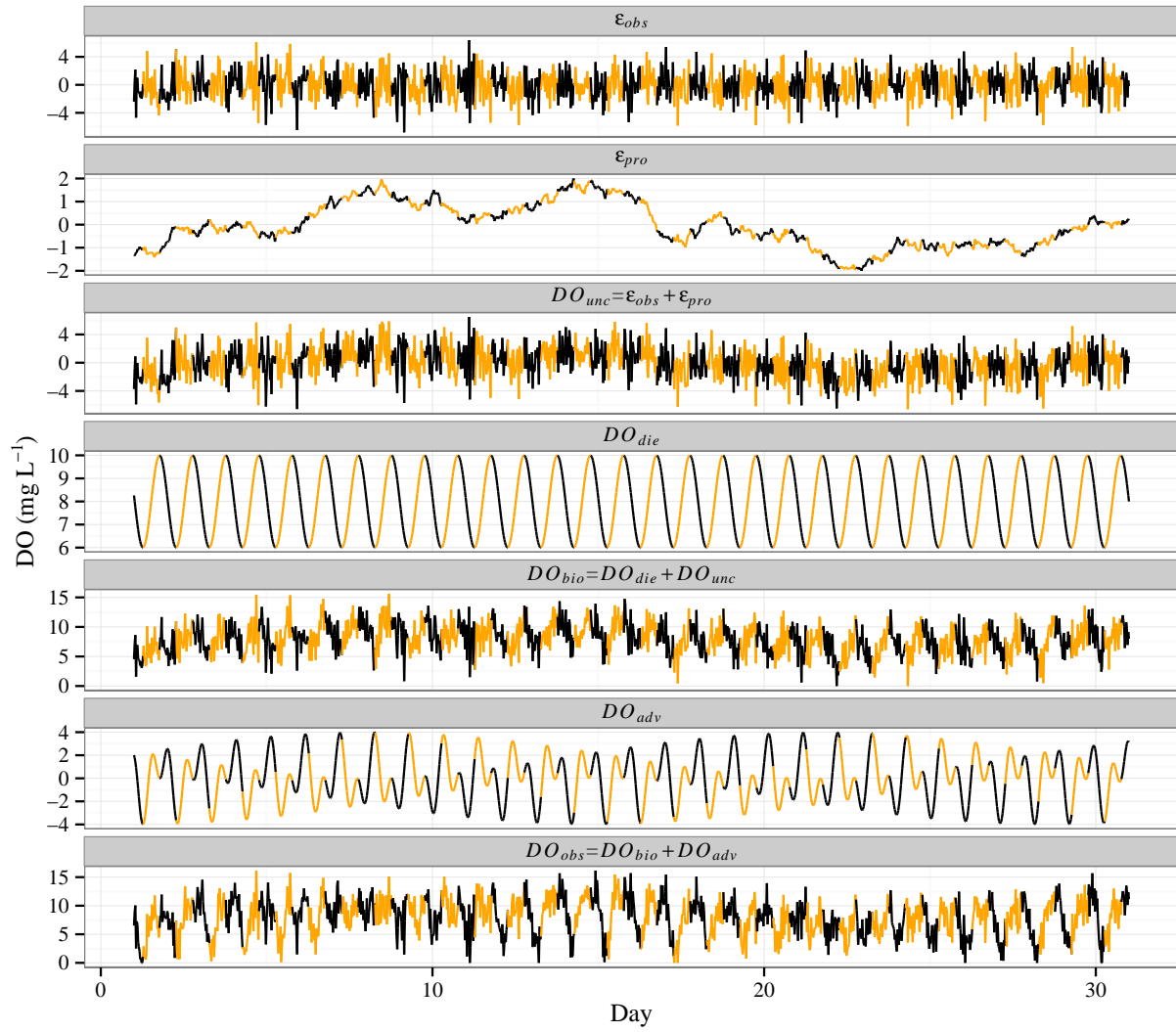


Fig. 2: Example of creating a simulated DO time series. Values were simulated every 30 minutes for 30 days. Yellow indicates daylight periods. ^{fig:do_sim}

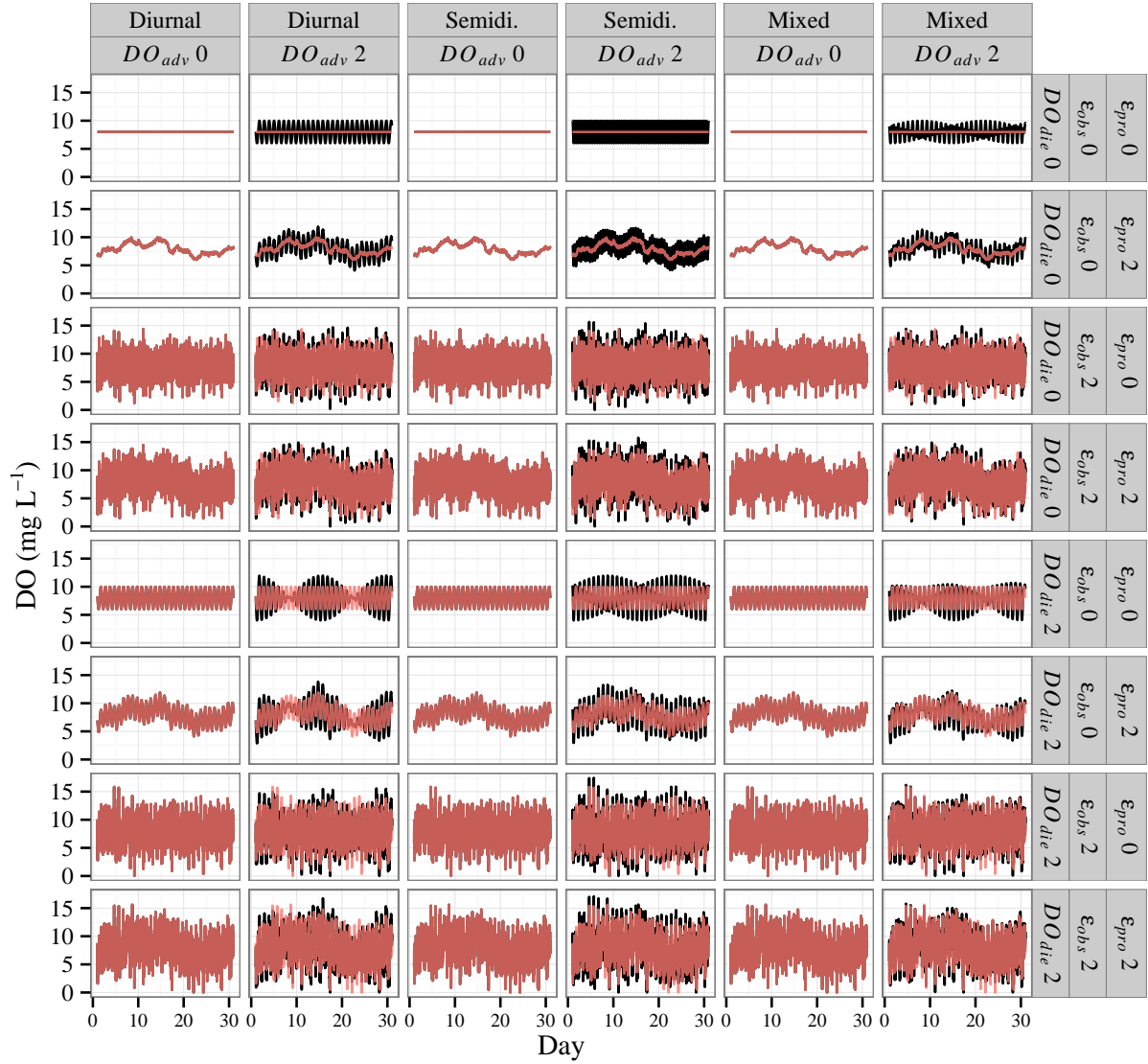


Fig. 3: Representative examples of simulated DO time series created by varying each of five parameters: tidal category (e.g., Mixed), strength of tidal association with DO signal using DO_{adv} , amount of process uncertainty ϵ_{pro} , amount of observation uncertainty ϵ_{obs} , and strength of diel DO component DO_{die} . Parameter values represent the extremes used in the simulation (i.e., minimum, maximum). Black lines are observed DO from eq. (8) and red lines are biological DO from eq. (6). fig:sim_ex

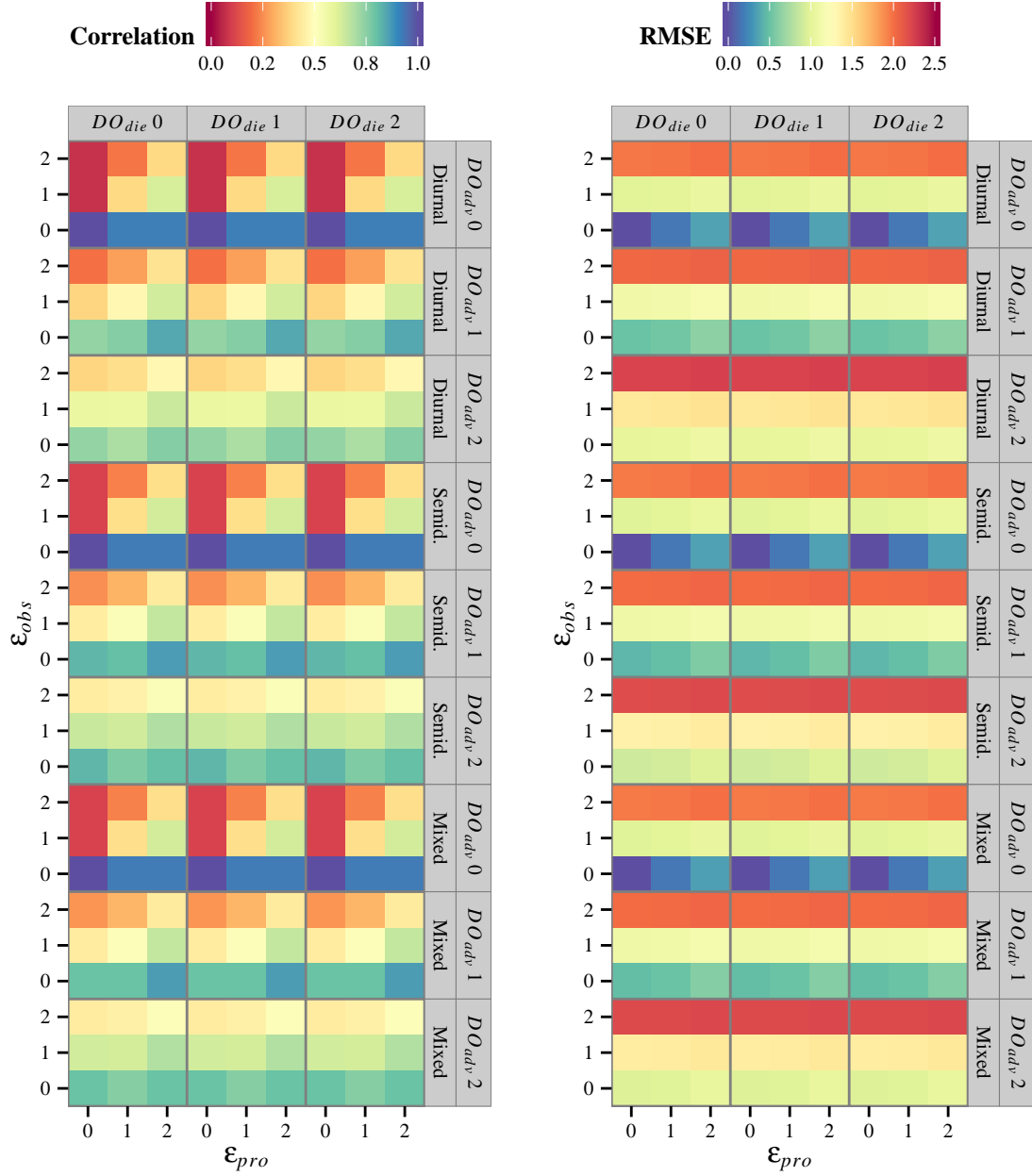


Fig. 4: Correlations and errors (RMSE) for detided DO time series, DO_{dtd} , from weighted regression with ‘true’ biological DO, DO_{bio} , for varying simulation parameters: tidal category (e.g., Mixed), strength of tidal association with DO signal DO_{adv} , amount of process uncertainty ϵ_{pro} , amount of observation observation uncertainty ϵ_{obs} , and strength of diel DO component DO_{die} . Each tile represents the correlation or error between detided and biological DO time series from results for a given combination of simulation parameters. Results are averaged for all window widths used to evaluate the regressions.

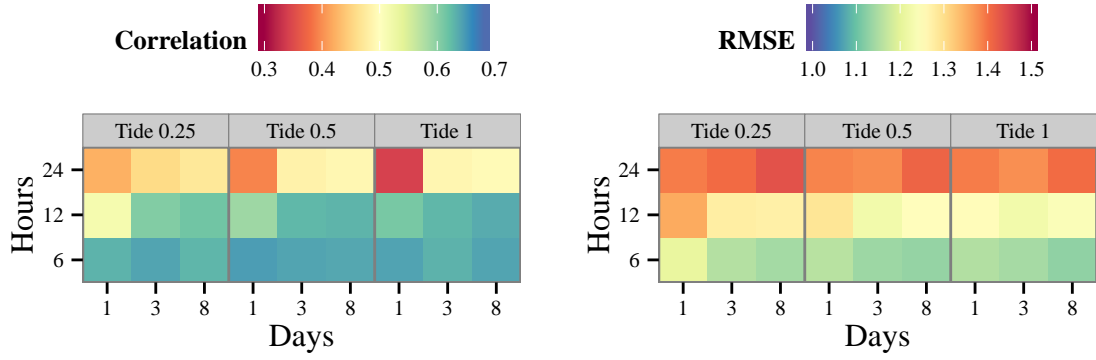


Fig. 5: Correlations and errors (RMSE) for detided DO time series, DO_{dtd} , from weighted regression with ‘true’ biological DO, DO_{bio} , for varying half window widths: days, hour of day, and proportion of tidal range. Each tile represents the correlation or error between detided and biological DO time series from results for a given combination of window widths. Results are averaged for all simulation parameters used to evaluate the regressions. fig:err_surf2

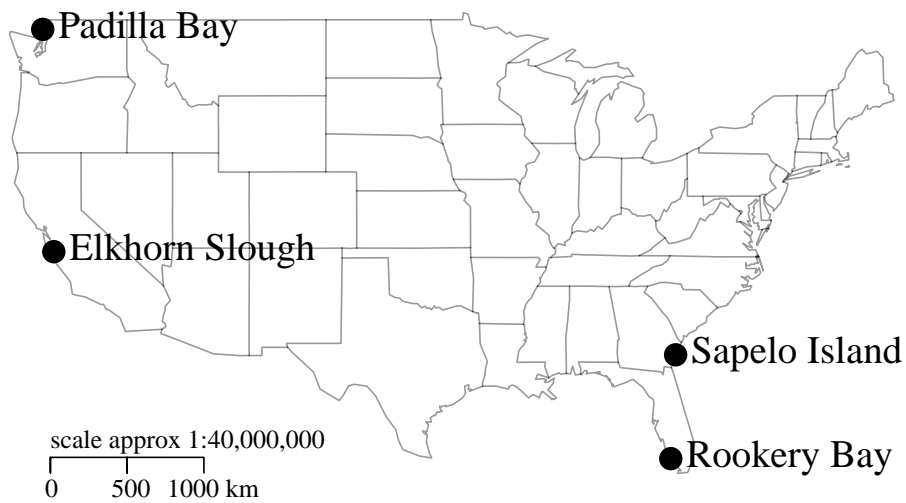


Fig. 6: Locations of NERRS sites used as case studies to evaluate of weighted regression. Individual stations at each reserve are PDBJE (Joe Leary Estuary at Padilla Bay), RKBMB (Middle Blackwater River at Rookery Bay), SAPDC (Dean Creek at Sapelo Island), and TJRBR (Boca Rio at Tijuana River).
fig:case_map

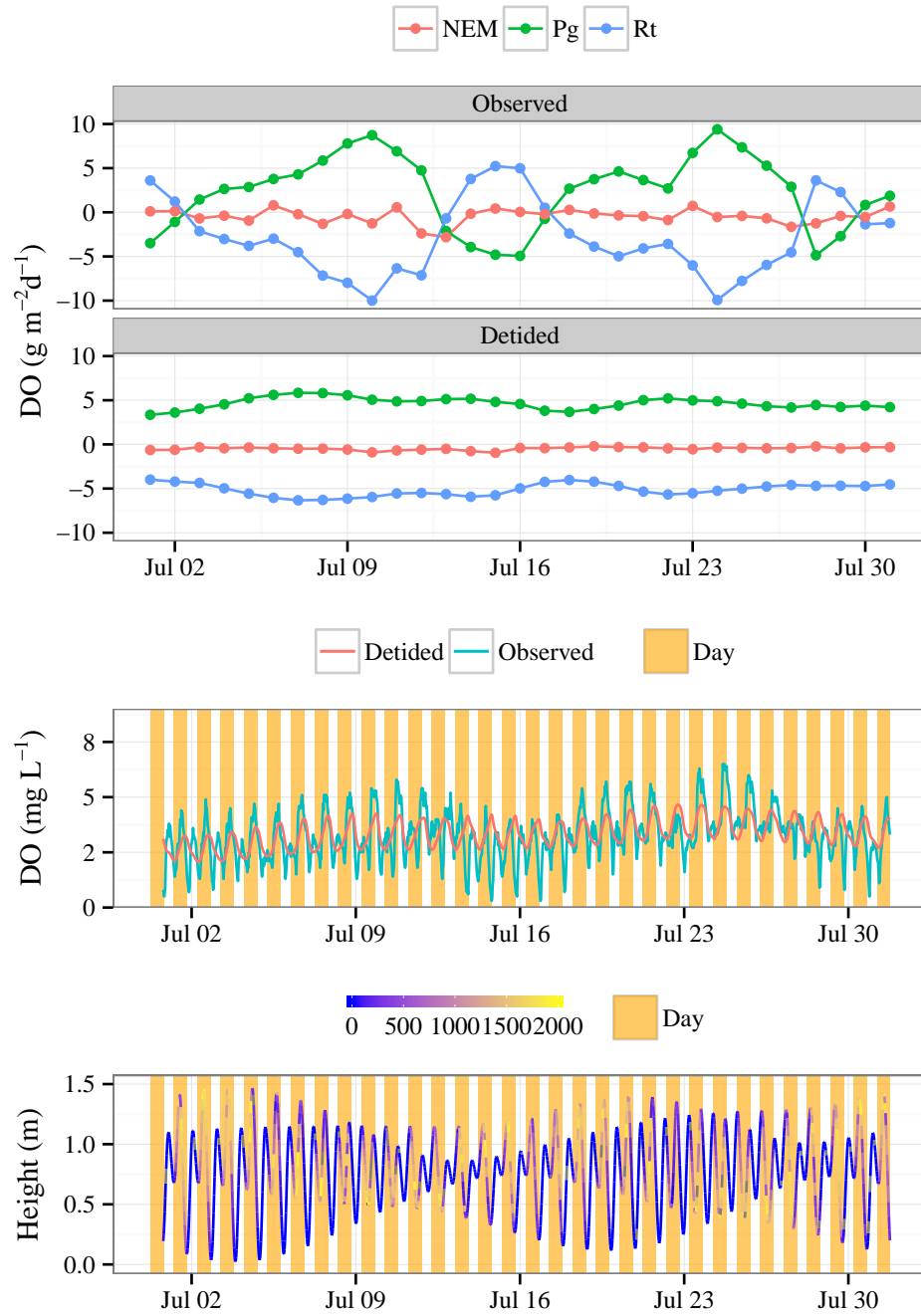


Fig. 7: Example of metabolism and DO time series before (observed) and after (detided) weighted regression. Results are for a ten day period in March for the Sapelo Island station using a weighted regression with a window of eight days, six hours within each day, and tidal height proportion of one.

Tables

Table 1: Summary (range, mean, percentiles) of correlations and error estimates comparing detided and biological DO time series for different simulation parameters (tidal category, DO_{die} , DO_{adv} , ϵ_{pro} , ϵ_{obs}). Values represent a combination of results from multiple simulations with the parameter value held constant for each row (e.g., row one is a summary of all simulations for which the tidal category was diurnal).
tab:dtd_perfl

Parameter	Correlation					RMSE				
	Min	25 th	Mean	75 th	Max	Min	25 th	Mean	75 th	Max
Tidal category										
Diurnal	-0.78	0.35	0.54	0.80	1.00	0.00	0.86	1.29	1.99	2.39
Semidiurnal	-0.28	0.37	0.58	0.84	1.00	0.00	0.73	1.25	1.97	2.40
Mixed Semidiurnal	-0.39	0.37	0.57	0.83	1.00	0.00	0.78	1.27	1.97	2.47
DO_{die}										
0	0.00	0.21	0.52	0.92	1.00	0.00	0.26	1.05	1.96	2.05
1	-0.78	0.36	0.55	0.74	1.00	0.12	0.68	1.23	2.00	2.13
2	-0.78	0.48	0.62	0.81	1.00	0.25	1.13	1.53	2.08	2.47
DO_{adv}										
0	-0.78	0.36	0.56	0.82	1.00	0.00	0.78	1.27	1.98	2.47
1	-0.78	0.36	0.56	0.82	1.00	0.00	0.78	1.27	1.98	2.47
2	-0.78	0.36	0.56	0.82	1.00	0.00	0.78	1.27	1.98	2.47
ϵ_{pro}										
0	-0.78	0.14	0.50	0.83	1.00	0.00	0.74	1.23	1.96	2.45
1	0.14	0.35	0.55	0.81	0.99	0.07	0.76	1.26	1.98	2.45
2	0.33	0.47	0.65	0.82	0.99	0.15	0.82	1.32	2.00	2.47
ϵ_{obs}										
0	-0.78	0.80	0.84	0.97	1.00	0.00	0.26	0.57	0.78	1.57
1	-0.07	0.39	0.51	0.67	0.84	0.96	1.01	1.18	1.25	1.82
2	0.00	0.22	0.34	0.44	0.63	1.93	1.98	2.07	2.11	2.47

Table 2: Summary (range, mean, percentiles) of correlations and error estimates comparing detided and biological DO time series for simulations using different half window widths in the weighted regressions (days, hours, and proportion of tidal range). Values represent a combination of results from multiple simulations with the window value held constant for each row (e.g., row one is a summary of all simulations for which the half window width was one day).^{tab:dtd_perf2}

Window	Correlation					RMSE				
	Min	25 th	Mean	75 th	Max	Min	25 th	Mean	75 th	Max
Days										
1	-0.78	0.30	0.53	0.77	1.00	0.00	0.95	1.29	1.96	2.40
3	0.00	0.39	0.58	0.83	1.00	0.00	0.75	1.26	1.98	2.43
8	0.03	0.36	0.58	0.85	1.00	0.00	0.78	1.27	1.99	2.47
Hours										
6	0.00	0.41	0.64	0.90	1.00	0.00	0.53	1.15	1.97	2.21
12	0.04	0.41	0.61	0.85	1.00	0.00	0.87	1.27	1.98	2.33
24	-0.78	0.24	0.45	0.60	1.00	0.00	0.98	1.40	1.98	2.47
Tide										
0.25	0.03	0.35	0.55	0.81	1.00	0.00	0.81	1.29	1.99	2.47
0.5	-0.10	0.37	0.57	0.82	1.00	0.00	0.78	1.26	1.97	2.40
1	-0.78	0.36	0.57	0.82	1.00	0.00	0.76	1.26	1.97	2.40

Table 3: Summary statistics of tidal component amplitudes (m), DO (mg L⁻¹), and metabolism estimates (gross production, respiration, and net ecosystem metabolism as g m⁻² d⁻¹) for each case study. Tidal components are principal lunar semidiurnal (O1, frequency 25.82 hours), solar diurnal (P1, 24.07 hours), lunar semidiurnal (M2, 12.42 hours), and solar semidiurnal (S2, 12 hours), estimated from harmonic regressions of tidal height (`oce` package in R, [Foreman and Henry 1989](#), [RDCT 2014](#)). DO range and mean are grand means of daily estimates for the entire period of record (30 minute observations) for each site. Metabolism estimates are means of daily integrated values.^{tab:case_att}

Site	Tidal amplitude				DO		Metabolism ^a		
	O1	P1	M2	S2	Range	Mean	Pg	Rt	NEM
ELKVM	0.24	0.12	0.48	0.13	6.79	7.86	8.14	-8.19	-0.05
PDBBY	0.46	0.23	0.63	0.15	7.53	8.97	5.95	-5.90	0.05
RKBMB	0.13	0.04	0.36	0.10	5.47	4.53	3.02	-3.62	-0.60
SAPDC	0.10	0.02	0.54	0.07	7.98	5.01	4.89	-6.04	-1.16

^aPg: gross production, Rt: respiration, NEM: net ecosystem metabolism

Table 4: Correlations of tidal changes at each site with continuous DO observations and metabolism estimates (gross production, respiration, and net metabolism) before (observed) and after (detided) detiding from weighted regression. DO values are correlated with predicted tidal height at each observation, whereas metabolism estimates are correlated with mean tidal height change between observations during day, night, or total day periods for production, respiration, and net metabolism, respectively.^{tab:cor_res}

Site	DO	Pg ^a	Rt	NEM
ELKVM				
Observed	0.47***	0.60***	0.73***	0.35***
Detided	-0.02*	-0.04	-0.17**	0.06
PDBBY				
Observed	-0.45***	-0.33***	-0.46***	-0.25***
Detided	0.09***	0.57***	0.51***	-0.12*
RKBMB				
Observed	0.28***	0.34***	0.39***	0.24***
Detided	-0.02*	-0.36***	-0.44***	0.11
SAPDC				
Observed	0.48***	0.54***	0.71***	0.41***
Detided	-0.03***	0.08	0.15**	-0.06

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$

^aPg: gross production, Rt: respiration, NEM: net ecosystem metabolism

Table 5: Summary of metabolism estimates (gross production, respiration, and net metabolism) for case studies using DO time series before (observed) and after (detided) application of weighted regression. Means and standard errors are based on daily integrated metabolism estimates. Anomalous values are the proportion of metabolism estimates that were negative for gross production and positive for respiration. Results are for weighted regressions with a window of thirty days and tidal height proportion of one.

Site	Pg^a			Rt			NEM	
	Mean	Std. Err.	Anom	Mean	Std. Err.	Anom	Mean	Std. Err.
ELKVM								
Observed	8.14	0.67	0.19	-8.19	0.69	0.21	-0.05	0.16
Detided	2.78	0.14	0.11	-2.83	0.15	0.12	-0.05	0.03
PDBBY								
Observed	5.95	0.69	0.22	-5.90	0.74	0.19	0.05	0.22
Detided	8.07	0.40	0.05	-8.04	0.39	0.06	0.04	0.06
RKBMB								
Observed	3.02	0.14	0.09	-3.62	0.15	0.08	-0.60	0.06
Detided	2.73	0.07	0.00	-3.34	0.07	0.00	-0.61	0.03
SAPDC								
Observed	4.89	0.23	0.13	-6.04	0.25	0.11	-1.16	0.09
Detided	4.40	0.08	0.00	-5.58	0.09	0.00	-1.18	0.05

^aPg: gross production, Rt: respiration, NEM: net ecosystem metabolism