

INORGANIC CARBON AND OXYGEN DYNAMICS IN A MARSH-DOMINATED  
ESTUARY

by

SHIYU WANG

(Under the Direction of Charles S. Hopkins)

ABSTRACT

We conducted a study to address uncertainties associated with the metabolism and net carbon fluxes for the tidal wetland and estuarine portion of the coastal ocean because of these zones disproportionately large role in ocean carbon dynamics. We measured open water diurnal O<sub>2</sub> and CO<sub>2</sub> dynamics seasonally in the Duplin River salt marsh-estuary in Georgia, USA with a particular focus on the marsh-estuary linkage associated with tidal flooding. We observed that the overall system was a net source of CO<sub>2</sub> to the atmosphere and adjacent coastal ocean and a net sink for oceanic and atmospheric O<sub>2</sub>. Rates of metabolism were extremely high, with respiration (R: 43 mol/m<sup>2</sup>/yr) exceeding gross primary production (GPP: 28 mol/m<sup>2</sup>/yr). Rates of metabolism measured with CO<sub>2</sub> were substantially higher than with O<sub>2</sub>. The net heterotrophy of the aquatic salt marsh-estuary system is supported primarily by the net production of the salt marsh proper.

INDEX WORDS: salt marsh; estuary; metabolism; CO<sub>2</sub> exchange; O<sub>2</sub> exchange; inundation

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MS, University of Georgia, 2016

BS, Ocean University of China, China, 2012

A Thesis Submitted to the Graduate Faculty of The University of Georgia in Partial Fulfillment  
of the Requirements for the Degree

MASTER OF SCIENCE

ATHENS, GEORGIA

2016

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May 2016

## DEDICATION

To people who live in poverty and never get a chance to receive an education.

## ACKNOWLEDGEMENTS

I would like to first thank my major professor Chuck Hopkinson, who always stops what he is doing and talks to me whenever I go to his office. I enjoyed every inspiring conversation with him regarding science, politics, cultures and life. I would also like to thank my committee members Daniela Di Iorio and Weijun Cai, for their constant patience, technical support, useful critiques and challenging insights, which greatly improved my work. I also want to thank Joel Craig, our GCE-LTER technician, who helped a lot during my field trips and kept me entertained during the long hours of sampling on the marsh. Special thanks to my lab mates, friends, and family who bore with me for the past years with great support and patience.

I could never finish my degree without these amazing people.

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## CHAPTER 1

### INTRODUCTION

Carbon dynamics of salt marsh-dominated estuaries have fascinated coastal ecosystem ecologists for more than half a century because of their tremendously high rates of primary production, their support for commercial fisheries, and their disproportionately large contribution to the global carbon budget relative to their size (Bauer et al. 2013). Early investigations documented their high rates of marsh primary production and concluded on the basis of little apparent grazing and organic matter burial that large quantities of macrophyte-derived organic matter were exported to tidal waters where it formed the basis of a rich detrital food web (Teal 1962, Darnell 1967, Odum 1968). Aquatic and benthic metabolism measurements of estuarine subsystems in bottles and chambers supported a marsh outwelling hypothesis by showing a deficit of production relative to respiration (e.g., Pomeroy and Wiegert 1981, Hopkinson 1985), but cross-system comparisons of coastal fisheries production found little evidence that it was higher in salt marsh-dominated estuaries (Nixon 1980). Carbon budgets became increasingly complex through the 1980's following decades of observations, but many fluxes, including those between marsh and tidal creeks, were calculated by mass balance (Hopkinson 1988) and oftentimes were quite large. More recently, mass balance analysis of CO<sub>2</sub> degassing from estuarine waters and dissolved inorganic carbon (DIC) export from salt marsh-dominated estuaries suggests large export of inorganic carbon from salt marsh-estuaries but how much of this carbon originates as respiration on the marsh proper as opposed to respiration in tidal creeks of organic matter exported from the marsh is not entirely clear (Cai 2011; Wang and Cai 2004).

Recent global syntheses of the coastal ocean carbon balance conclude that tremendous spatial heterogeneity in carbon processing and fluxes results in high levels of uncertainty in estuarine net carbon balances and that climate change, land-use change, and sea-level rise will likely decrease net carbon burial in estuaries and adjacent tidal wetlands in the future (Bauer et al. 2013).

Further progress in refining marsh-estuarine carbon fluxes and reducing uncertainty in metabolic balance will be made by reducing 3 major constraints: 1) chamber and bottle approaches to measuring metabolism of marsh-estuarine subsystems (e.g., intertidal benthos and marsh platform) likely severely underestimate true rates, as they artificially separate local sources and sinks of nutrients, reduce mixing, reduce macrofaunal feedbacks and lack the tidal dynamics of intertidal flat and marsh platform flooding and draining (Montague 1980, Smith and Hollibaugh 1997), 2) scaling plot-based measures (e.g., subtidal benthos, water column, creekbank) to the whole system typically misrepresents the high spatial heterogeneity of salt marsh estuaries (Cai 2011; Bauer et al. 2013), and 3) calculating whole system net carbon balance from many independent measures of production and respiration, each of which has a high uncertainty, typically results in a small value for net ecosystem metabolism with high variance and even higher uncertainty (Hopkinson 1988).

One way to overcome the constraints of containerization, component isolation and high variance is to directly conduct whole system measures of metabolism including net ecosystem production, using eddy covariance approaches to measure marsh metabolism (Forbrich and Giblin 2015) and open water diurnal approaches to measure estuarine metabolism (Vallino et al. 2008, Swaney et al. 1999, Odum 1956). With the open water diurnal approach, the metabolism of the multi-component, coupled marsh-estuary system is calculated from the diurnal changes in

CO<sub>2</sub> and/or O<sub>2</sub> after correcting for atmospheric exchange and mixing with adjacent water masses. The free water diurnal approach, apart from providing direct measures of whole system metabolism without constraint, also yields measures of estuarine O<sub>2</sub> and CO<sub>2</sub> exchange with the atmosphere and exchange with coastal ocean waters, which are of great importance in understanding the global atmospheric CO<sub>2</sub> budget and the exchange of carbon between terrestrial and oceanic realms (Frankignoulle et al. 1998; Cai 2011; Cai and Wang 1998; Raymond et al. 2000, Bauer et al. 2013).

In the ocean, known CNSPO stoichiometry of metabolism suggests that O<sub>2</sub> and CO<sub>2</sub> can be used interchangeably to measure metabolism (Redfield 1958). Indeed stoichiometrically linked whole-system budgets of C, N and P have been used to directly measure net ecosystem production of coastal systems (*sensu* Smith and Hollibaugh 1997). Most often however CO<sub>2</sub> and O<sub>2</sub> are used to measure metabolism, but usually separately - <sup>14</sup>CO<sub>2</sub> to measure production because of its sensitivity and O<sub>2</sub> to measure respiration because of its simplicity and sensitivity. With recent interest in understanding the role of various aquatic ecosystems in controlling atmospheric CO<sub>2</sub> levels, prior metabolism studies based on O<sub>2</sub> are being used to calculate CO<sub>2</sub> dynamics. Frequently respiratory and photosynthesis quotients (RQ and PQ) of 1 are used to convert from O<sub>2</sub> to CO<sub>2</sub> (Boynton & Kemp, 1985; Hopkinson, 1987; Banta et al. 1995), but evidence suggests great caution is required in making this assumption. In shallow water systems, a large percentage of metabolism is benthic and dependent on alternative electron acceptors to O<sub>2</sub>, such as NO<sub>3</sub><sup>-</sup>, reduced Fe and Mn, and SO<sub>4</sub><sup>2-</sup>. Respiration in salt marsh and estuarine sediments is dominated by SO<sub>4</sub><sup>2-</sup> reduction, thus decoupling of O<sub>2</sub> and CO<sub>2</sub> at least temporally. The decoupling of O<sub>2</sub> and CO<sub>2</sub> can also be a result of differences in thermodynamic and gas exchange dynamic controls of these two gases as CO<sub>2</sub> is buffered by a vast marine HCO<sub>3</sub><sup>-</sup> system

while  $O_2$  is the sole molecule. It is essential that we understand the temporal and spatial variability in the stoichiometry of  $O_2$  and  $CO_2$  if we continue to use  $O_2$  to measure coastal metabolism for use in global C budgets.

In one of the first inorganic carbon balance studies of salt marsh estuaries, Wang and Cai (2004) found that inorganic carbon was exported at high rates from estuarine waters, both in terms of  $CO_2$  flux to the atmosphere and dissolved inorganic carbon (DIC) transport to the coastal ocean. In comparison to bottle measures of estuarine aquatic respiration, Wang and Cai concluded that an important source of the exported DIC was the salt marsh. Previous organic carbon budgets had ignored inorganic carbon and concluded that the super-saturation of estuarine waters with  $CO_2$  and under-saturation with  $O_2$  was the sole result of the decomposition of organic carbon exported from the marsh. The open water diurnal approach to salt marsh estuarine metabolism directly incorporates some contribution of salt marsh metabolism to adjacent tidal waters, as twice daily high tides flood the marsh platform resulting in either the uptake or release of DIC and oxygen as a result of metabolism on the marsh.

In this study, we used the open water diurnal approach to study the seasonal metabolism of a hydrodynamically linked salt marsh – estuary, the Duplin River in Georgia, USA. We used simultaneous measurements of  $CO_2$  and  $O_2$  along the entire 12 km length of this system to examine the stoichiometry of  $CO_2$  and  $O_2$  and to integrate across a highly heterogeneous complex of open water, intertidal flats, marsh creekbanks, tidal creeks, and marsh platform environments. We also measured directly the flux of DIC and  $O_2$  between the Duplin River and an adjacent first-order tidal creek and its watershed in order to evaluate the contribution of marsh flooding to the metabolism of the Duplin River. In addition, we measured the air to water and marsh-estuary to coastal ocean exchange of  $CO_2$  and  $O_2$ . This work was done in parallel with

eddy covariance measures of net ecosystem exchange of CO<sub>2</sub> between a Duplin River marsh and the atmosphere.

## CHAPTER 2

### DESCRIPTION OF THE AREA AND METHODOLOGY

#### 2.1 Description of the area

We conducted our study in the Duplin River salt marsh - estuary, adjacent to Sapelo Island, Georgia, a coastal ecosystem representative of the broad intertidal, wetland macrophyte-dominated estuaries of the Carolinian biogeographic province of the southeastern USA (Fig. 1). The ecosystem is relatively pristine as local coastal development is low.

The Duplin salt marsh–estuary ecosystem includes the Duplin River estuary and the adjacent intertidal salt marsh that floods at high tide (consider the intertidal marshes as the catchment or watershed for the Duplin River). The ecosystem is approximately 12-km long and 11.4 km<sup>2</sup> in area of which about 30% is aquatic (20% permanently aquatic with depths below mean low water (-1.02 m) (MLW) (NOAA – relative to MSL at 0 m) and 10% intertidal mudflats between MLW and mean sea level (MSL – 0 m)) and 70% is intertidal salt marsh. The marsh, which is dominated by *Spartina alterniflora*, extends from near 0 m MSL to form a broad relatively flat platform between about 0.8 to about 1.2 m in elevation. Mean high water is at 1.00 m.

The meso-tidal Duplin River is well-mixed (Type 1B by the Hansen and Rattray classification criteria) with minimal freshwater input that is mostly via groundwater runoff from Sapelo Island (Imberger et al. 1983). Salinity varies seasonally in relation to discharge of the Altamaha River about 10 km to the south (Fig. 1). The Duplin has a large tidal excursion that decreases along its length from about 3.9km at the mouth to about 1 km at its upper end

(Ragotskie and Bryson 1955, Imberger et al. 1983, this study). We identified two water masses within the Duplin River based on whether the water mass remains in the system at low tide or exchanges with Dobby Sound and the coastal ocean. Our study was conducted in the “resident” water mass that remains within the Duplin at low tide.

Our study measured metabolism and CO<sub>2</sub> and O<sub>2</sub> dynamics in the “resident” water along its 12 km length. We also measured the metabolism and CO<sub>2</sub> and O<sub>2</sub> dynamics of water when it floods the marsh by focusing on a first order tidal creek that is the main source of water that floods the marsh where the GCE LTER project operates an eddy covariance tower. The small tidal creek connects directly with the Duplin River about three kilometers from its mouth (Fig. 1). The creek is about 400m long and floods a marsh of 0.043 km<sup>2</sup>. The creek drains completely at low tide, with only a trickle of water flowing during lowest stages of the tide as a result of creek-bank drainage.

## **2.2 Methodology**

We investigated carbon dynamics and ecosystem metabolism of “resident water” of the Duplin River salt marsh - estuary seasonally by analyzing the open water (Odum and Hoskin 1958; Odum and Wilson 1962, Balsis et al. 1995) diurnal changes in dissolved inorganic carbon (DIC or TCO<sub>2</sub>) and dissolved oxygen (DO) along the entire length of the system. We also examined the contribution of intertidal marshes to carbon and oxygen dynamics of the salt marsh-estuary by analyzing the net transport of DIC and O<sub>2</sub> through a small, ephemeral tidal creek that floods a defined salt marsh catchment adjacent to the main Duplin River channel.

Three processes contribute to the diurnal change in DIC and DO concentrations: gas exchange across the air-water surface, longitudinal dispersion or mixing with adjacent water

masses and metabolism by the pelagic, benthic, and intertidal communities of the salt marsh – estuary ecosystem when inundated (Eq. 1):

$$\Delta[\text{DIC (DO)}] * V = F * A_S * T + M * A_C * T + \text{Metabolism} \quad (\text{Eq. 1})$$

where  $\Delta[\text{DIC (DO)}]$  is the diurnal change in DIC or DO concentration ( $\text{mol m}^{-3}$ );  $V$  is the water volume ( $\text{m}^3$ );  $F$  is vertical gas flux across air-water surface ( $\text{mol m}^{-2} \text{hr}^{-1}$ );  $A_S$  is the water surface area ( $\text{m}^2$ );  $M$  is longitudinal mixing flux with adjacent water masses ( $\text{mol m}^{-2} \text{s}^{-1}$ );  $A_C$  is cross section area ( $\text{m}^2$ ) of the water channel,  $T$  is the time interval (hr) for a diurnal cycle.

Water of the Duplin is our reference for Eq. 1 such that positive values for terms increase the concentration of  $\text{CO}_2$  or  $\text{O}_2$ . For example, a calculated air-water flux of  $\text{CO}_2$  of  $-10 \text{ mol m}^2 \text{ day}^{-1}$  would lead to a decrease in DIC for a water mass during a diurnal period.

### **2.2.1 Spatial sampling along the Duplin – the open-water diurnal approach**

Discrete samples for DIC and alkalinity (Alk) were collected at twelve 1 km equidistantly spaced stations, while DO concentration, DO percent saturation (DO%) and partial pressure of  $\text{CO}_2$  ( $\text{pCO}_2$ ) were continuously measured along the length of the Duplin. Each transect was run within about one hour of dawn, dusk and the next dawn on February 21-22, May 19-20, August 15-16 and October 29-30, 2014. Sampling days were chosen so that sunrise was within 2 hours of low tide to facilitate matching of dawn-dusk and dusk-dawn sampling station water masses. Synoptic transects typically took 1 hour to complete. Details of DIC and Alk sampling, storage and analysis and  $\text{pCO}_2$  measurements are described fully in Cai et al. 2003. DO and its percent saturation were continuously measured with a YSI-6920 along with ancillary data such as temperature, salinity, and chlorophyll fluorescence by pumping water while underway from below the boat hull (Vallino et al. 2005). The same water was also analyzed for  $\text{pCO}_2$  with an onboard equilibrator and LICOR MODEL IRGA. The YSI was calibrated in moist air at sea

level just prior to sampling. Salinity was calibrated against KCl standards. Additional discrete samples were collected for dissolved organic carbon (DOC). DOC samples were filtered through Whatman GF/F filters (nominal 1  $\mu\text{m}$  pore size), stored frozen and analyzed on a Shimadzu TOC-Vcph using NPOC\_low2.met and NPOC\_low2.cal, paying careful attention to blank correction. Wind velocity and photosynthetically active radiation (PAR) were obtained from continuous measurements made and archived by the GCE-LTER program.

Next, we explain how each term in equation 2.2 was estimated for each of the 12 discrete sampling segments of the Duplin River.

### 2.2.1.2 Air-water exchange estimation

$\text{CO}_2$  and  $\text{O}_2$  air-water fluxes were estimated with the one-dimensional bulk flux equation (Wanninkhof 2014):

$$F_{\text{CO}_2} = K_H * K_T * ( p\text{CO}_{2\text{water}} - p\text{CO}_{2\text{atm}} ) \quad (\text{Eq. 2})$$

$$F_{\text{O}_2} = K_T * ( \text{DO}_{\text{water}} - \text{DO}_{\text{atm}} ) \quad (\text{Eq. 3})$$

where  $K_H$  is the  $\text{CO}_2$  solubility coefficient calculated as a function of water temperature and salinity (Weiss, 1974);  $K_T$  is gas transfer velocity as a function of wind speed at 10m above the water surface (Wanninkhof et al. 2009- eq. 36);  $p\text{CO}_{2\text{water}}$  and  $p\text{CO}_{2\text{atm}}$  are the partial pressure of  $\text{CO}_2$  of Duplin water and the atmosphere measured underway.  $\text{DO}_{\text{water}}$  is the dissolved oxygen concentration measured in water.  $\text{DO}_{\text{atm}}$  is the saturated dissolved oxygen concentration calculated from the percent saturation measured with the YSI and takes into consideration temperature and salinity.

We calculated the air-water fluxes of gases separately for when water was in-channel and over the marsh because wind speed is likely to be substantially different at the bottom of a *Spartina alterniflora* canopy versus over an open water body. Over open water, we used the

average wind speed during each dawn-dusk interval measured at the LTER meteorological station located at the mouth of the Duplin. Wind was assumed to be still ( $0 \text{ m s}^{-1}$  wind) at the air-water surface within the marsh canopy. Thus we used the intercept value for  $K_T$  when the marsh was flooded.

Areal rates of gas flux were determined taking into consideration the areas of “open water” and flooded marsh as determined from ARC-GIS and the detailed GCE-LTER vegetation corrected DEM. The “open water” surface area (Appendix A - Table 6) was determined for each segment at its mid-tide location (Appendix B) and elevation (0 MSL). The flooded marsh area (Appendix A – Table 7) was also measured for each segment based on the observed high tide level during each sampling interval. We used half of the maximum marsh area flooded to represent the average amount of marsh flooded during each 6 hours interval when water level is  $\geq 0$  MSL. Further details on calculating air-water exchange surface areas are described in Appendix A.

### **2.2.1.3 Longitudinal mixing estimation**

The longitudinal mixing or dispersion ( $M$ ) is calculated as the product of the horizontal dispersion coefficient ( $\varepsilon - \text{m}^2/\text{s}$ ), the along-stream concentration gradient ( $\delta[\text{DIC (DO)}]/\delta x$ ) and cross-sectional area  $A_c$  for each sampling segment (Eq. 2.4):

$$M = A_c * \varepsilon * \delta[\text{DIC (DO)}] / \delta x \quad (\text{Eq. 4})$$

A cross-sectional area of  $979 \text{m}^2$  was estimated from a high resolution Digital Elevation Model (Daniela et al, not published). As there is an extreme paucity of information on effective dispersion coefficients for meso-tidal salt marsh estuaries, we used the value determined by Imberger et al. (1983) for the upper Duplin River following a rainstorm freshening event and ramped it up towards the ocean as determined by Vallino and Hopkinson (1998) for the very

similar upper 15 km of the Parker River estuary using water mass tracers and hydrodynamic modeling. In our study,  $\epsilon$  ranges from 27.4 to 35.9  $\text{m}^2 \text{s}^{-1}$ , increasing downstream along the length of the Duplin. Further details are described in Appendix C.

#### 2.2.1.4 Metabolism estimation

Metabolism is calculated as the balance between the diurnal rate of change in DIC and DO concentration \* volume and air-water exchange and longitudinal mixing (Eq. 1). Following Odum's convention (1956) the balance rate of change calculated between sunset and sunrise is defined as ecosystem respiration (R) and the balance rate of change between sunrise and sunset is defined as net daytime production (NDP). NDP reflects the balance between gross primary production (GPP) and R:

$$\text{NDP} = \text{GPP} + \text{R} \quad (\text{Eq. 5})$$

Assuming the rate of R measured at night holds throughout daytime, GPP is calculated as  $\text{NDP} + \text{R}$  (during daytime hours only).

Recalling that the water in the Duplin River is our reference system, GPP is a positive number with respect to the  $\text{O}_2$  mass balance, as it adds  $\text{O}_2$  to the water, and GPP is a negative number with respect to the  $\text{CO}_2$  mass balance, as it removes DIC from the water. Similarly, R is a negative number for  $\text{O}_2$  consumption and a positive number for  $\text{CO}_2$  production.

Daily net ecosystem production (NEP) reflects the balance of GPP and R for 24 hours:

$$\text{NEP} (\text{mol day}^{-1}) = \text{GPP} * \text{Daytime hrs} + \text{R} * 24 \text{ hrs} \quad (\text{Eq. 6})$$

We report metabolism several ways:

Spatial distribution (Fig. 8&9):

- Metabolism of each segment per unit volume along the Duplin ( $\text{mol m}^{-3} \text{ day}^{-1}$ ) = Daily metabolism of each segment ( $\text{mol day}^{-1}$ )/water volume of each segment ( $\text{m}^3$ ) (Appendix A- Table 5).

Seasonal pattern (Fig. 10)

- Seasonal daily areal rates of metabolism for the entire Duplin salt marsh - estuary ( $\text{mol m}^{-2} \text{ day}^{-1}$ ) = sum of the daily metabolism for the 12 segments/ the annual averaged total water area (Appendix A)

Annually (Table 3):

- Annual metabolism for the entire Duplin River salt marsh – estuary = averaged seasonal daily areal rates \* 365 days\* the annual average total water area

The respiratory quotient (RQ,  $\text{CO}_2$  produced/  $\text{O}_2$  consumed through respiration) and photosynthetic quotient (PQ,  $\text{O}_2$  produced/  $\text{CO}_2$  consumed through primary production) were calculated for the entire Duplin seasonally using the median of values calculated for each of the 12 Duplin River water mass segments.

### **2.2.2 Estimation of the marsh contribution to entire salt marsh – estuary metabolism**

While for most of the tidal cycle and dawn-dusk interval the Duplin River water is within channel, during at least part of the tidal cycle, water floods over creek banks onto the marsh platform. Thus some aspects of marsh metabolism are incorporated into metabolism as measured in the water. To quantify the contribution that the marsh makes to the entire Duplin River marsh-estuary ecosystem metabolism, we separately measured the net horizontal transport flux of DIC and  $\text{O}_2$  and estimated air-water exchange during marsh inundation. The balance between the net transport and the air-water exchange is a measure of marsh metabolism. We extrapolated results

for the single tidal creek study to the entire Duplin salt marsh – estuary by taking into consideration the relative areas of marsh flooded during our seasonal sampling trips.

### 2.2.2.1 Horizontal transport of DO and DIC

The net horizontal transport of DIC and DO in and out of the small tidal creek that floods the flux tower marsh platform,  $Q_{M-H}$ , is estimated as the product of water transport ( $m^3 s^{-1}$ ) and [DIC] or [DO] over an entire tidal cycle.

$$Q_{M-H} = \int_{LT_1}^{LT_2} [DIC (DO)](t) * \text{transport} (t) * dt \quad (\text{Eq. 7})$$

Where LT1 and LT2 are the times when a tidal cycle started at the first low tide and ended at the next low tide. Samples for DO and DIC concentration analysis were collected at the mouth of the tidal creek ½-hourly for a complete tidal cycle, the day after the Duplin dawn-dusk transects were conducted. In the winter we conducted a second flux study when tides were higher (March 18), because less than 10% of the marsh was flooded during the February trip. Tidal creek sampling was conducted only when high tide occurred during daylight.

Water transport was determined as the quarter-hourly changes in water storage (ArcMap) in the tidal creek and its catchment over a complete tidal cycle. Water transport in the thalweg of the tidal creek was measured with an ADCP, but because it missed water entering the catchment directly from the Duplin via overbank, marsh sheetflow flooding, we considered the approach inadequate for our purposes.

The ARCMAP 10.2.2 Surface Volume Functional Surface Tool was used to estimate volume for 15 minute records of tidal height within the tidal creek catchment. The catchment boundaries were defined by field surveys of where adjacent creek waters met at high tide for the northern and eastern boundary, by the top of the natural levee along the Duplin River to the west, and by a location midway to the adjacent tidal creek to the south. The change in volume over 15

minutes was used to develop water transport as a function of tidal stage, transport(t) in Eq. 7. Our ARC map layers were the high precision (2 cm), vegetation corrected (Hladik et al. 2013) Duplin River marsh DEM and water levels recorded in the flux tower tidal creek (GPS surveyed and tied into local MSL) by the GCE-LTER.

### 2.2.2.2 Vertical air-water transport of CO<sub>2</sub> and O<sub>2</sub>

The vertical transport  $Q_{M-v}$  was estimated as the product of air-water flux over the tidal creek ( $F_{tc}$ ) and the inundated marsh area ( $A_{tc}$ ) over an entire tidal cycle:

$$Q_{M-v} (\text{mol tide}^{-1}) = \int_{LT_1}^{LT_2} F_{tc}(t) * A_{tc}(t) * dt \quad (\text{Eq. 8})$$

$F_{tc}$  was estimated the same way as described in Eq. 2&3, except that, rather than measure pCO<sub>2</sub>, we calculated it with the online CO<sub>2</sub> system calculation tool---CO2SYS\_V2.1.xls with measured DIC and Alk from the discrete water samples collected ½ hourly during the rising and fall tide. We assumed still winds at the base of the marsh grass canopy in our calculation of the gas transfer velocity,  $K_T$ . The inundated area  $A_{tc}$  as a function of tidal stage was also determined with the ARCMAP 10.2.2 Surface Volume Functional Surface Tool with 15 minute records of tidal height within the defined catchment.

### 2.2.2.3 Metabolism of inundated marsh

The net daytime production,  $NDP_{\text{marsh}}$ , of the inundated marsh (including platform, creek bank, and water components) was calculated as the net tidal horizontal transport of DIC or DO from the tidal creek catchment ( $Q_{M-l}$ ) corrected for the vertical air-water transport ( $Q_{M-v}$ ).

$$NDP_{\text{marsh}} = Q_{M-H} + Q_{M-v} \quad (\text{Eq. 9})$$

Areal rates of lateral transport, vertical transport and metabolism were calculated by dividing  $Q_{M-H}$ ,  $Q_{M-v}$  and  $NDP_{\text{marsh}}$  by the average flooding area of tidal creek catchment during each sampling trip. The average was calculated as ½ the maximum area flooded for each sampling

tide: 2600, 21500, 11000, 21800, 21500 m<sup>2</sup> for Feb, Mar, May, Aug, Oct, respectively. To express the relative contribution of marsh NDP to metabolism of the entire Duplin salt marsh – estuary, we scaled results on the basis of 2 flood tides per day and the relative extent of marsh in the flux tower creek catchment compared to the area of marsh flooded by “resident” water for the entire Duplin.

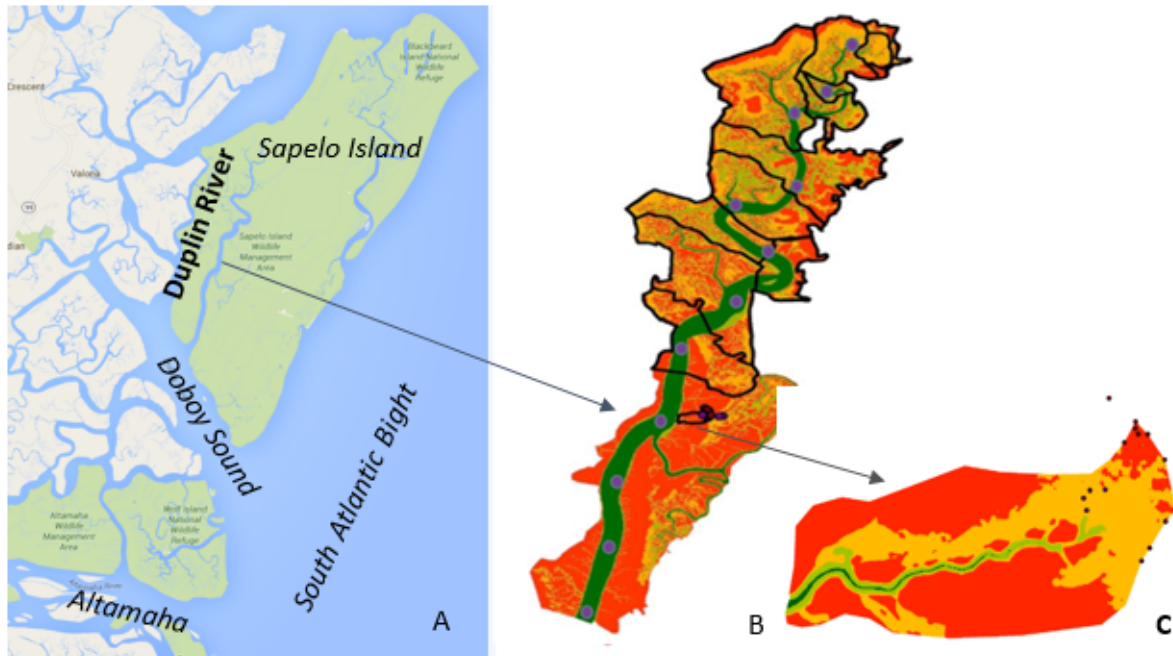


Figure 1: Study site and sampling stations. A. Sapelo Island, B. the Duplin River and its salt marsh catchment: The low-tide locations (purple dots on green river) and mid-tide catchment (black catchment lines crossing green river) of the 12 water masses we sampled. The black lines define the catchment boundaries for each water mass when they flood the marsh at high tide. C. Flus tower tidal creek and its marsh catchment: Dots to the far right show where GPS sampling confirmed catchment boundaries. Dots near the head of the creek show the end of the boardwalk that accesses the eddy covariance flux tower. The color scheme shows elevation in 4 categories: dark green: -5 to 0 m, light green: 0 to 0.80 m; orange: 0.80 to 0.94 m, red: 0.94 to 1.2 m.

## CHAPTER 3

### RESULTS

#### **3.1 Environmental conditions during the study**

Our sampling design enabled us to capture the full seasonal range of metabolically significant physical and ecological drivers likely to control ecosystem metabolism in the Duplin River system (Table 1). Water temperatures during our sampling trips were within a standard deviation of the 10-yr seasonal averages for each season, ranging from a low of 13.6 °C in winter (Feb) to a high of 30.0 °C in summer (Aug). Similarly, we captured the full seasonal range in solar insolation, although being less than average during our cloudy February sampling (11.7 mol m<sup>-2</sup>d<sup>-1</sup>) and slightly above average during our cloud-free May sampling (44.8 mol m<sup>-2</sup>d<sup>-1</sup>). Variations in salinity reflect primarily variations in Altamaha river discharge. Wind speed was low and stable for our trips with a mean value of 3.0 ± 0.4 m s<sup>-1</sup>, compared to the ten-year mean value of 3.8 ± 0.5 m s<sup>-1</sup>. Chlorophyll-*a* concentrations ranged from a seasonal low of 6.9 ug l<sup>-1</sup> in February to a high of 13.6 ug L<sup>-1</sup> in May and were within a standard deviation of the 10-yr mean for each season. DOC concentrations were similar to previous reports (Sottile, 1973; Imberger et al. 1983) showing little annual variation (323 to 428 μM DOC). There are no long-term data available for DOC in this system. The close adherence to seasonal trends observed through long-term monitoring suggests that carbon and oxygen dynamics and ecosystem metabolism we observed over the course of 2014 are typical and adequately captured seasonal patterns.

### 3.2 Seasonal and spatial patterns for DIC and DO

We observed similar spatial, seasonal and diurnal patterns for pCO<sub>2</sub> and DIC along the length of the Duplin River that were inverse the patterns for DO. The DIC distribution along the Duplin River was similar during all months (Fig. 2): typically increasing with distance upriver and away from the ocean especially in the final kilometer. Overall, levels were lowest in the coldest month (February), increasing from about 1600 - 1700 μmol L<sup>-1</sup> at the mouth to 1850-1950 μmol L<sup>-1</sup> at the head. Concentrations of DIC reached their highest levels in the warmest months (August and October), increasing from about 2200-2350 μmol L<sup>-1</sup> at the mouth to as high as 2650 μmol L<sup>-1</sup> at the head. There was also a strong diurnal signal, with values highest just after sunrise and lowest in late afternoon at sunset. The diurnal range in values was least in February (25-100 μmol L<sup>-1</sup>) and greatest in August (up to 300 μmol L<sup>-1</sup>). The diurnal range was also greater at the head of the estuary than it was near the mouth. The positive up-estuary gradient in DIC shows that the estuary is a source of DIC to the coastal ocean. The increase in diurnal amplitude up-estuary suggests that metabolic activity increases up the estuary and during the warmer months of the year.

Duplin pCO<sub>2</sub> had spatial, diel and seasonal patterns similar to DIC (Fig. 3). Overall pCO<sub>2</sub> levels were lowest in the coldest month (February), increasing from about 500 ppm at the mouth to 3000 ppm at the head, and highest in the warmest month (August), increasing from 3500 ppm at the mouth to 7500 ppm at the head. The diel difference in pCO<sub>2</sub> was most prominent in May and August and least prominent in February. Throughout the year, pCO<sub>2</sub> levels for all stations were higher than in the atmosphere (400 ppm), showing that waters of the Duplin River estuary were a net source of CO<sub>2</sub> to the atmosphere year round.

DO distributions were typically inverse those observed for inorganic carbon (Fig. 4). For most transects, DO typically decreased with distance upriver and away from the ocean especially in the last kilometer and for sunrise transects. For each station, the diurnal range was greater at the head of the estuary than it was near the mouth. The 100% saturated DO levels along river varied by month and with distance upriver in accordance with seasonal patterns in temperature and salinity (Table. 1). Duplin water was under-saturated in DO year-round especially upriver and during the warmest month of the year (August - <10% of saturation). The annual and diurnal spatial patterns of DO under-saturation suggest that the Duplin River is a net sink of atmospheric O<sub>2</sub> year round and that metabolic activity increases up the estuary and during the warmest months of the year.

### **3.3 DIC and DO tidal exchange in the flux tower creek**

DIC concentrations in the flux tower tidal creek varied substantially over a flood-ebb tidal cycle but minimally from season to season (Fig. 5-a). During all seasons the tidal pattern was similar: high DIC concentration at low tide (ranging from 2500  $\mu\text{mol L}^{-1}$  in March to 4300  $\mu\text{mol L}^{-1}$  in August), a sudden drop as creek bank drainage water was replaced with low DIC water flooding in from the Duplin, low concentrations near high tide (ranging from 1500  $\mu\text{mol L}^{-1}$  in Feb to 2250  $\mu\text{mol L}^{-1}$  in October), and a slow continual rise during ebbing tide back to initial levels. The greatest difference between high and low tide DIC concentrations was in August when metabolism of the flooded marsh community was expected to be most active. We note that the marsh platform is typically completely drained within 3 hours of high tide, thus much of the DIC draining during the final stages of the ebb tide likely originates from drainage of creek bank pore waters (*sensu* Gardner and Gaines, 2008). The total length of creekbank edge upstream of where we collected samples is 862 m.

Calculated pCO<sub>2</sub> levels in tidal creek water showed tidal and seasonal patterns similar to DIC (Fig. 5-b). pCO<sub>2</sub> values in the tidal creek dropped rapidly as Duplin River water entered the tidal creek, remained relatively low during high tide and then rebounded during marsh platform and creek bank pore water drainage. The change between low tide and high tide was most prominent in August and least prominent in February. Overall pCO<sub>2</sub> levels were lowest in the coldest month (February), ranging from 500 ppm at high tide to 4000 ppm at low tide, and highest in the warmest month (August), ranging from 1600 ppm at high tide to 12000 ppm at low tide. Throughout the year, pCO<sub>2</sub> levels in the tidal creek were higher than in the atmosphere (400 ppm), showing that tidal creek water was a net source of CO<sub>2</sub> to the atmosphere, especially the final portion of water draining from creek banks in the summer.

The seasonal and tidal patterns of DO concentrations in the flux tower creek were typically inverse those observed for DIC and pCO<sub>2</sub> (Fig. 5-c). For each sampling month, the low DO concentration at low tide typically had a sudden jump as high-DO water flooded into and onto the marsh from the Duplin. The pattern thereafter varied seasonally, sometimes reaching highest levels prior to high tide near midday (e.g., May and August) and sometimes several hours after high tide, as in October. As with inorganic carbon, DO slowly returned to initial low tide values. Only once during our study did we observe super-saturated levels of DO in tidal creek water. In October concentrations increased after high tide reaching a level of 240 μmol L<sup>-1</sup> (vs a saturation level of 220 μmol L<sup>-1</sup>). Total PAR reaching flood tide waters was higher in October than any other month. During the October trip the timing of high tide most closely coincided with peak PAR at midday and the October trip was cloud-free.

### 3.4 Water transport estimation in the flux tower creek

Volume transport and catchment area flooded were directly related to high tide water level (Table 2). High tide water levels and the resultant areal extent of marsh flooded varied substantially during our 5 sampling trips. In February high tide reached just over 0.8 m (MSL), while in March it exceeded 1.3 m (MSL). The amount of marsh flooded increases rapidly once water level reaches the marsh platform at about 0.8 m (MSL). With a 0.84 m water level in February only 4494 m<sup>2</sup> of marsh flooded, while at 0.95 m in May over 20,000 m<sup>2</sup> flooded. Once water level reached about 1.2 m, the entire tidal creek catchment of 43,327 m<sup>2</sup> flooded. This occurred in March, August and October.

Water transport volumes in the flux tower tidal creek was proportional to water level and ranged from as little as 1,132 m<sup>3</sup> per flood and ebb tide in February to 18,341 m<sup>3</sup> in March. Transport was twice as high in May (2,282 m<sup>3</sup>) as in February and was 10,229 and 11,617 m<sup>3</sup> in August and October (Table 2).

With each tidal cycle, there is a complete draining of all water that enters during flood tide, thus there is a zero net flux of water for a tidal cycle. The exception to this would be if there was significant evaporation or rainfall during the tidal cycle. Under certain wind conditions it is also likely that flux tower tidal creek water mixes with water from adjacent tidal creeks. However all our observations were conducted on relatively low wind days, so exchange with adjacent creeks was likely minimal.

Table 1. Physical and ecological conditions observed in the Duplin River salt marsh – estuary in 2014. Seasonal means and standard deviations were calculated by averaging 2002-2011 monthly water quality, meteorological, and nutrient data collected at either Marsh Landing (Station 0) or Hunt Dock (between Stations 8 & 9) by the Sapelo Island NERR and the GCE-LTER. In situ data were collected for our four field trips. Where data are available for multiple stations, values reported represent the arithmetic mean.

Sampling Season	Sampling Month	Salinity Psu (In situ)	Water Temp °C		PAR mol m <sup>-2</sup> day <sup>-1</sup>		Wind Speed m s <sup>-1</sup>		Chl µg L <sup>-1</sup>		DOC µmol L <sup>-1</sup>
			Seasonal Mean	In Situ	Seasonal Mean	In Situ	Seasonal Mean	In Situ	Seasonal Mean	In Situ	In Situ
Winter	Feb	21.3	12.8±2.4	13.6	19.3±3.7	11.7	3.6±0.6	3.4	8.3±1.9	6.9	323
Spring	May	19.2	20.3±4.1	23.2	36.7±6.7	44.8	3.9±0.5	3.3	7.4±1.4	13.6	380
Summer	Aug	26.8	29.0±1.5	30.0	38.3±5.6	35.8	3.8±0.4	2.9	11.9±2.7	10.2	428
Fall	Oct	28.9	22.6±4.6	22.8	26.1±5.8	33.3	3.7±0.5	2.6	7.9±1.4	8.6	375

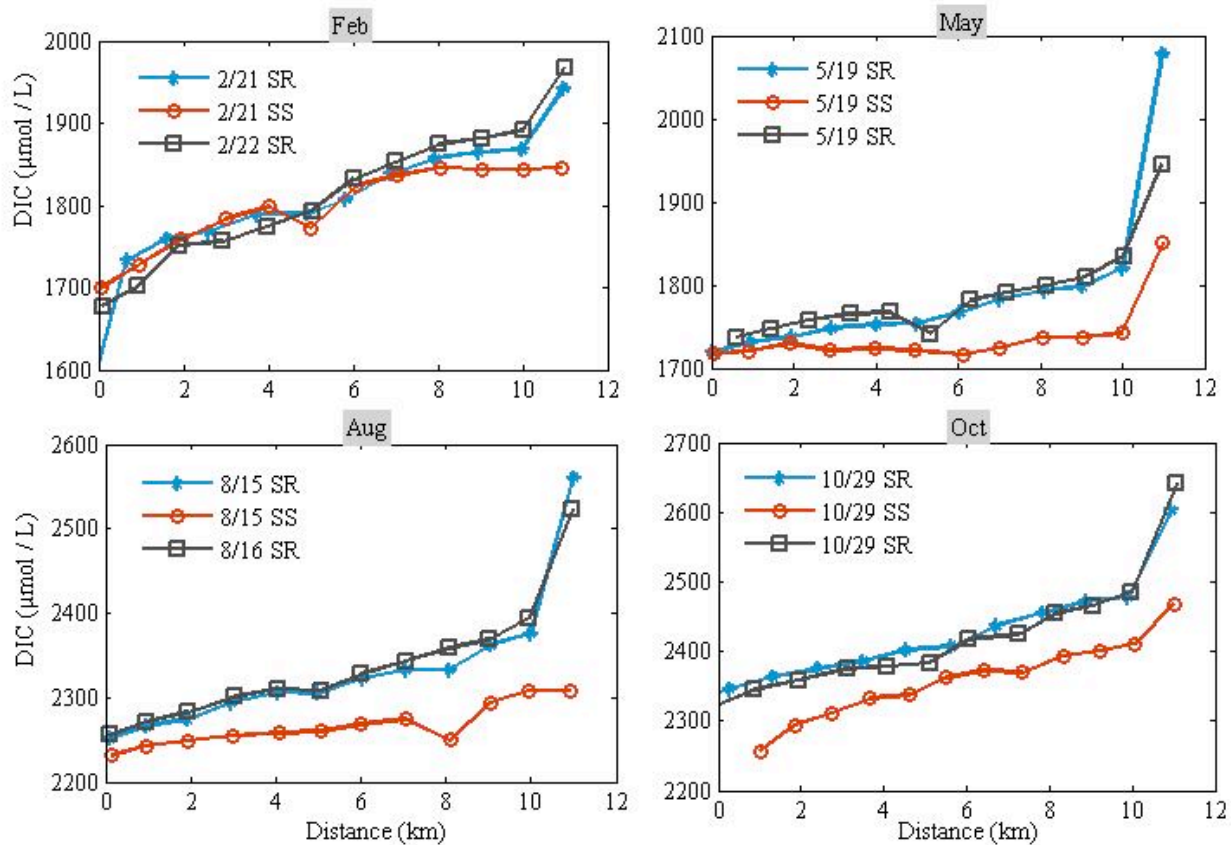


Figure 2: Diurnal DIC distribution along the Duplin estuary for each season: For each trip, measurements were taken at sunrise, sunset and the next sunrise at twelve stations equally spaced along the river.

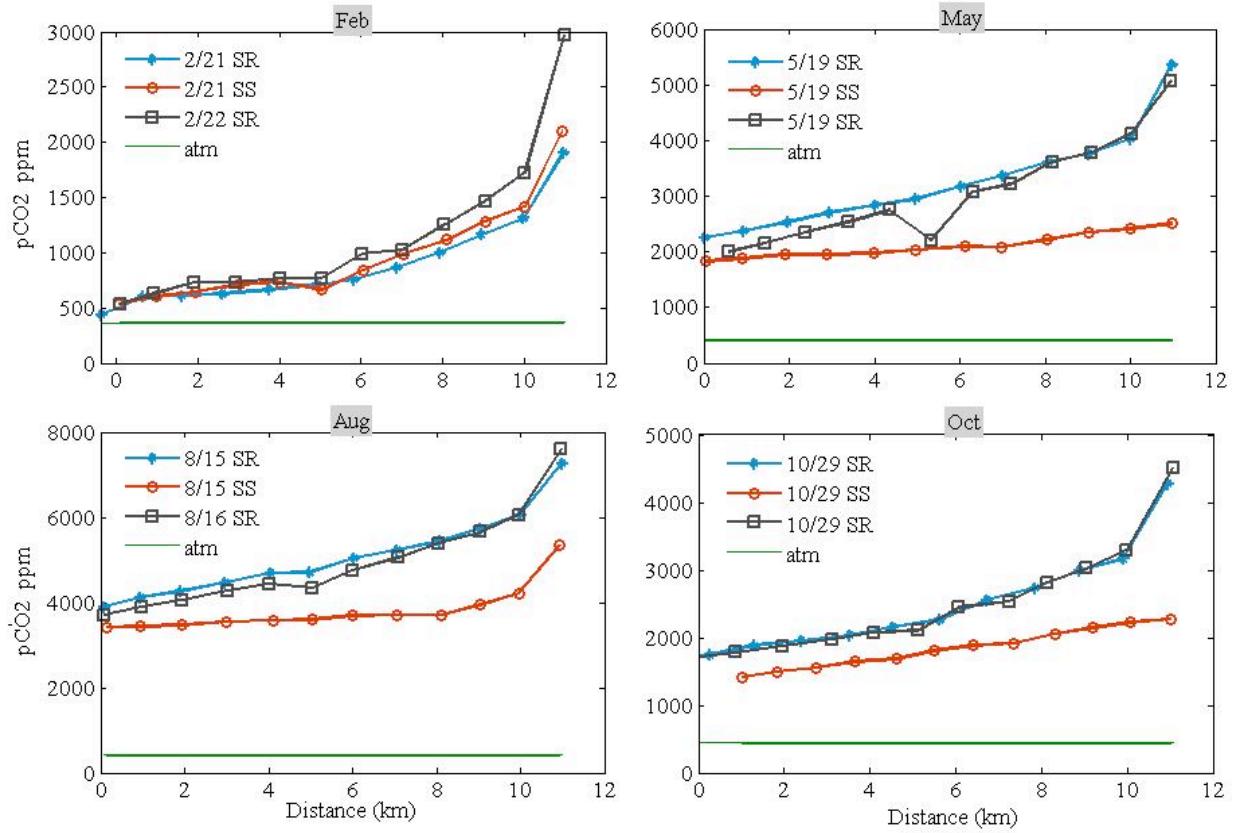


Figure 3: Diurnal pCO<sub>2</sub> distribution along the Duplin estuary for each season: Green line is the average measured pCO<sub>2</sub> level in the atmosphere.

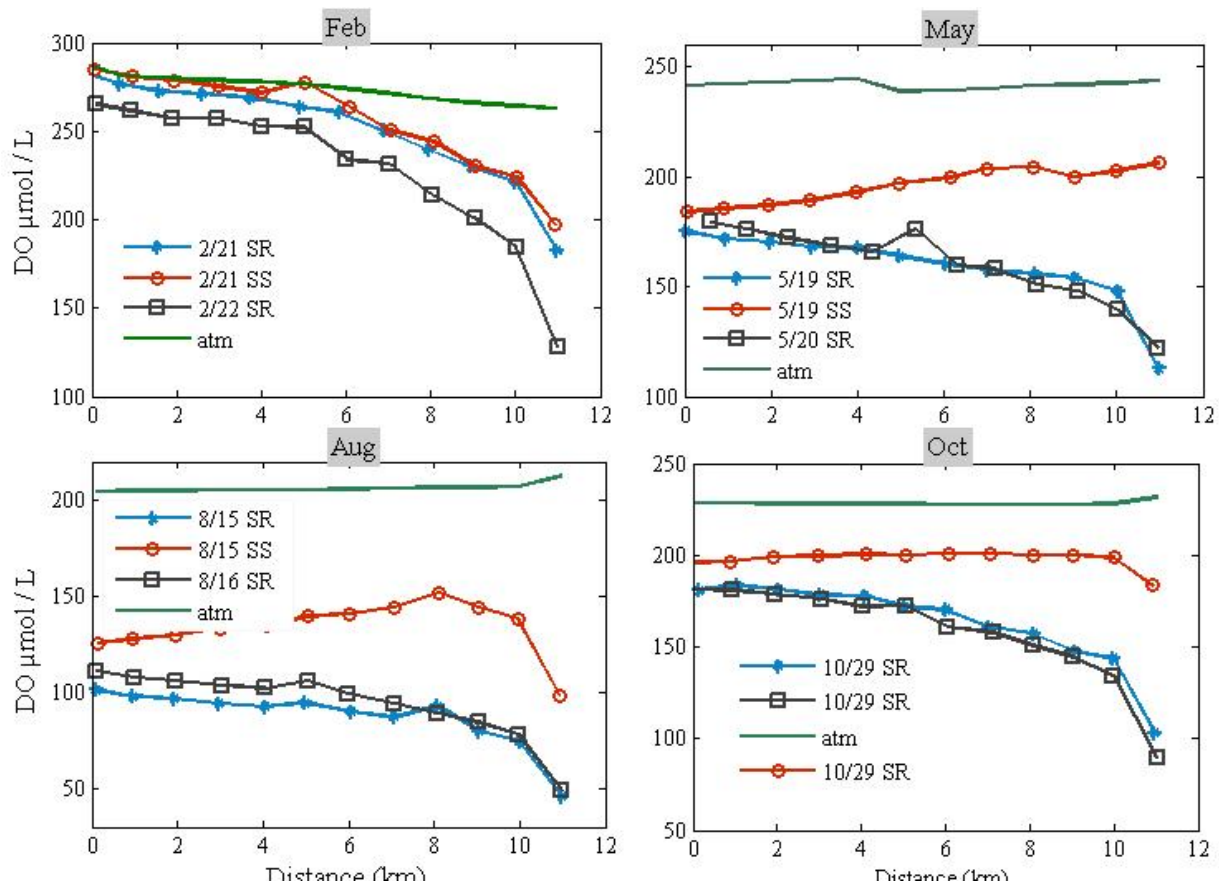


Figure 4: Diurnal O<sub>2</sub> distribution along the Duplin estuary for each season. Green line is the 100% saturated DO level in the atmosphere.

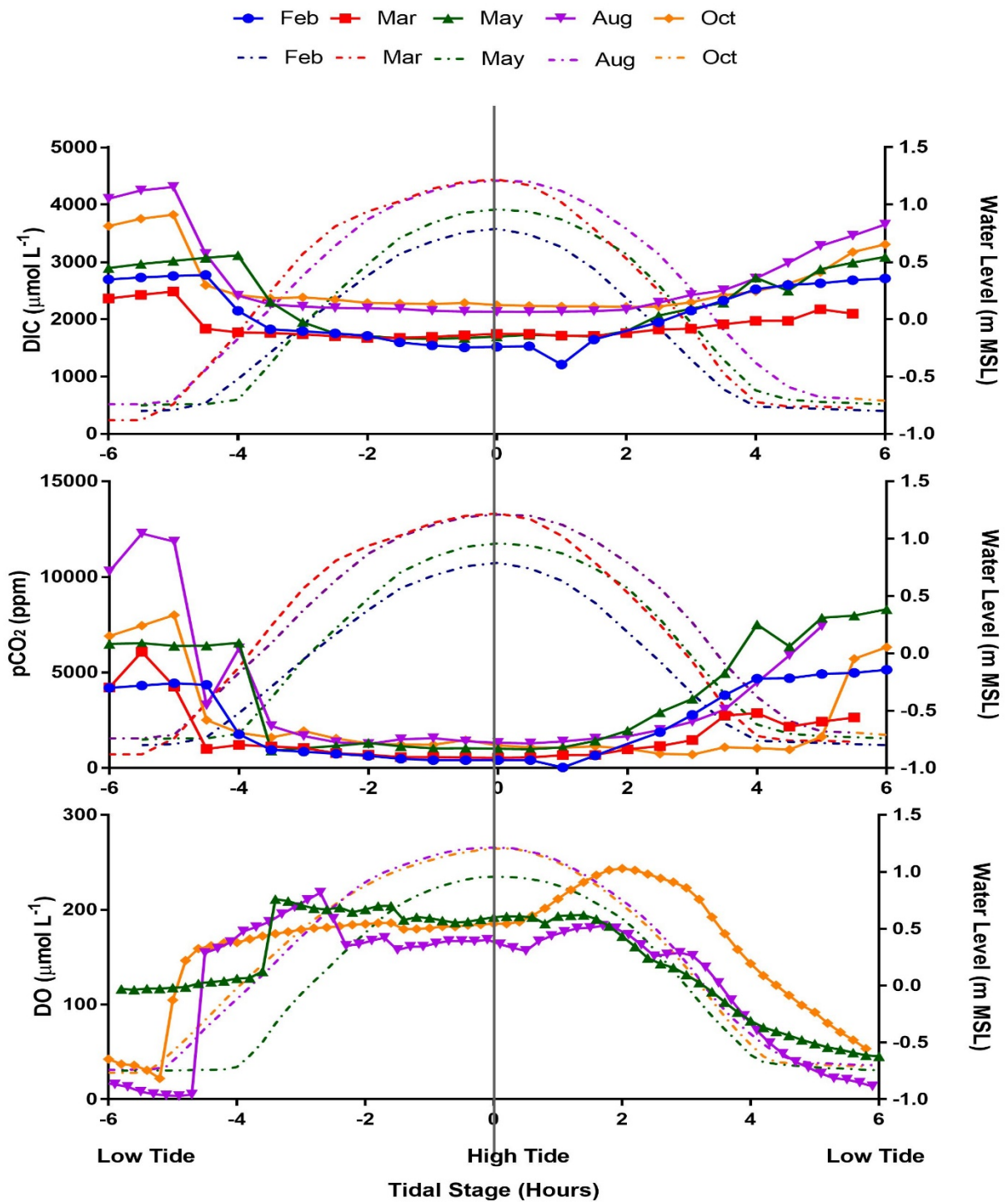


Figure 5. Water levels and DIC, pCO<sub>2</sub> and DO concentrations over a tidal cycle at the flux tower creek: Water depth is relative to 0 m MSL. The elevation of the marsh platform here ranges from about 0.8 to 1.2 m. At levels less than 0.8 m, all water is confined within the tidal creek, which is up to 20 m wide and heavily vegetated except for about a 2 m wide thalweg. We did not collect DO data in February and March.

Table 2. Water level, volume transport and flooded area estimation for the flux tower tidal creek

Month	High Tide Water depth (m)	Flood/Ebb Volume (m <sup>3</sup> )	Max Flood Area (m <sup>2</sup> )
Feb	0.84	1132	4494
March	1.34	18341	43327
May	0.95	2282	20178
Aug	1.17	10299	43327
Oct	1.20	11617	43327

## CHAPTER 4

### DISCUSSION

#### 4.1 Air-water exchange

The spatial distribution of air-water fluxes was similar to that for the along-estuary distribution of pCO<sub>2</sub> and DO concentrations, with increasing exchange rates from the mouth to headwaters (Fig. 3&4). The seasonal pattern of air-water exchange was similar for the two gases: strongest in August and weakest in February (Fig. 6). The seasonality reflects the deviation from saturation values, which in turn is related to the balance between mixing and ecosystem metabolism. Deviation from saturation values is greatest in summer and least in winter (Fig 3&4) because of the effect of temperature on solubility and temperature and light on rates of photosynthesis and respiration.

We calculate that areal gas exchange rates from channel water (-0.7 ~ -5.5 mmol CO<sub>2</sub> m<sup>-2</sup> hr<sup>-1</sup>, 0.6 ~ 4.5 mmol O<sub>2</sub> m<sup>-2</sup> hr<sup>-1</sup>) are higher than from flooded-marsh water (-0.6 ~ -3.9 mmol CO<sub>2</sub> m<sup>-2</sup> hr<sup>-1</sup>, 0.5 ~ 3.7 mmol m<sup>-2</sup> hr<sup>-1</sup>) (Fig. 6 -a,c). This is a direct result of our assumption that wind speeds within the marsh canopy during marsh flooding are still, thus the gas transfer velocity, K<sub>T</sub>, used to calculate air-water exchange is low (the wind speed vs K<sub>T</sub> intercept value) and invariable with respect to wind velocity.

DO and CO<sub>2</sub> fluxes are almost mirror images for each other – CO<sub>2</sub> to atmosphere and O<sub>2</sub> to the Duplin River. On average rates of CO<sub>2</sub> flux are about 20% higher than for O<sub>2</sub>, ranging from as little as 6% to as high as 30%. This near balance of O<sub>2</sub> and CO<sub>2</sub> fluxes in estuaries with high pCO<sub>2</sub> was also observed in the marsh-dominated Satilla River estuary (Cai and Wang 1998;

Cai et al. 1999). In low pCO<sub>2</sub> estuarine and coastal waters, this is often not the case (Omstedt et al. 2014; Zhai et al. 2009).

The seasonal pattern of the total air-water exchange of CO<sub>2</sub> and DO followed the same seasonal pattern observed for areal rates in either marshes or channel waters, but the relative importance of gas fluxes over the marshes and open channel waters differs (Fig. 6 -b,d). This is because the flux when water is over the marsh reflects not only the amount of time the marsh was flooded but also the absolute area of marsh flooded. This changes as a function of tide height, which varies twice daily, forth-nightly in conjunction with the spring-neap tidal cycle and seasonally in relation to coastal climatology. Marsh surface water accounted for 14%-36% of the total CO<sub>2</sub> flux and 16%-39% of the total O<sub>2</sub> flux depending on corresponding areal gas exchange rate and inundation area and duration. Considering the relative importance of this process and that occurs for such a short interval but over such a large area, it is remarkable how limited our understanding is of the mechanisms controlling gas exchange from flooded wetland surfaces. Although our equation for transfer velocity includes a nonzero intercept to account for the K<sub>T</sub> in a zero-wind speed situation, it is still insufficient to capture processes such as canopy characteristics (Lightbody & Nepf 2006), buoyancy (McGillis et al., 2004), surface water turbulence (Zappa et al. 2007), rain (Ho, 2004), etc, that may dominate vertical gas transfer in a non-wind condition. Future studies on generating models based on non-wind factors would enable us to better understand gas flux across the air-water boundary for a wetland.

Annually, the entire Duplin system degassed  $7.4 \cdot 10^7$  mol yr<sup>-1</sup> of CO<sub>2</sub> to the atmosphere and absorbed  $6.1 \cdot 10^7$  mol yr<sup>-1</sup> of O<sub>2</sub> from the atmosphere, of which one third of these fluxes occurred over the inundated marsh water surface (Fig. 13). To express these fluxes in mol m<sup>-2</sup> yr<sup>-1</sup>

<sup>1</sup>, 18 mol CO<sub>2</sub> m<sup>-2</sup> yr<sup>-1</sup> was lost and 15 mol O<sub>2</sub> m<sup>-2</sup> yr<sup>-1</sup> was gained across the entire Duplin's air-water surface.

#### 4.2 Mixing with coastal water

The Duplin estuary exported DIC and imported DO to and from Doboy Sound and the coastal ocean during each sampling trip in all four seasons of the year (Fig. 7). The Duplin exported DIC at high rates in February and October to Doboy sound (10.3 \*10<sup>4</sup> mol day<sup>-1</sup> and 15.1\*10<sup>4</sup> mol day<sup>-1</sup>) and at lower rates in May and August (2.8 \*10<sup>4</sup> mol day<sup>-1</sup> and 3.4 mol \*10<sup>4</sup> day<sup>-1</sup>) (Fig. 7-a), reflecting the seasonal variation in the along-estuary DIC gradient (Fig. 2). The Duplin imported DO from Doboy sound and coastal water year round, but to a much lower extent compared to DIC export (Fig. 7 - b), ranging from 0.02 \*10<sup>4</sup> mol day<sup>-1</sup> in August to 1.0 \*10<sup>4</sup> mol day<sup>-1</sup> in February. While the seasonality was similar for DIC and O<sub>2</sub>, they differed by at least an order of magnitude. This inconsistency in the mixing of the two gases with coastal water is interesting and requires further study. We note that as the air-water flux of CO<sub>2</sub> and O<sub>2</sub> dominates the total exchange with adjacent systems (atmosphere and oceanic water), the combined total exchange does not disagree greatly. We suggest that this inconsistency is a result of a greatly imbalanced ratio of air-water exchange surface (channel and flooded marsh 4.1 \* 10<sup>6</sup> m<sup>2</sup>) relative to a very limited channel cross-sectional area through which mixing occurs (979 m<sup>2</sup>).

The temporal pattern of mixing of DIC and DO is opposite in direction to the air-water flux (Fig. 7). This pattern may reflect the balance between metabolism, air-water exchange and mixing. Net ecosystem metabolism (NEP) should have a similar seasonal pattern as air-water flux since they are both mainly driven by temperature variation. Thus air-water flux dominates total system loss or gain of the metabolic gas, whereas the lateral transport to coastal water

reflects the residual after correcting for the vertical transport. This may partially explain why the lateral transport showed the opposite temporal pattern to air-water flux. Another explanation for the high DIC export relative to DO import in February could be related to the strong DIC and O<sub>2</sub> gradients in February as a result of high Altamaha River discharge and concomitantly low DIC and high O<sub>2</sub> concentrations. However, this cannot explain the high DIC export in October.

Integrated annual DIC export from the Duplin River to the coastal ocean was estimated as  $2.9 \times 10^7 \text{ mol yr}^{-1}$  (Fig. 13), which is about three times higher than a previous estimate of  $0.96 \times 10^7 \text{ mol yr}^{-1}$  (Wang, 2003). Our more accurate estimation of cross-sectional area for the Duplin mouth (979 m<sup>2</sup> vs Wang's 654 m<sup>2</sup> from Imberger, 1983) and our refined model of how dispersion increases along the length of the Duplin estuary (vs a uniform and lower  $\epsilon$  from Imberger (1983) certainly contribute to the difference in estimates. In addition our estimate of the concentration gradient is based on the concentration between adjacent water masses at the mouth of the Duplin, whereas Wang and Cai used a gradient that ranged from the upper reaches of the Duplin at low tide to the oceanic water at the mouth of the Duplin at high tide.

The combined air-water exchange and horizontal diffusive mixing flux of TCO<sub>2</sub> from the Duplin system was  $25 \text{ mol m}^{-2} \text{ yr}^{-1}$  of CO<sub>2</sub> to adjacent systems, of which 72% was to the atmosphere and 28% was to the coastal ocean. The gain of O<sub>2</sub> from adjacent oceanic and atmospheric systems was  $15 \text{ mol m}^{-2} \text{ yr}^{-1}$ , which is smaller than the loss of CO<sub>2</sub>, mainly due to the much lower longitudinal mixing of O<sub>2</sub>. The total loss of TCO<sub>2</sub> from the Duplin salt marsh estuary is about two times larger than the  $8.3 \text{ mol m}^{-2} \text{ yr}^{-1}$  estimated for the York River estuary, within the Chesapeake Bay system (Raymond, 2000). This may reflect the much smaller ratio of marsh to river area and the greater freshwater input in the York compared to the Duplin. However, the degassing flux in the Duplin River is similar to that of the upper and mid parts of

the Satilla River estuary, a Georgia riverine estuary with a similarly large marsh to open water ratio but a much greater freshwater input (Cai and Wang 2003).

### **4.3 Metabolism of the Duplin salt marsh-estuary**

#### **4.3.1 Communities of the salt marsh-estuary that contribute to metabolism as measured with the open water approach**

The environment that contribute to the metabolism measured by the open water approach include the water column and permanently flooded subtidal benthos and the intermittently flooded intertidal flats and creek banks below mean sea level and the marsh creek banks and marsh platform above mean sea level. Autotrophic communities include phytoplankton in the water column, benthic micro algae on creek bottoms, banks and marsh platform and perhaps those portions of emergent marsh macrophytes that are flooded at high tide. Communities that contribute to respiration other than the autotrophs include heterotrophic plankton and mobile macrofauna in the water column, benthos of creek bottoms, creek banks and marsh surface, aufwuchs associated with live and dead-standing marsh macrophytes and perhaps flooded portions of marsh macrophytes. Quite likely the open water technique measures some aspects of intertidal marsh respiration that occurs even when the marsh is not flooded, as DIC, DOC and other dissolved metabolites (e.g.,  $\text{HS}^-$ ) that build up to extremely high concentrations in marsh sediments (Koretsky, et al. 2000, Neubauer and Anderson 2003) diffuse into overlying flood waters during high tide or drain from creekbanks into creek waters at low tide (Raymond and Hopkinson 2003, Gardner and Gaines 2008). Our definition of aquatic salt marsh-estuarine metabolism needs to include not only estuarine water bodies and their sediments, but also some portion, in space and time, of the intertidal marshes. This blending of the marsh with estuarine

creeks, bays, and sounds blurs the lines between how salt marsh estuaries have been conceptualized historically in text books and the literature.

#### **4.3.2 Spatial and seasonal patterns of metabolism along the Duplin**

There was a pronounced spatial pattern of metabolic activity that held from season to season for both CO<sub>2</sub> and DO approaches (Fig. 8 & 9): community respiration and gross primary production typically increased 2-5 fold and uniformly with distance along the Duplin, then abruptly increased up to 10-fold in the final kilometer. Exceptions to this pattern were seen in October for CO<sub>2</sub>-based metabolism, where GPP and R actually decreased along the 4.5 km from the mouth of the estuary, then increased until the final station. Such results were not seen with oxygen however as metabolism increased 2-3 fold up-estuary in October. The upstream enhancement of metabolism most likely reflects gradients in marsh density (marsh area/ channel water area, see Cai et al. 1999), temperature, inorganic nutrient concentrations, DOC, and chlorophyll-a (Pomeroy and Wiegert 1981). Water residence time is also longer in the upper estuary, which promotes the accumulation of materials upstream. The marsh has been shown previously to be a source of DOC and DIC to estuarine waters (Peterson et al. 1994, Sottile 1973, Imberger 1983, Cai and Wang 2004), which is likely to be enhanced in the upper portion of the Duplin River where the drainage density of tidal creeks and flooding extent is highest (Frey and Basan 1978, Wadsworth 1980). Along the Duplin, R was consistently greater than GPP indicating that the system was heterotrophic during all seasons. Thus, more CO<sub>2</sub> was produced than consumed and vice versa for DO— more O<sub>2</sub> consumed than produced. These patterns are consistent with our observations that the Duplin was a source of CO<sub>2</sub> to the atmosphere and a sink for O<sub>2</sub>, and thus dependent on allochthonous organic matter to fuel the respiration in excess of GPP.

An exception to the pattern of increasing GPP with distance up estuary was seen at the upper- most station (Fig. 8 & 9). GPP became negative (CO<sub>2</sub> production and O<sub>2</sub> consumption) during 2 seasons for CO<sub>2</sub> and 3 seasons for DO. This is unexpected and unrealistic. It occurred during the warmer times of the year, which leads us to suspect a diurnal temperature effect on respiration as described by Tobias et al. (2007) using oxygen stable isotopes – enhanced during the day when flooding a hot marsh surface exposed to full sunlight and reduced at night, when tidal water likely cooled during marsh inundation. The open water approach calculates GPP as NDP measured during the day adjusted for respiration measured at night. If temperature enhances respiration during the day, then we underestimate the respiratory correction of NDP. We timed our field trips so that our dawn sampling was close to low tide, thus high tide would have occurred when marsh surface temperatures were greatest. This effect was seen only in the final kilometer of the Duplin, because the entire low tide volume of that reach moves onto the marsh at high tide. Only a fraction of the main channel water volume moves onto the marsh surface at stations further downstream, as most of the water movement is up and down the channel of the Duplin. We note however, that NDP and NEP are not biased by the applicability of the night time respiration assumption as both are measured directly as the residual change in CO<sub>2</sub> or DO during the daytime and 24 hours respectively without applying nighttime measures of R to estimate daytime gross production.

#### **4.3.3 Integrated seasonal pattern of metabolism**

The metabolism of the Duplin marsh-estuary reflected seasonal patterns for GPP, R, and NEP: maximal during warmer months and minimal during the colder months (Fig. 10). GPP was highest in summer and fall ( $-0.10\sim-0.13 \text{ mol m}^{-2} \text{ day}^{-1}$ ) and lowest in winter ( $-0.01 \text{ mol m}^{-2} \text{ day}^{-1}$ ) as expected, as photosynthesis is typically positively related to light intensity and temperature

(Whitney, 1983; William, 1962; Darley, 1981). GPP was positively related to temperature ( $R^2=0.58$ ) and PAR ( $R^2=0.43$ ). Respiration peaked in August in response to the higher temperature and DOC availability (Table. 1). Regression analysis showed that R is positively related to temperature ( $R^2=0.86$ ) and DOC ( $R^2=0.82$ ), which is consistent with previous studies showing that respiration rate in marshes and estuaries is regulated by temperature and labile carbon availability (Pomeroy, 2000). NEP was always net heterotrophic - highest in August ( $0.06 \text{ mol CO}_2 \text{ m}^{-2} \text{ day}^{-1}$ ) and lowest February ( $0.02 \text{ mol CO}_2 \text{ m}^{-2} \text{ day}^{-1}$ ).

The seasonal pattern of metabolism calculated from DO was typically inverse that calculated by DIC and showed similar spatial and temporal trends, albeit at lower rates (Fig. 10). The metabolic rates calculated by DO were usually 30%-50% lower than DIC, except for February, when rates based on DO were almost 3 times higher. This could partially be due to our underestimation of the air-water gas exchange coefficient when intertidal marshes are flooded. This would affect  $\text{O}_2$  measures of metabolism more than  $\text{TCO}_2$  measures as the  $\text{O}_2$  inventory in water is more sensitive to gas exchange than that of  $\text{CO}_2$ , which is more sensitive to lateral transport (Cai et al. 1999). However, we suspect the primary reason why  $\text{O}_2$  underestimates metabolism is that  $\text{O}_2$  underestimates anaerobic respiration on the short term and completely misses anoxygenic photosynthesis, which we know is substantial in salt marsh systems where redox potentials are strong in sediments and there is ample light availability.

#### **4.3.4 Respiratory and photosynthetic quotient**

For the open ocean, the stoichiometry of aerobic respiration is 118 moles of  $\text{O}_2$  consumed and 106 moles of  $\text{CO}_2$  produced, which gives a respiratory quotient (RQ –  $\text{CO}_2:\text{O}_2$ ) close to 1 (0.90 - Redfield 1958). In salt marsh and estuarine sediments however, anaerobic respiration raises the RQ as the process does not require  $\text{O}_2$  as the terminal electron acceptor yet still

releases CO<sub>2</sub>. However, anaerobic respiration usually generates reduced metabolic end products (e.g., HS<sup>-</sup>) that are ultimately reoxidized (thus consuming O<sub>2</sub>). Thus, the deviation of RQ from 1 is dependent on the magnitude of anaerobic respiration and the fate of metabolic end-products.

The mean RQ estimated in this study was 1.2 (1.2 mol CO<sub>2</sub> produced per 1 mol O<sub>2</sub> consumed) but in the metabolically most active seasons (spring, summer and fall) it ranged up to 1.5 (Fig. 11). This is not surprising as salt marsh and estuarine sediments are typically anaerobic within mm's of the surface (Wiebe, et al, 1981) with respiration dominated by sulfate reduction (Howarth, 1983) and the rapid seasonal storage of reduced sulfur and pyrite. In winter however, the RQ was as low as 0.5 indicating less CO<sub>2</sub> production than O<sub>2</sub> consumption. While both aerobic and anaerobic respiration undoubtedly both decreased during the cold season, enhanced O<sub>2</sub> consumption most likely reflects the reoxidation of end-products of summertime anaerobic metabolism.

Due to the technical difficulty of TCO<sub>2</sub> measurement, most previous estuarine metabolism and carbon budget studies were achieved by converting O<sub>2</sub>-based measures to C units assuming an RQ of 1 (Boynton & Kemp, 1985; Hopkinson, 1987; Banta et al. 1995). In the few coastal studies where O<sub>2</sub> and CO<sub>2</sub> were both measured, RQ was often reported greater than 1. For example, Dollar et al. (1991) found a RQ of 1.3 by comparing the DIC and O<sub>2</sub> fluxes in Tomales Bay. In Boston Harbor sediments, RQs ranged from 1.2 to 2.0 as DIC fluxes were greater than O<sub>2</sub> uptake at two stations in all three study years (Giblin et al. 1997). Hopkinson et al (2001) also reported that rates of O<sub>2</sub> consumption were nearly always lower than the release of CO<sub>2</sub> from sediments of Massachusetts Bay. With an increasing concern of climate change due to rising atmospheric CO<sub>2</sub> levels from fossil fuel combustion, there is great interest in evaluating the role of the coastal ocean in the global C balance. Our study and others suggest we should be

cautious in converting previous metabolic studies from O<sub>2</sub> to CO<sub>2</sub> units and that an RQ of 1 will likely underestimate actual CO<sub>2</sub> production rates.

The photosynthetic quotient (PQ) indicates the balance of O<sub>2</sub> production and the CO<sub>2</sub> consumption through photosynthesis and at Redfield stoichiometry using NH<sub>3</sub> should be 1.1. The calculated PQ for the Duplin system ranged from 0.5~0.7 through the year (Fig. 11). This result was unexpected but reasonable given the light environment and extreme redox gradients near the sediment surface in intertidal mudflats and on the marsh surface. These are ideal conditions for anoxygenic photosynthesis. A variety of bacteria can perform anoxygenic photosynthesis to fix CO<sub>2</sub> to biomass without producing O<sub>2</sub>. They use reverse electron transport from electron donors such as sulfide (Kuenen et al 1975, Tuttle & Jannasch 1977, Cohen et al 1975) or ferrous iron (Widdel et al 1993, Lliros et al 2014), which are abundant in the salt marsh sediment due to anaerobic respiration, to produce NADPH. Kearns et al. (in revision) showed that purple sulfur bacteria (Chromatiales) were the 3<sup>rd</sup> most abundant group of bacteria in salt marshes in the Plum Island Sound estuary. Green sulfur bacteria as well as purple non-sulfur bacteria were common as well. All these groups can express non-oxygenic photosynthesis.

#### **4.3.5 Comparisons between metabolism of the Duplin marsh-estuary with previous studies**

We find discrepancies between our results and previous studies in the Duplin River estuary and marshes that differ for GPP and R and for O<sub>2</sub> vs CO<sub>2</sub> approaches. To make comparison, we scaled up previous component measures, which were usually reported as g C m<sup>-2</sup> d<sup>-1</sup> to moles C yr<sup>-1</sup> for the entire Duplin salt marsh-estuary using areas we measured in this study. To scale previous measures of intertidal benthic metabolism on the marsh, we multiplied daily rates by a half year to account for water levels being > 0MSL only half the time.

For the entire Duplin salt marsh-estuary system, we calculated GPP of  $116 \times 10^6 \text{ mol yr}^{-1}$  in  $\text{CO}_2$  and  $75 \times 10^6 \text{ mol yr}^{-1}$  in  $\text{O}_2$  (Table 3). Ragotzkie measured annual phytoplankton gross production of  $41 \times 10^6 \text{ mol C yr}^{-1}$  from the light-dark bottle with a PQ of 1.25 (Ragotzkie, 1959), which is about a third of our total GPP measured with  $\text{CO}_2$  and about half of our total GPP measured with  $\text{O}_2$ . Benthic algae contributed  $25 \times 10^6 \text{ mol C yr}^{-1}$  of GPP with  $\text{O}_2$  measures in chambers at high tide and  $\text{CO}_2$  measures at low tide with a PQ of 1 (Pomeroy 1959). A similar annual areal production rate was reported by Whitney, who measured production in bottles using the  $^{14}\text{CO}_2$  tracer addition approach (Christian et al 1983). Pomeroy's and Whitney's estimates of benthic algal production accounted for about 22% of our total GPP measures with  $\text{CO}_2$  and 33% of total GPP with  $\text{O}_2$ . The sum of the two component measures ( $66 \times 10^6 \text{ mol yr}^{-1}$  including phytoplankton and intertidal benthic algae) is about 57% of our estimate of total GPP using  $\text{CO}_2$  and 80% of our total GPP using  $\text{O}_2$ . To some extent this discrepancy reflects the inconsistent PQ conversion factors used in each study (Ragotzkie used 1.25 while Pomeroy used 1) and different measuring techniques ( $\text{O}_2/\text{CO}_2$  light-dark, isotopic uptake ( $^{14}\text{C}$ ), bottles and chambers).

We estimate total aquatic respiration of the Duplin salt marsh-estuary to be  $176 \times 10^6 \text{ mol CO}_2 \text{ yr}^{-1}$  and  $124 \times 10^6 \text{ mol O}_2 \text{ yr}^{-1}$ . As expected respiration rates of the various components of the entire system are less than the rates we measured: submerged sediment respiration of  $71 \times 10^6 \text{ mol C yr}^{-1}$  (Pomeroy, 1972) and planktonic respiration of  $44 \times 10^6 \text{ mol C yr}^{-1}$  (Ragotzkie, 1959; Wang and Cai, 2003). Christian et al. (1983) estimated total aquatic respiration for the Duplin by integrating rates determined with a combination of various techniques and relative areas of marsh (79%) and open water (21%). We extrapolated his areal rate of R to  $116 \times 10^6 \text{ mol C yr}^{-1}$  with areas measured in this study. This is very similar to the sum of the component measures of Pomeroy, Ragotzkie and Wang and Cai ( $115 \times 10^6 \text{ mol C yr}^{-1}$ ). Our measures of respiration are

substantially higher than the sum of the component measures, as we found for GPP: using O<sub>2</sub> our estimate is 7% higher and using CO<sub>2</sub> our estimate is 51% higher. We assume the differences reflect biases in bottle and chamber approaches and arbitrary selection of RQ conversion factors.

It has frequently been observed that rates of metabolism measured in bottles and chambers are consistently less than whole-system measures. We agree with many previous studies that open water measures of metabolism are higher than measures based on bottle and chamber approaches (Cox et al. 2015., Boynton and Kemp 1985, Balsis et al. 1995, Hopkinson and Smith 2005). Some reasons contributing to differences include the artifacts associated with containers – reduced turbulence, reduced grazing, unvarying light fields, removal of nutrient supplies from adjacent systems (e.g., benthic recycling for plankton uptake) (Cox et al. 2015), and the lack of system dynamics such as tidal interaction and mixing in component measures.

Overall we calculate the Duplin River salt marsh-estuary to be net heterotrophic with R exceeding GPP by  $60 \cdot 10^6$  mol CO<sub>2</sub> yr<sup>-1</sup> and  $49 \cdot 10^6$  mol O<sub>2</sub> yr<sup>-1</sup> (Table 3). The O<sub>2</sub>-based measure of NEP is the same as the sum of component measures of GPP and R  $49 \cdot 10^6$  mol CO<sub>2</sub> yr<sup>-1</sup>. Cai and Wang (2003) estimated Duplin River net heterotrophy at  $30 \cdot 10^6$  mol C yr<sup>-1</sup>. They likely underestimated air-water exchange as they neglected exchange from the flooded marsh and overestimated mixing because they based their DIC gradient on upper estuary vs oceanic water masses. Component measures of GPP, R and NEP are consistently in better agreement with our measures based on O<sub>2</sub> than they are with CO<sub>2</sub>. But this agreement is dependent on previous researchers using too low an RQ and too high a PQ, compared to what we actually measured them to be in the Duplin system.

There are few measures of NEP for other marsh-dominated estuaries. In the York River in Virginia, USA, NEP was estimated to be  $8.2$  mol CO<sub>2</sub> m<sup>-2</sup> yr<sup>-1</sup>. This is substantially lower than

the areal rates we found for the Duplin ( $14 \text{ mol CO}_2 \text{ m}^{-2} \text{ yr}^{-1}$  and  $12 \text{ mol O}_2 \text{ m}^{-2} \text{ yr}^{-1}$ ). Lower rates in the York may reflect lower temperatures year-round, a shorter growing season, and a lower marsh: water area ratio.

#### **4.3.6 Uncertainties Associated with Metabolism Estimation**

There are two parameters used in calculating air-water gas exchange and dissolved constituent mixing for which there is a considerable uncertainty expressed in the literature: the gas transfer velocity,  $K_T$ , and the longitudinal mixing coefficient,  $\epsilon$ . To assess the impact of uncertainty in calculations of metabolism, we varied both parameters by what we consider reasonable upper and lower bounds. We varied  $K_T$  by a factor of 2 and  $\epsilon$  by a factor of 10.

Taking August for example, a 10X increase in  $\epsilon$  increased R-35% , GPP-15% and NEP-66%. A 10X reduction decreased R-3%, GPP-0% and NEP-7%. Multiplying  $K_T$  by a factor of 2 gave a 5% increase of GPP, 38% increase of R and 91% increase of NEP. Dividing  $K_T$  by a factor of 2 reduced R 19%, GPP 2% and NEP 45%. These results show the importance of correctly choosing both these terms, especially for estimates of respiration and net ecosystem production. We have confidence in the mixing coefficient for the upper Duplin as it was previously measured empirically by Imberger et al. (1983), but we base our estimate on how the mixing coefficient increases downstream from another system. Our sensitivity analysis shows that increases in the gas transfer velocity impacts estimates of metabolism the most. The factor of 2 range in  $K_T$  likely overestimates our uncertainty as the empirical “scatter” in  $K_T$  vs wind speed reported in Wanninkhof (2009) is only 0.5 to 1.2 X the rate we chose. If we assume that the marsh canopy does not influence wind speed at the air-water interface and use the Wanninkhof relation to calculate  $K_T$ , our annual total system estimates of metabolism change little - 9% increase of R, 1% increase in GPP and 21% increase in NEP (Data not shown). However, we

again note that NEP is more affected than GPP or R. As it is the difference in GPP and R that is critical in assessing allochthonous organic carbon inputs to the aquatic system and ultimately export to adjacent systems, it is important that we increase our understanding of these critical parameters.

#### **4.4 Contribution of the inundated marsh to the Duplin salt marsh-estuary**

It is challenging to evaluate the relative importance of the marsh community to overall estuarine aquatic metabolism. Prior attempts have focused on direct quantification of marsh creek bank drainage (Gardner and Gaines, 2008) or on quantifying DIC export to the ocean from headwater portions of the Duplin River estuary where the relative area of flooded marsh to open water is very large (e.g., Imberger et al 1983, Cai et al 2003). Another approach, which we take in this study, is to mass balance DIC and DO inputs and outputs over an entire tidal cycle for a very small tidal creek that floods a large marsh platform area. The change in  $\text{CO}_2$  or  $\text{O}_2$  after correcting for air-water exchange, is a measure of marsh metabolism in estuarine waters. When scaled to the entire Duplin system, we can assess the relative importance of the marsh compared to the whole salt marsh estuary.

##### **4.4.1 Vertical and lateral $\text{CO}_2/\text{O}_2$ loss/gain over the tidal creek marsh catchment.**

The  $\text{CO}_2$  and  $\text{O}_2$  contents of the Duplin River water change when spread out across the tidal creek and its marsh platform or creekshed (Fig. 5) as a result of air-water exchange that is enhanced as the floodwater spreads out across the broad area of the marsh platform and as a result of the metabolism of creek and marsh platform organisms. We estimated the net  $\text{CO}_2$  and DO exchange based on time-course measures of  $\text{TCO}_2$  and DO concentrations and water volume transport calculated from measures of water level height using ARCMAP. Even though the

Duplin DEM was corrected for a vegetation bias on bare earth elevations, we consider the ARCMAP-calculated transport to be a conservative estimate, as the DEM correction may be biased upward slightly because of the extremely dense and tall *Spartina alterniflora* in the creek channel we studied.

The net lateral transport of DIC between marsh and estuary showed large variation in magnitude and direction for our trips (Fig. 12-a. purple bars). DIC was exported from the creekshed for four out of five sampling months (February, March, May and August), ranging from 81-406 mol per tide (Fig. 12-a). The total lateral transport of O<sub>2</sub> was to the creekshed in May (42 mol tide<sup>-1</sup>) and from the creekshed to the Duplin in August and October (-69 and -401 mol O<sub>2</sub> tide<sup>-1</sup>) (Fig. 12-b). While the magnitude and direction were as expected in October based on the CO<sub>2</sub> transport, the magnitude was lower than expected in May and August and in the opposite direction to CO<sub>2</sub> in August. No data were collected in February and March for DO.

We calculated a loss of CO<sub>2</sub> to the atmosphere from the tidal creekshed year-round as supersaturated Duplin River water flooded the flux tower creek and spread out across the marsh platform (Fig. 12-a. green bars). As expected, the O<sub>2</sub> atmospheric exchange was in the opposite direction of CO<sub>2</sub> year-round due to it being under-saturated when entering (Fig. 12-b). For CO<sub>2</sub>, the air-water loss from the creek ranged from 40 to 577 mol per tide: lowest in February and highest in August. For O<sub>2</sub> the creek gained 237 to 529 mol per tide over three seasons without winter data. Seasonal variations reflect not only variations in metabolism of the marsh-dominated tidal creek but also variations in extent of marsh and marsh organisms flooded.

Areal rates of lateral transport from the marsh and tidal creek to the Duplin River ranged from 0.005 to 0.031 mol CO<sub>2</sub> m<sup>-2</sup> tide<sup>-1</sup> for 4 of 5 observation periods (Fig. 12-c). The average magnitude of this flux is very similar to the reduction in marsh-air flux as measured with the

eddy covariance approach when the marsh floods (Kathilankal et al. 2008):  $0.023 \text{ mol CO}_2 \text{ m}^{-2} \text{ day}^{-1}$  DIC export (taking into account 2 tides per day) vs  $0.019 \pm 0.02 \text{ mol CO}_2 \text{ m}^{-2} \text{ day}^{-1}$  net ecosystem exchange reduction in a Virginia salt marsh. The areal transport of  $\text{O}_2$  from the tidal creek was to the creekshed from the Duplin in May ( $0.004 \text{ mol m}^{-2} \text{ tide}^{-1}$ ) and from the creekshed to the Duplin in August and October ( $-0.003$  to  $-0.019 \text{ mol O}_2 \text{ m}^{-2} \text{ tide}^{-1}$ ) (Fig. 12-d).

Flux tower measures of salt marsh net ecosystem exchange (NEE) miss any measure of marsh metabolism into floodwater at high tide and exported during ebb tide. Indeed, tidal marsh flux tower studies show a sizeable reduction in NEE fluxes when the marsh is inundated (e.g., see Forbrich and Giblin 2015). To estimate true marsh net ecosystem production, flux tower NEE measures must be corrected for lateral exchange as measured in our study.

The metabolism of the tidal creek – marsh platform system, estimated from balancing lateral transport and air-water exchange, revealed a strong seasonal pattern of being heterotrophic for most of the year (negative NDP with respiration exceeding GPP in February, March, May and August, ranging from  $0.031\sim 0.049 \text{ mol CO}_2 \text{ m}^{-2} \text{ tide}^{-1}$ ), and autotrophic to October (positive NDP with GPP exceeding R  $0.007 \text{ mol CO}_2 \text{ m}^{-2} \text{ tide}^{-1}$ ) (Fig. 12-c, orange line). In October, the net consumption of DIC (generation of DO) occurred during a cloudless day when cumulative PAR was 28% higher than typical for this time of year and when high tide coincided with peak solar radiation. The net uptake of DIC suggests an autotrophic marsh platform during the hours the marsh was flooded in October. It would appear that for most of the year the marsh-creek system is heterotrophic ( $R > \text{GPP}$ ) even during the daytime. Only when photosynthetic conditions are ideal such as we found in October (highest daily PAR of entire study and perfectly matched with time of high tide) is the marsh-creek system autotrophic.

Measures in the winter (Feb and Mar) give us some insight into the relative influence of the marsh platform versus the vegetated intertidal creekbank on DIC dynamics. In February ONLY the intertidal marsh creekbank was flooded (0.84 m MSL high tide), while in March both creekbank and platform marshes were flooded (1.34 m MSL high tide). We assume little change in metabolism between these two months as weather conditions were similar. Net DIC export was 81 mol/tide in Feb and 406 mol/tide in March. Thus the marsh platform contributes 80%  $((406-81)/406)$  compared to 20% for the marsh creekbank. Taking into consideration the total tidal creek shoreline length 862m (both sides of creek), the creek bank exported 0.094 mol DIC per meter shoreline and the marsh platform exported 0.019 mol DIC per m<sup>2</sup> (based on 43000 m<sup>2</sup> of marsh platform flooded). Thus a meter of marsh edge contributes about 5x more DIC to the overall Duplin saltmarsh estuary, than a m<sup>2</sup> of marsh platform. If salt marshes do not keep up with sea-level rise and they begin to fragment as described by Reed (2002) and Day and Hopkinson. (1977), we can expect tidal creek density to increase while total marsh area decreases. Our results suggest this pattern will lead to more DIC export to the estuary at least until marsh area loss becomes really large.

#### **4.4.2 Relative importance of the marsh to aquatic metabolism of the Duplin salt marsh-estuary**

As mentioned earlier, for the most part the tidal creek – marsh platform system was heterotrophic, even during daytime hours. Assuming net daytime heterotrophy on the marsh in this study is a minimal estimate of respiration and that the flux tower creek marsh is representative of marshes throughout the entire Duplin, we find that flooding marshes contribute from 12% to 35% of total respiration measured for the entire Duplin (Table 4). We note that this

influence reflects the marsh only being flooded for 3 to 4.2 hours out of the total 12 hours day/night interval.

Under the ideal conditions observed in October the marsh was net autotrophic during the day, which enables us to estimate the extent to which the marsh can contribute to total Duplin system GPP. GPP equals NDP plus night R. Tidal creek – marsh platform NDP in October was  $-0.2 \times 10^6$  mol CO<sub>2</sub> per tide (net autotrophic). Estimating marsh R as 12-35% of measured whole system night respiration in October (from above) and adding to October tidal creek – marsh platform NDP yields an estimate of tidal creek - marsh platform GPP ranging from  $-0.8$  to  $-2.0 \times 10^5$  mol CO<sub>2</sub> tide<sup>-1</sup>. Scaled to all marshes of the Duplin marsh-estuary, we estimate that the marsh can contribute 10 to 24% of the total system GPP under ideal conditions.

These estimates of the relative contribution of the marsh to total Duplin aquatic system metabolism are first approximations and we assume conservative. Marsh respiration at night is undoubtedly higher than that estimated from the net change in DO or DIC during day. Nevertheless, these are the first ever estimates of the extent to which aquatic metabolism as measured by the free-water approach integrates a portion of overall marsh metabolism.

We can conceptualize the marsh community to include emergent macrophytes, here *S. alterniflora*, the micro-, meio-, and macrofauna of the marsh sediments and surface muds, organisms suspended in the floodwaters, and epiphytic algal and bacterial organisms on and in surface sediments and live and dead-standing marsh macrophytes. When flooded, these sub-communities metabolize directly into flood waters, with the exception of the marsh macrophytes themselves. It is unclear to what extent, if any, macrophytes exchange CO<sub>2</sub> or oxygen with flood waters as opposed to the atmosphere. With the exception of air-breathing organisms, the vast majority of metabolism will be attributable to bacteria, which when active are primarily moist

and thus producing metabolic gases directly into water. As a result, gas exchange is limited and DIC concentrations and oxygen deficits accumulate in sediment porewaters. High concentration gradients in metabolites such as carbonate alkalinity and reduced Fe, Mn, and S (Koretsky et al. 2000, Faber et al. 2014) can result in sediment to floodwater fluxes when the marsh is inundated. Koretsky et al. (2000) showed pore water concentrations of  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{H}_2\text{S}$  and alkalinity to exceed 450, 200, 4000 and 24000  $\mu\text{M}$ , respectively in saltmarsh sediments at Sapelo Island, which can result in sediment to floodwater fluxes when the marsh is inundated. These fluxes are the result of prior metabolism and therefore represent more than just the 3 to 4.2 hours during which the marsh platform is inundated.

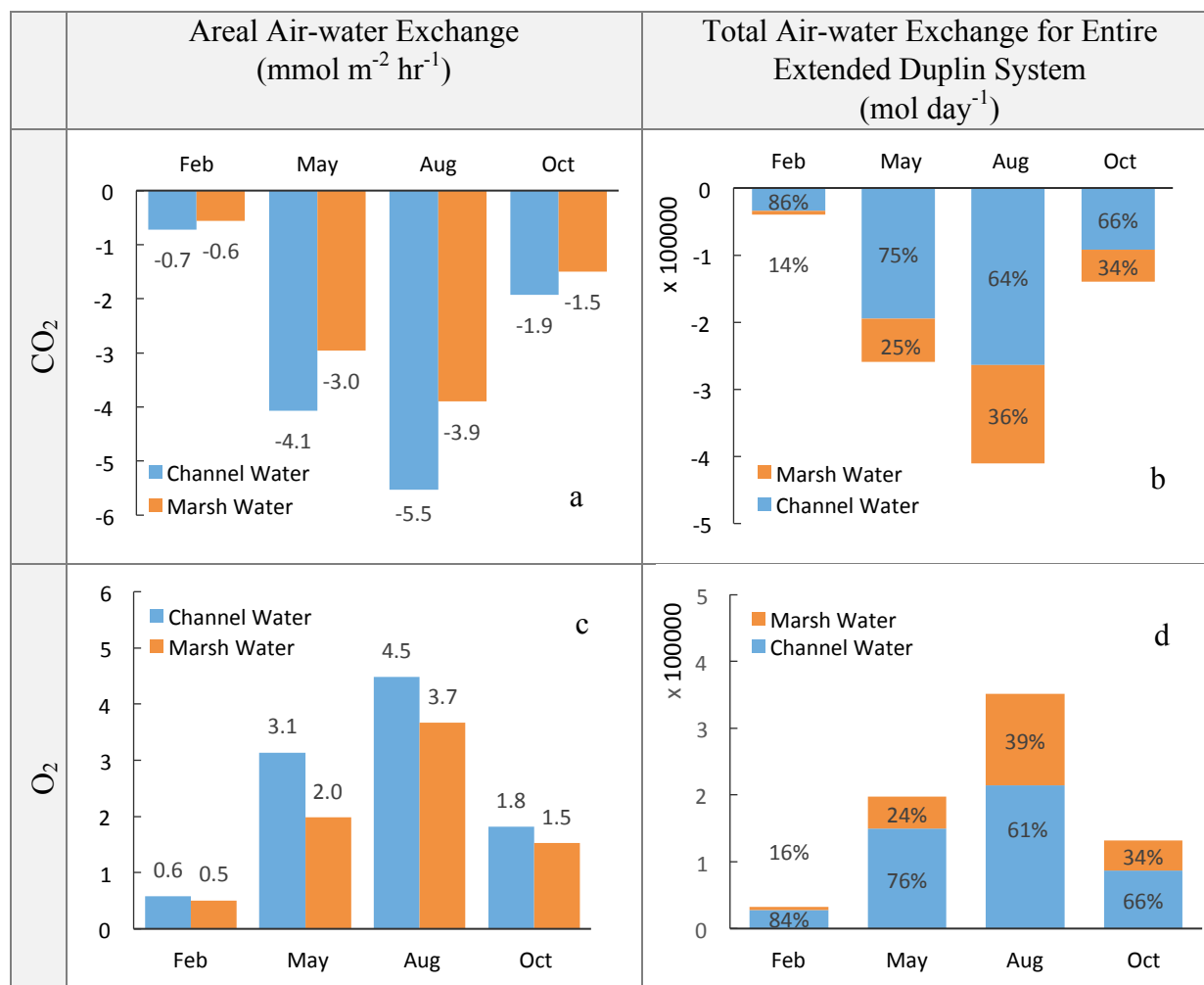


Figure 6: Seasonal air-water exchange: Areal air-water flux of CO<sub>2</sub> (a). Areal air-water flux of O<sub>2</sub> (b). Daily air-water CO<sub>2</sub> flux over the Duplin marsh-estuary (c). Daily air-water O<sub>2</sub> flux over the Duplin marsh-estuary (d).

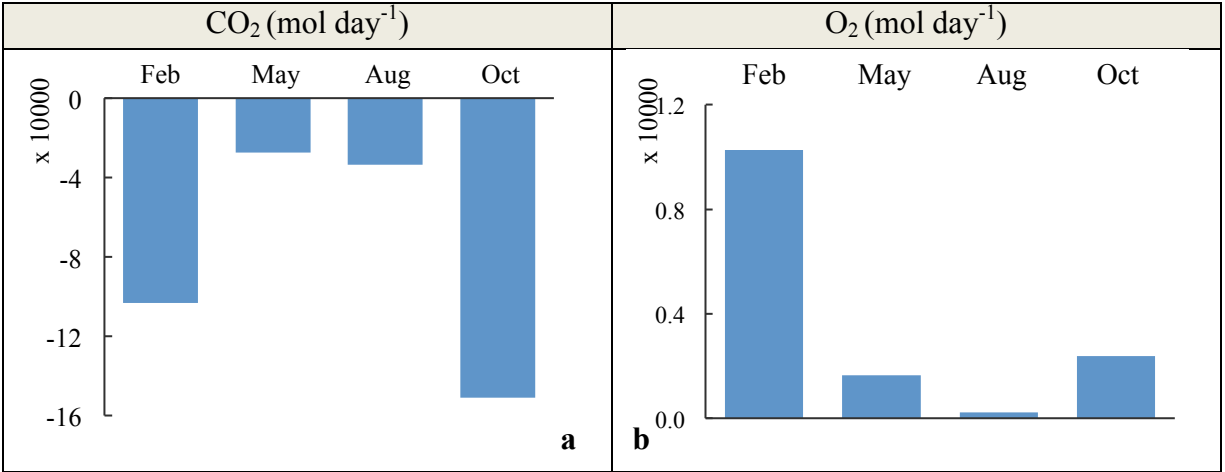


Figure 7: Seasonal mixing with coastal water: Daily DIC and DO mixing at the mouth of the Duplin estuary with the adjacent coastal waters of Doboy Sound and the ocean. Negative transport represents export from the Duplin to coastal water, and positive transport represent import from the coastal water to the Duplin.

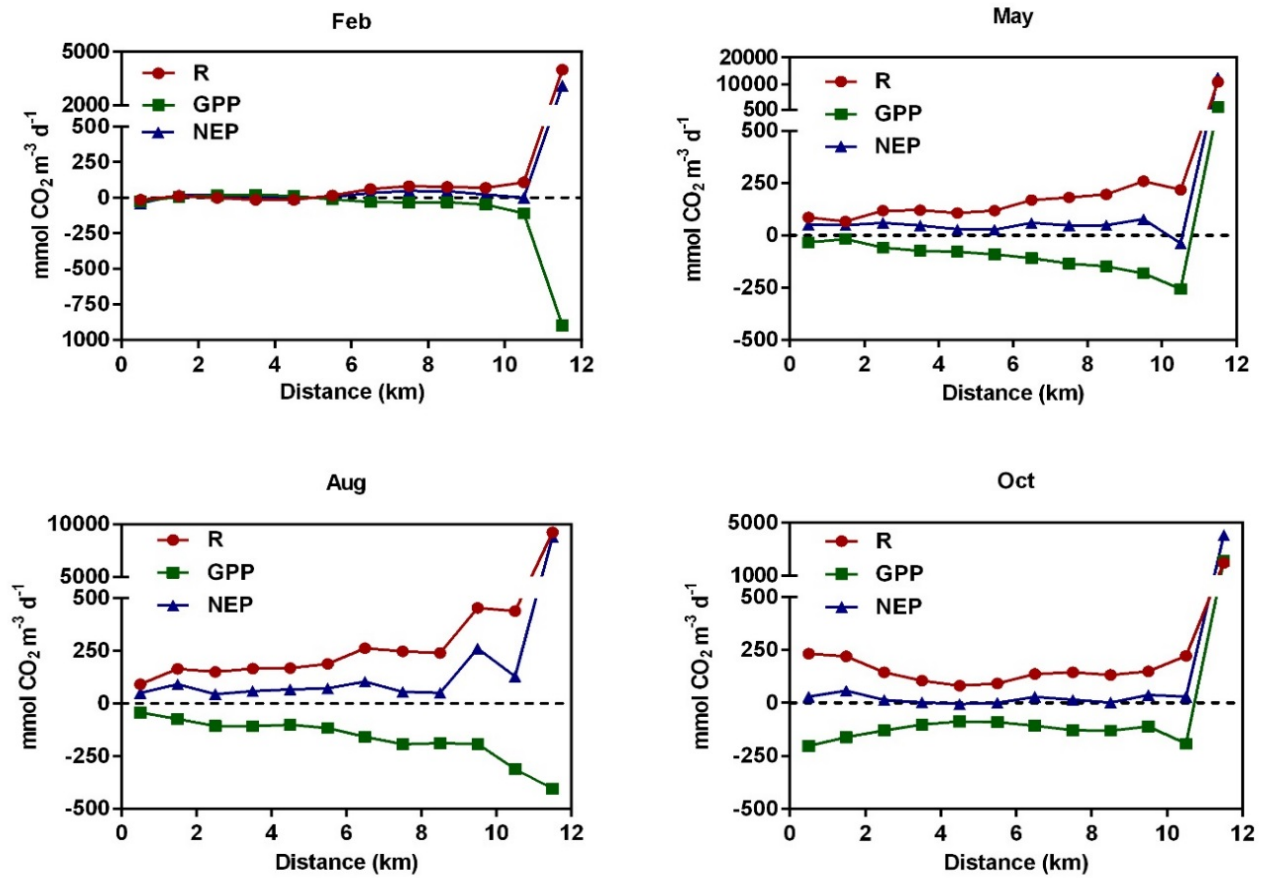


Figure 8: Metabolic rates calculated with  $\text{CO}_2$  distribution along Duplin..

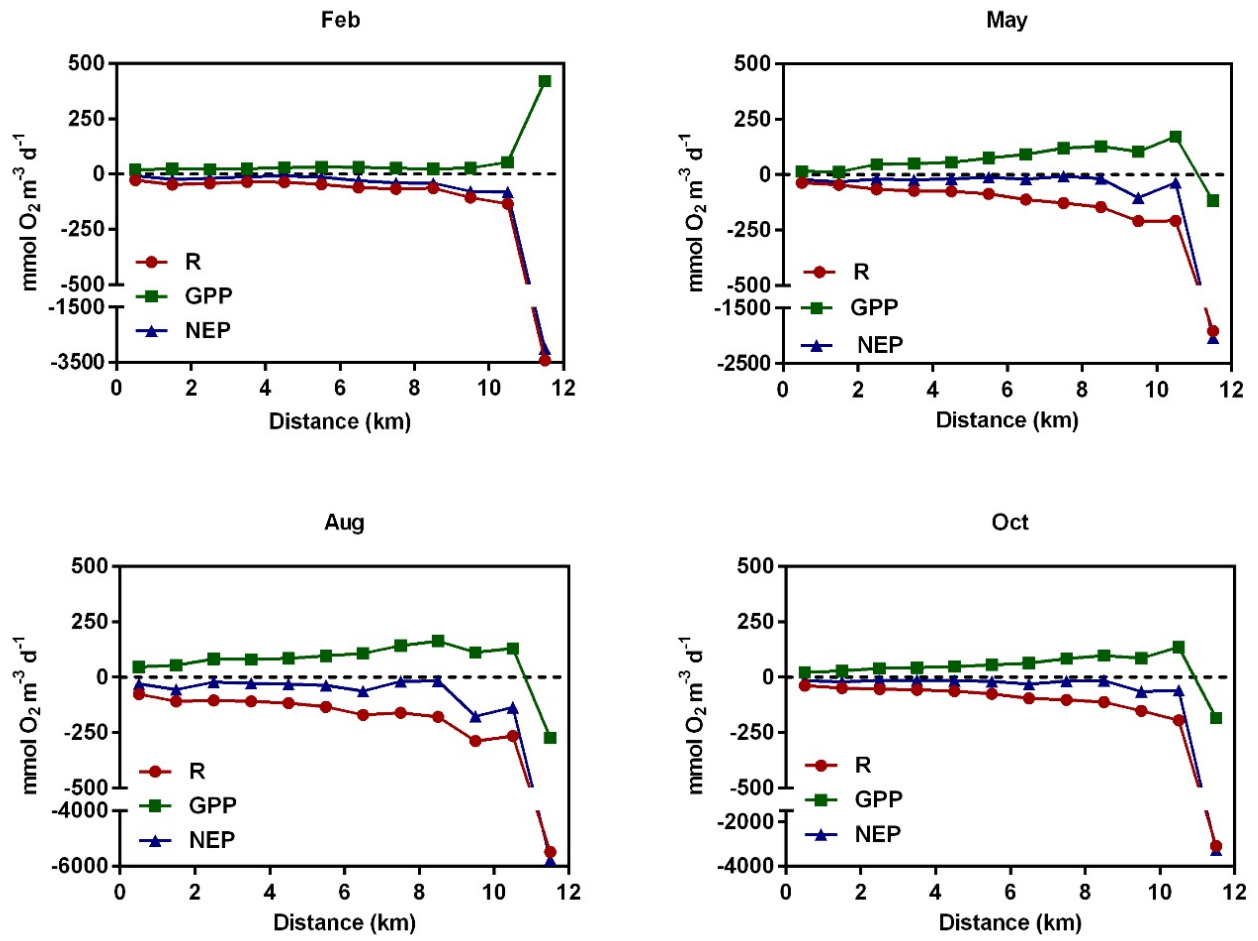


Figure 9: Metabolic rates calculated with  $\text{O}_2$  distribution along Duplin.

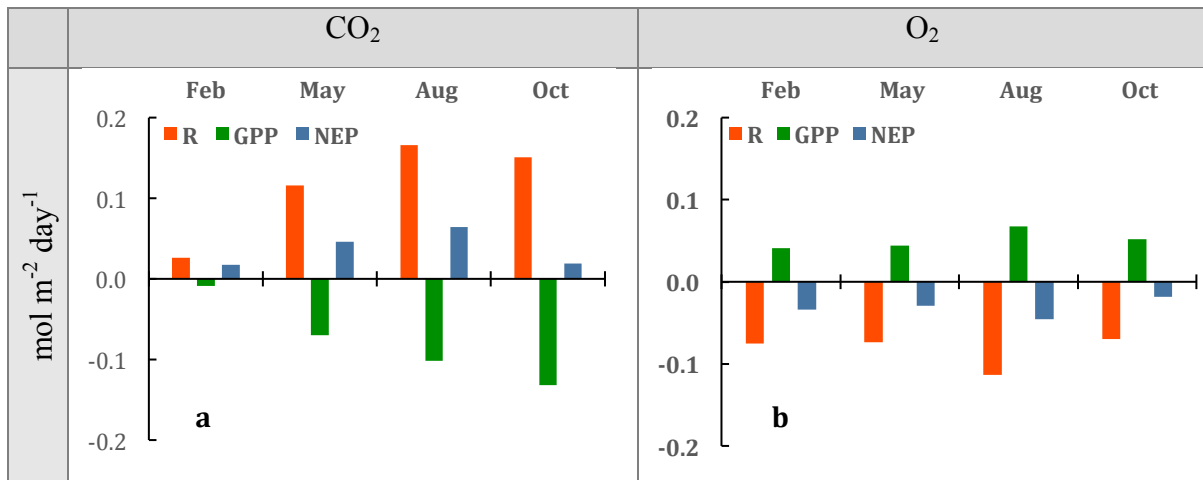


Figure 10: Seasonal metabolism for the entire Duplin marsh-estuary.

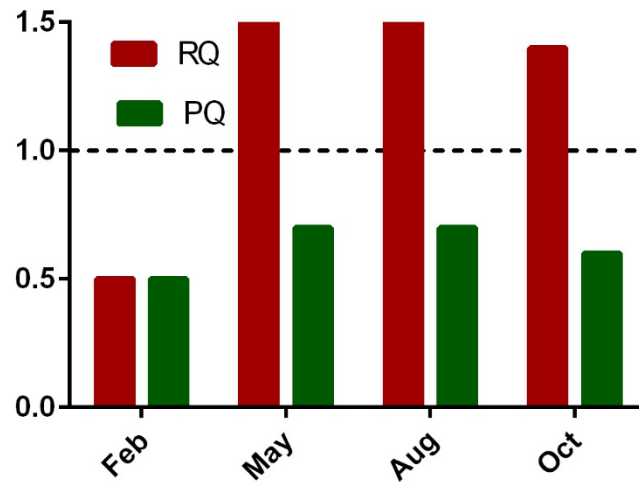


Figure 11: Seasonal respiratory quotient (RQ) and photosynthetic quotient (PQ) of the entire Duplin marsh-estuary system.

Table 3. Comparison of aquatic salt marsh-estuarine metabolic rates between this study and the literature. . Rates scaled up to the whole system were calculated from previous studies by multiplying their annual areal rates by the relative areas measured in this study.

Process – region or community	Annual total $10^6 \text{ mol yr}^{-1}$	Areal rates $\text{mol m}^{-2} \text{ yr}^{-1}$	Area estimated in this study $10^6 \text{ m}^2$	Reference
<b>GPP – Duplin salt marsh-estuary</b>	116 –CO <sub>2</sub> 75 –O <sub>2</sub>	28.3 –CO <sub>2</sub> 18.25 –O <sub>2</sub>	Marsh + estuary area: 4.1	This study: open water
GPP- phytoplankton	41	21	Aquatic area ( $\leq 0\text{m MSL}$ ): 2.0	Ragotzkie, 1959: bottles, light-dark O <sub>2</sub>
GPP- intertidal benthic algae	25	8	Marsh platform plus creek bank area: 3.1	Pomeroy, 1959: Chamber low tide with O <sub>2</sub> High tide with CO <sub>2</sub> Whitney, 1983 (C14)
<b>R- Duplin salt marsh-estuary</b>	176 –CO <sub>2</sub> 124 –O <sub>2</sub>	43 –CO <sub>2</sub> 30 –O <sub>2</sub>	Marsh + estuary area: 4.1	This study: open water
R-intertidal benthos	71	23	Marsh platform plus creek bank area: 3.1	Pomeroy 1972: chamber with O <sub>2</sub>
R-Plankton	44	22	Aquatic area ( $\leq 0\text{m MSL}$ ): 2.0	Ragotzkie 1959: bottles with O <sub>2</sub>
R-Total aquatic respiration of Duplin estuary	116	28	Marsh + estuary area: 4.1	Christian et al 1981: sum of multiple components
R-plankton (mouth only)	45	23	Estuary area ( $\leq 0\text{m MSL}$ ): 2.0	Wang & Cai, 2003: bottles with CO <sub>2</sub>
<b>NEP –Duplin salt marsh-estuary</b>	60 –CO <sub>2</sub> 49 –O <sub>2</sub>	14 –CO <sub>2</sub> 12 –O <sub>2</sub>	Marsh + estuary area: 4.1	This Study

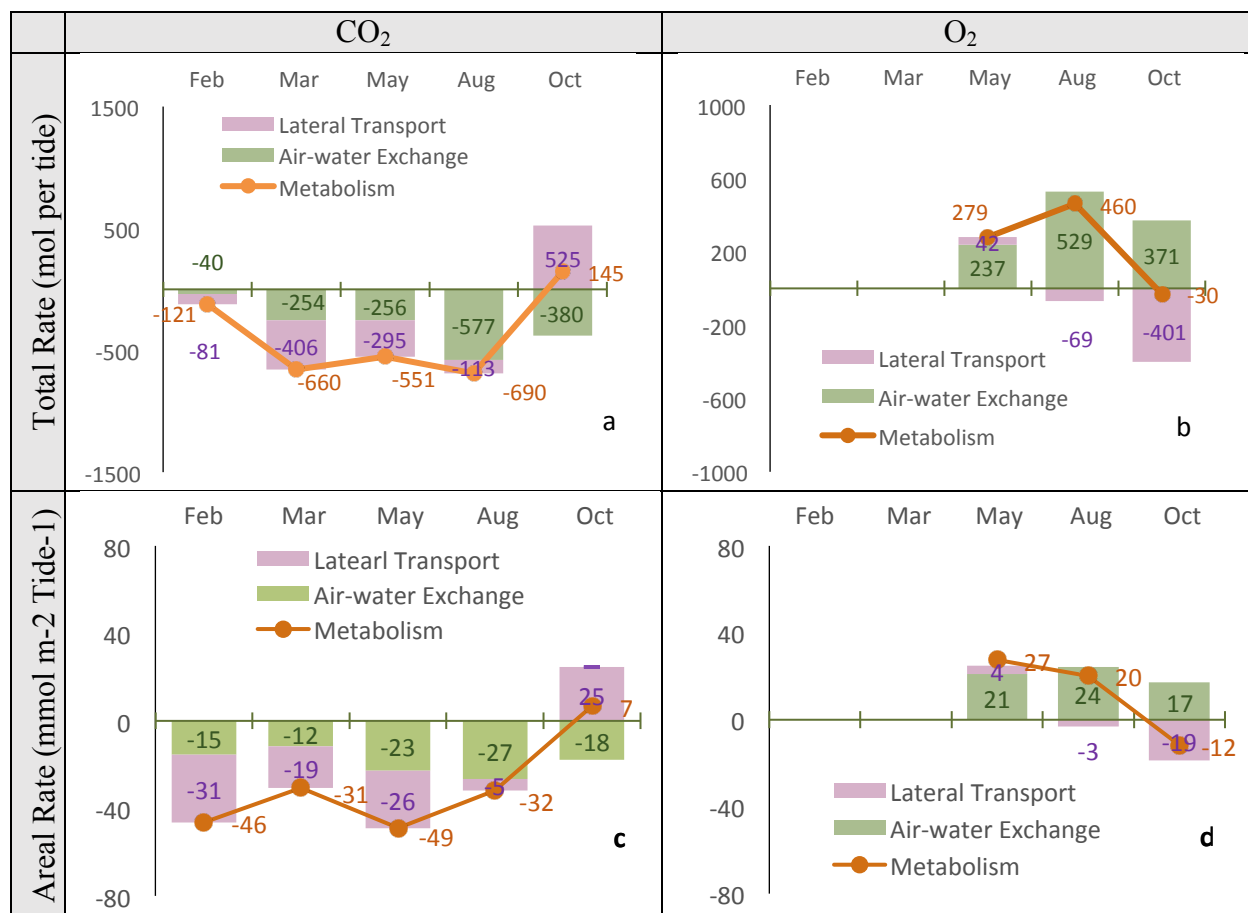


Figure 12: Air-water exchange, lateral transport and metabolism of the inundated marsh. Negative transport indicates loss from the marsh to the estuary or the atmosphere and vice versa for positive transport. Areal rates were calculated by dividing the total rates with  $\frac{1}{2}$  the maximum area of marsh flooded for each month: 2600, 21500, 11000, 21800, 21500 m<sup>2</sup> for Feb, Mar, May, Aug, Oct, respectively. We did not collect DO data in February and March. Net day production of marsh (NDP) was calculated as the sum of vertical flux and averaged lateral transport.

Table 4: Comparisons between marsh NDP and the total systematic R.

	May	Aug		Oct
Marsh NDP (*10 <sup>5</sup> mol CO <sub>2</sub> tide <sup>-1</sup> )	1.2	0.8	Marsh NDP	-0.2
Total Daytime R (*10 <sup>5</sup> mol CO <sub>2</sub> tide <sup>-1</sup> )	4.7	6.6	Total Night R	5.1
% marsh NDP of total daytime R	26%	12%	Marsh R (assuming 12%~36% of total R)	0.61~1.8
Total Nighttime R (*10 <sup>5</sup> mol CO <sub>2</sub> tide <sup>-1</sup> )	3.4	5.3	Marsh GPP (= NDP-R )	0.81~2.0
% marsh NDP of total nighttime R	35%	15%	% marsh contributed GPP	10%~24%

## CHAPTER 5

### SUMMARY

Metabolism dominated  $\text{CO}_2$  and  $\text{O}_2$  dynamics within the overall Duplin River salt marsh-estuary, with respiration greatly exceeding gross primary production in both  $\text{CO}_2$  and  $\text{O}_2$  based measures (Fig. 13). Overall the system was net heterotrophic demonstrating a strong dependence on excess primary production by marsh macrophytes. The aquatic system is strongly linked to the adjacent tidal marshes via the twice daily tidal flooding. During flooding tidal waters capture a portion of the metabolism occurring on the marsh resulting in a loss of  $\text{CO}_2$  to the atmosphere (or gain of  $\text{O}_2$ ) and an export of DIC to the Duplin (or import of  $\text{O}_2$ ). A large percentage of overall air-water exchange of dissolved gases in the estuary occurs from waters when they flood the marsh. We have likely underestimated the air-water flux because we have assumed no effect of wind on the exchange rate. This is one of the largest sources of uncertainty in our analysis. The Duplin estuary is also a source of DIC to the coastal ocean (and sink for  $\text{O}_2$ ), but at a greatly reduced magnitude relative to the air-water flux. We found that the C:O stoichiometry of metabolism deviates substantially from oceanographic Redfield ratios with an average RQ of 1.2 and PQ of 0.6. We attribute the high RQ to the importance of sulfate reduction and the burial of pyrite in salt marsh sediments. We attribute the low PQ to the importance of anoxygenic photosynthesis. We suggest that future work in developing C budgets for coastal ecosystems be careful in choosing factors to convert from  $\text{O}_2$  to  $\text{CO}_2$  units.

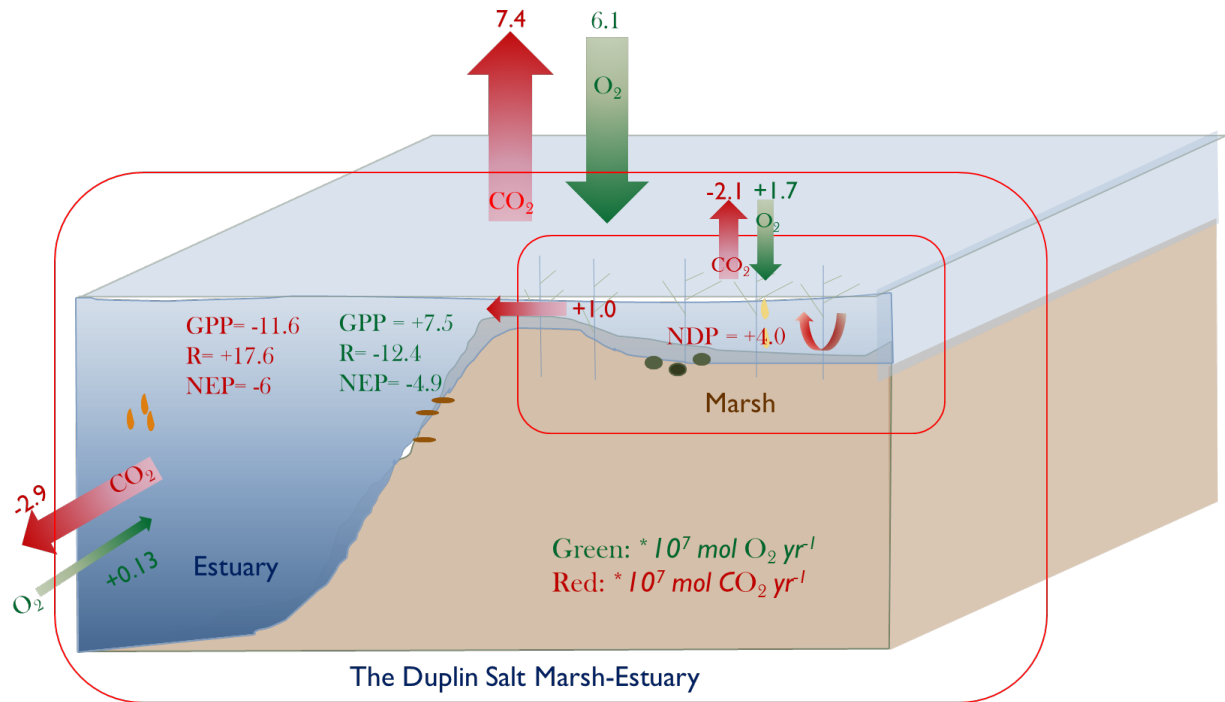


Figure 13: A conceptual representation of the metabolism and CO<sub>2</sub> and O<sub>2</sub> dynamics: highlighting the exchange between the marsh and tidal waters, the exchange between the entire Duplin marsh-estuary with the atmosphere and the coastal ocean water.

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## APPENDIX A

### WATER SURFACE AREA AND VOLUME CALCULATION

Annual averaged inundated marsh surface area -  $2.1 \times 10^6 \text{ m}^2$ : half of surface area when marsh was flooded at mean high water level (MHW -- 1.0m relative to MSL 0 m) as reported by NOAA, calculated by ArcMap surface area tool at mid-tide location.

Annual averaged total water area: the sum of total open water surface area ( $2.0 \times 10^6 \text{ m}^2$ ) and average inundated marsh surface area ( $2.1 \times 10^6 \text{ m}^2$ ).

Table 5: Water volumes for 12 segment along the Duplin estuary: Calculated by integrating the bathymetry employed in the FVCOM model to MLW (MSL -1.02m), at the initial location of each water segment at low tide.

Segment #	Water volume m <sup>3</sup>
0	828471
1	818605
2	1073074
3	702280
4	793361
5	766682
6	543742
7	474912
8	307803
9	94895
10	63663
11	1709

Table 6: Open water surface area: Determined by ArcMap surface area tool at mid-tide location and 0m MSL water depth. Used to calculate air-water flux for channel water.

Segment #	Open water area (m <sup>2</sup> )
0	204029
1	285710
2	267123
3	207519
4	267563
5	238514
6	186682
7	129627
8	94326
9	80670
10	29673
11	1674
Sum	1993108

Table 7: Inundated marsh water surface area: Calculated as ½ of the total area of marsh inundated at highest tidal level observed during each dawn-dusk interval with ArcMap surface area tool. Used to calculate air-water flux for marsh over-lying water.

ST #	Feb Inundated marsh area (m <sup>2</sup> )		May Inundated marsh area (m <sup>2</sup> )		Aug Inundated marsh area (m <sup>2</sup> )		Oct Inundated marsh area (m <sup>2</sup> )	
	Day	Night	Day	Night	Day	Night	Day	Night
0	6,337	12,681	38,252	47,740	48,163	46,627	45,874	28,071
1	35,568	46,530	58,213	58,366	58,366	58,366	58,365	54,994
2	83,006	106,954	177,217	188,301	188,551	187,859	187,275	149,162
3	11,134	12,787	20,613	21,080	21,163	20,906	20,857	16,346
4	38,041	45,417	74,766	78,786	79,201	77,812	77,488	60,165
5	170,021	230,963	462,645	479,084	479,225	478,537	477,845	348,851
6	132,072	158,590	313,656	385,873	388,147	371,181	362,002	220,449
7	117,071	138,117	256,501	277,583	277,755	274,561	271,200	191,785
8	87,118	116,295	195,288	196,655	196,650	196,656	196,509	165,030
9	25,629	30,765	81,249	110,035	110,933	107,025	103,640	44,654
10	139,261	185,220	438,734	464,846	465,857	462,558	461,090	308,452
11	54,368	89,240	278,514	299,047	299,255	298,137	296,972	181,964

## APPENDIX B

### TIDAL EXCURSION AND WATER MASS MATCHING

**Tidal excursion and water mass matching:** In the meso-tidal Duplin the location of discrete water masses move substantially over a tidal cycle (tidal excursion distance). We estimated the location of our initial 12 discrete water masses on subsequent transects using simulations from a Lagrangian particle tracer hydrodynamic model (FVCOM and Daniela et al, not published). As samplings following the initial dusk transect were within 5 minutes to 2 hours of subsequent low tides, site locations did not differ considerably. We used model simulations that showed locations over a tidal cycle of 200 particles input at each station along the Duplin. Third or fourth order polynomials were constructed for particle movement for each station in order to predict where initial sampling locations were on subsequent transects (Fig.15).

**Mid-tide locations** were based on the average of total excursion distance as estimated by other researchers (Ragotzkie, etc) and this study. For this study, we estimated excursion distance as the up-estuary travel distance of a volume of water at high tide equivalent to the volume measured at low tide. We then used the rate of change in velocity following high tide obtained from ADCP current meters at several locations in the thalweg of the Duplin River to estimate the location of water 3 hr after high tide.

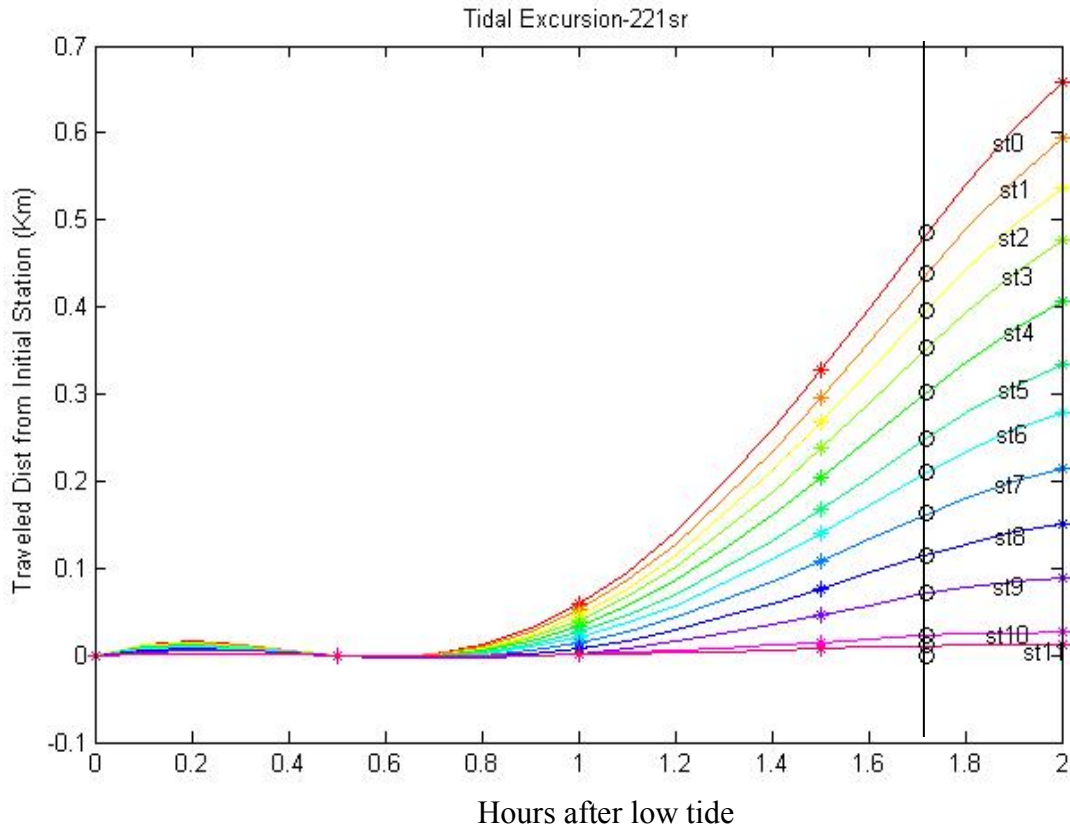


Figure 14: An example of matching water masses--- 2/21/2014 sunrise transect. The colored curve are the polynomial relationships between the tidal stage and the traveled distance from low tide location. The water mass are labeled on the curves, e.g.: st0 represents the water mass that start at station 0 at low tide. In this transect, our averaged sampling time is about 1.75 hours later than the low tide time, where the black line illustrate. The y coordinate of each circles are the traveled distance for the 1.75 hours since low tide for each water mass.

## APPENDIX C

### DIFFUSION COEFFICIENT

Diffusion coefficient:  $\varepsilon = -0.0041*D^3 + 0.1439*D^2 - 1.8575*D + 35.855$

D is the distance from the mouth of Duplin.  $\varepsilon$  is the dispersion coefficient