

## OCEAN ACIDIFICATION BUFFERING EFFECTS OF SEAGRASS IN TAMPA BAY

Kimberly K. Yates, Ryan P. Moyer, Christopher Moore, David Tomasko, Nathan Smiley, Legna Torres-Garcia, Christina E. Powell, Amanda R. Chappel and Ioana Bociu

### **ABSTRACT**

The Intergovernmental Panel on Climate Change has identified ocean acidification as a critical threat to marine and estuarine species in ocean and coastal ecosystems around the world. However, seagrasses are projected to benefit from elevated atmospheric pCO<sub>2</sub>, are capable of increasing seawater pH and carbonate mineral saturation states through photosynthesis, and may help buffer against the chemical impacts of ocean acidification. Additionally, dissolution of carbonate sediments may also provide a mechanism for buffering seawater pH. Long-term water quality monitoring data from the Environmental Protection Commission of Hillsborough County indicates that seawater pH has risen since the 1980's as seagrass beds have continued to recover since that time. We examined the role of seagrass beds in maintaining and elevating pH and carbonate mineral saturation state in northern and southern Tampa Bay where the percent of carbonate sediments is low (<3%) and high (>40%), respectively. Basic water quality and carbonate system parameters (including pH, total alkalinity, dissolved inorganic carbon, partial pressure of CO<sub>2</sub>, and carbonate mineral saturation state) were measured over diurnal time periods along transects (50-100 m) including dense and sparse *Thalassia testudinum*. seagrass beds, deep edge seagrass, and adjacent bare sand bottom. Seagrass density and productivity, sediment composition and hydrodynamic parameters were also measured, concurrently. Results indicate that seagrass beds locally elevate pH by up to 0.5 pH unit and double carbonate mineral saturation states relative to bare sand habitats. Thus, seagrass beds in Tampa Bay may provide refuge for marine organisms from the impacts of ocean acidification.

### **INTRODUCTION**

The IPCC has confirmed that ocean acidification (OA) has a profound effect on ocean and coastal ecosystems and communities around the globe (IPCC, 2014). Many marine and estuarine species will be negatively impacted (Barton et al., 2012; Gazeau et al., 2007; Fabry et al., 2008; Kurihara, 2008; Kroecker et al., 2010; Narita et al., 2012; Waldbusser et al., 2011); and it is projected that some species (especially calcifying species) may become locally and/or globally extinct. Management strategies have focused on reducing local stressors to reduce the impact of multiple stressors on ecosystems, and on identifying and establishing protected areas with environmental conditions that promote resiliency to marine organisms (Salm et al., 2006).

Long-term water quality monitoring data from the Environmental Protection Commission of Hillsborough County (EPC-HC: <http://www.epchc.org/index.aspx?nid=219>) indicates that daytime values of seawater pH in Tampa Bay decreased from approximately 1970 to the early 1980's when the rate of seagrass habitat loss was at its peak. However, these same daytime pH values have steadily risen in Tampa Bay since the early 1980's when local management strategies improved water quality and seagrass beds have continued to recover since that time (Sherwood et al., 2016). Seagrasses are projected to benefit from elevated atmospheric pCO<sub>2</sub> (Kleypas and Yates,

2009), are capable of increasing seawater pH and carbonate mineral saturation states through photosynthesis, and may help provide protection to organisms living in close association with seagrass beds (e.g. Semesi et al., 2009; Anthony et al., 2011; Manzello et al., 2012; Hendriks et al., 2014).

We hypothesized that the recovery of seagrass in Tampa Bay has helped buffer against the chemical impacts of ocean acidification, may confer some resiliency to organisms (such as shellfish and other economically important fish species) that are particularly sensitive to OA, and may serve as an important regional OA refuge. Additionally, dissolution of carbonate sediments may also provide a buffering mechanism for seawater pH (Kleypas and Yates, 2009). Tampa Bay is characterized by a natural gradient in sediment composition with upper portions of the bay dominated by siliciclastic sediments and lower portions of the bay dominated by carbonate sediments (Edgar et al., 2007). This mineralogical gradient in Tampa Bay provides a unique opportunity to examine the role of carbonate sediments in the ocean acidification process. To further examine these hypotheses, we performed a pilot study to examine the potential role of seagrass beds in elevating pH and carbonate mineral saturation state by measuring carbonate system parameters and related water quality parameters in representative habitats of Tampa Bay including seagrass beds and sand bottom communities and in siliciclastic and carbonate sediment dominated regions.

## METHODS

Upper and lower Tampa Bay study sites were selected based on minimum and maximum carbonate sediment content, similarity of seagrass species and light availability. Lower bay study sites were located near Ft. Desoto Park where carbonate content of seafloor sediments is approximately 57% (Edgar et al., 2007). A 98 m shore-perpendicular transect was established beginning at the seaward extent on bare sand, near the deep edge of seagrass, and ending at the shoreward edge in a dense (80-90% estimated) seagrass bed (Table 1). Seagrass consisted primarily of *Thalassia testudinum* with scattered *Syringodium filiforme*. Characteristics of the seagrass meadows at the different locations are shown in Table 2. Upper bay study sites were located near the east end of Courtney Campbell Causeway where carbonate content of seafloor sediments is approximately 1-2% (Edgar et al., 2007). A 72 m shore-perpendicular transect was established beginning at the seaward extent on bare sand near the deep edge of seagrass, and ending at the shoreward edge in a dense seagrass bed. Seagrass consisted primarily of *T. testudinum* with scattered *S. filiforme* and *Halodule wrightii*.

**Table 1. Location of Tampa Bay Study Sites.**

Description	Latitude	Longitude	Depth (m)
Upper Tampa Bay Transect			
Bare sand	N 27.96120	W 82.55422	2.4
Deep edge	N 27.96120	W 82.55421	2.1
Transitional	N 27.96125	W 82.55417	1.5
Dense seagrass	N 27.96150	W 82.55393	0.9
Lower Tampa Bay Transect			
Bare sand	N 27.63576	W 82.69315	2.4
Deep edge	N 27.63584	W 82.69322	2.4
Transitional	N 27.63611	W 82.69355	1.8
Dense seagrass	N 27.63622	W 82.69365	1.2

**Table 2. Characteristics of *T. testudinum* at study sites (data from May 2015, Tomasko et al., this issue).**

Description	Mean shoot density (no. m <sup>-2</sup> )	Mean biomass per shoot (mg dw shoot <sup>-1</sup> ± stdev)	Depth (m)
Upper Tampa Bay Transect			
Deep edge	43	64.7 ± 26.2	2.1
Transitional	77	67.1 ± 42.6	1.5
Dense seagrass	488	190.0 ± 66.4	0.9
Lower Tampa Bay Transect			
Deep edge	19	202.5 ± 52.4	2.4
Transitional	384	237.0 ± 53.7	1.8
Dense seagrass	454	516.6 ± 125.6	1.2

We measured small-scale, spatial variability (sub-100 m) in basic and carbonate system parameters [including temperature (T), salinity (S), dissolved oxygen (DO), pH on the total pH scale (pHT), total alkalinity (TA), dissolved inorganic carbon (DIC), and aragonite saturation state ( $\Omega_A$ )] along transects from shallow, dense seagrass, to transitional and deep-edge seagrass, to bare sand during May 14-15, 2015 in Upper Tampa Bay and during May 20-21, 2015 in Lower Tampa Bay. We installed duplicate water sampling tubes at each study site by attaching the tube ends to cement blocks positioned in each substrate type approximately 16 cm above the seafloor and affixing the

sampling end to a moored research vessel at the surface. Discrete seawater samples were collected for TA, DIC, and pHT analyses from each site every 4 h ( $n = 7$ ) throughout 24 h periods. A peristaltic pump was used to pump seawater through a 0.45  $\mu\text{m}$  filter into 500 ml borosilicate glass bottles. Samples for TA and DIC were preserved by adding 100  $\mu\text{L}$  saturated  $\text{HgCl}_2$  solution. Bottles were positive-pressure sealed with ground glass stoppers coated with Apiezon grease. Seawater samples for pHT were collected from the same peristaltic pump and filtered into 30mL glass optical cells, and were analyzed within 1 h of collection. Samples were analyzed for TA ( $\pm 1 \mu\text{mol kg}^{-1}$ ) using spectrophotometric methods of Yao and Byrne (1998) with an Ocean Optics USB2000 spectrometer and bromocresol purple indicator dye, for DIC ( $\pm 3 \mu\text{mol kg}^{-1}$ ) using a UIC carbon coulometer model CM5014 and CM5130 acidification module using methods of Dickson et al. (2007), and for pHT ( $\pm 0.005$ ) via spectrophotometric methods of Zhang and Byrne (1996) with an Ocean Optics USB2000 spectrometer and thymol blue indicator dye. Dissolved oxygen ( $\pm 0.1 \text{ mg l}^{-1}$ ), temperature ( $\pm 0.01 \text{ }^\circ\text{C}$ ), and salinity ( $\pm 0.01$ ) were measured using a YSI ProDSS multi-meter calibrated daily. Certified reference materials (CRM) for TA and DIC analyses were from the Marine Physical Laboratory of Scripps Institution of Oceanography (A. Dickson). Duplicate or triplicate analyses were performed on at least 10% of samples. Carbonate system parameters for all study sites including aragonite mineral saturation state ( $\Omega\text{A}$ ) and  $\text{pCO}_2$  were calculated from TA and pHT (or TA and DIC), temperature, and salinity measurements using the carbonate speciation program CO2sys (Pierrot et al., 2006) with dissociation constants  $K_1$  and  $K_2$  from Merbach et al. (1973) refit by Dickson and Millero (1987),  $\text{KSO}_4$  from Dickson (1990), and using the total pH scale. A 1200 kHz RDI Workhorse Monitor Acoustic Doppler Current Profiler was installed at the seaward end of each transect in bare sand to collect water current profiles at each study site.

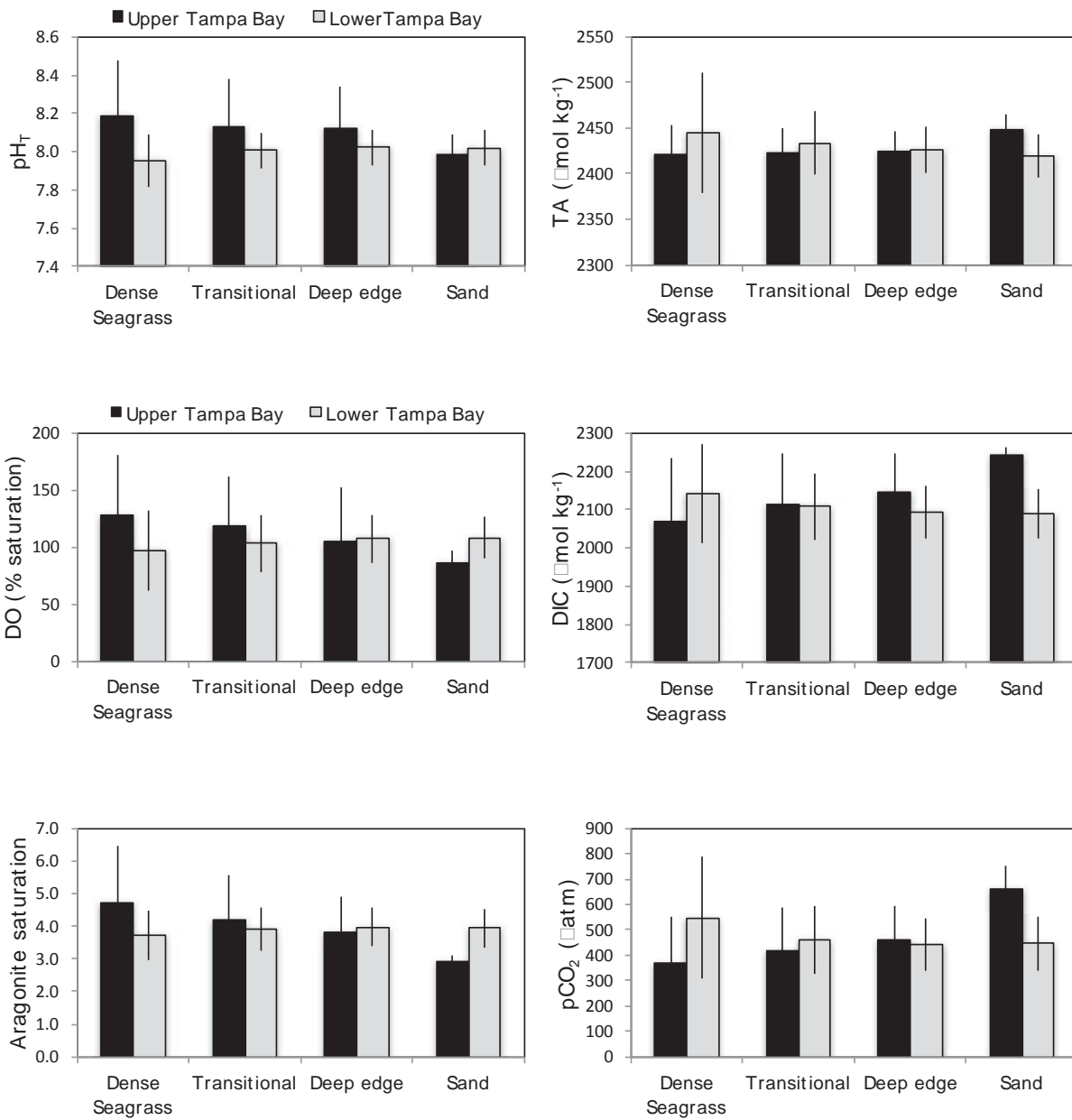
## PRELIMINARY RESULTS AND DISCUSSION

Preliminary results indicate considerable heterogeneity in all water chemistry parameters over small spatial scales (meters) and diurnal time periods (Table 3, Figure 1). Greatest spatial and temporal variability occurred along the Upper Tampa Bay transect where average current magnitude was slowest ( $0.02 \text{ ms}^{-1}$ ). Average pHT, DO, and  $\Omega\text{A}$  were higher and DIC,  $\text{pCO}_2$  and TA were lower at all seagrass sites than in bare sand at the Upper Tampa Bay study site. Spatial and temporal gradients were generally lower along the Lower Tampa Bay transect where average current magnitude (of  $0.1 \text{ ms}^{-1}$ ) was 5 times greater than at the Upper Tampa Bay study site, and average pH and  $\Omega\text{A}$  were slightly lower in dense seagrass than in bare sand.

**Table 3. Average values for discrete sample parameters at each study site in Upper and Lower Tampa Bay.**

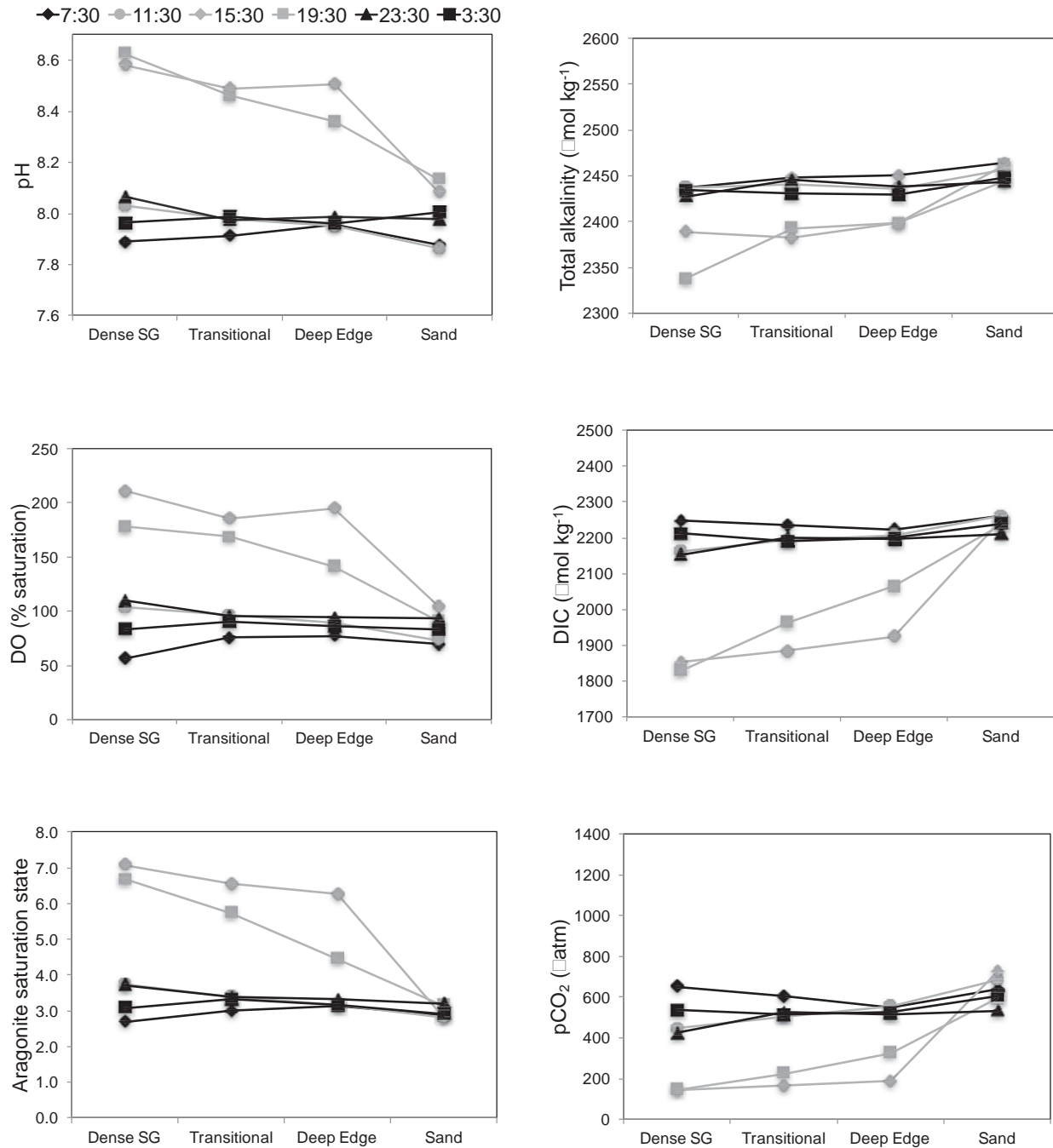
Description	pHT	stdev	DO	stdev	TA	stdev	DIC	stdev	pCO <sub>2</sub>	stdev	ΩA	stdev
Upper Tampa Bay Transect												
Dense seagrass	8.188	0.288	127.8	53.4	2420.7	32.2	2070.0	165.5	367.8	185.5	4.7	1.7
Transitional	8.134	0.244	118.9	42.3	2423.4	26.2	2112.8	135.5	419.1	166.0	4.2	1.4
Deep edge	8.123	0.218	105.0	46.6	2424.9	21.3	2144.9	103.7	459.0	133.8	3.8	1.1
Sand	7.985	0.104	86.2	10.9	2448.7	15.5	2243.8	19.0	658.0	91.3	2.9	0.2
Lower Tampa Bay Transect												
Dense seagrass	7.951	0.137	96.7	35.3	2445.2	66.0	2141.1	128.2	545.9	239.9	3.7	0.8
Transitional	8.006	0.094	103.2	25.1	2433.4	34.3	2107.7	86.7	460.4	131.5	3.9	0.7
Deep edge	8.023	0.092	107.1	20.7	2426.0	25.9	2093.0	69.2	441.9	104.6	4.0	0.6
Sand	8.020	0.093	108.2	18.4	2419.4	24.0	2089.5	65.8	446.4	105.1	3.9	0.6

*stdev = standard deviation*



**Figure 1. Average  $pH_T$ , DO, aragonite saturation state ( $\Omega_A$ ), TA, DIC, and  $pCO_2$  for each substrate type along sampling transects in Upper (black) and Lower (gray) Tampa Bay. Vertical lines indicate plus and minus one standard deviation.**

Greatest spatial variability occurred during afternoon (15:30) and evening hours (19:30) in Upper Tampa Bay (Figure 2). During these time periods, pH, DO, and  $\Omega_A$  were as much as 0.5 pH unit, 107% saturation, and 4.2 higher (and  $pCO_2$  and total alkalinity were as much as



**Figure 2. Time series for pH, DO, aragonite saturation state ( $\Omega_A$ ), TA, DIC, and  $pCO_2$  for each substrate type along sampling transects in Upper Tampa Bay. Black lines indicate dark and early morning hours. Gray lines indicate day light and evening hours.**

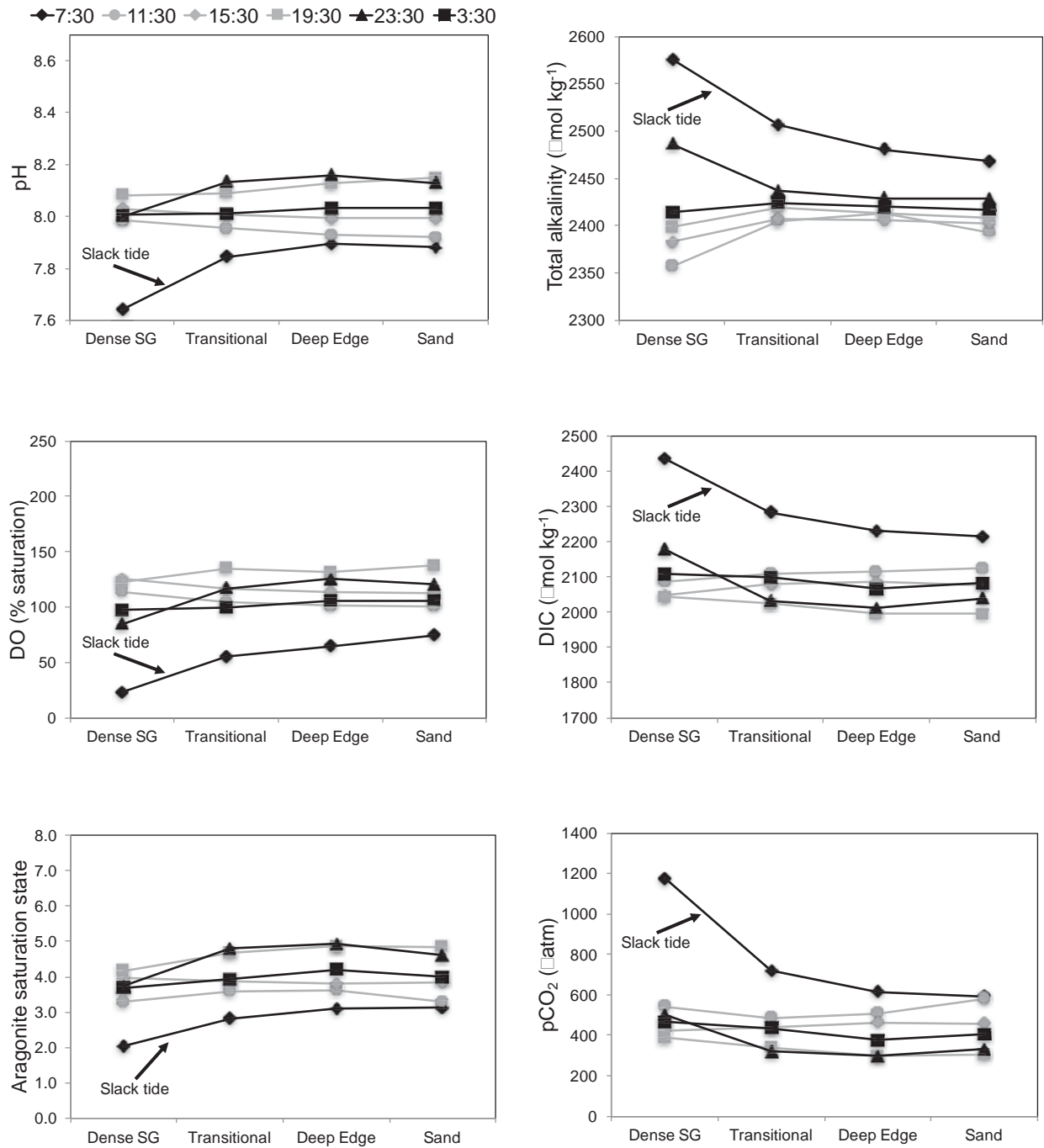
580  $\mu\text{atm}$  and 123  $\mu\text{mol kg}^{-1}$  lower) in dense seagrass than in sand, respectively. Greatest temporal variability occurred in dense seagrass beds with highest pH and DO, and lowest  $\text{pCO}_2$  occurring during late afternoon and evening hours likely due to seagrass photosynthesis. Lowest TA also occurred during late afternoon and evening hours, possibly due to calcification by seagrass epiphytes. However, little variation occurred in TA at the sand site possibly due to a lack of calcifying organisms and carbonate sediments and, therefore, little calcification or dissolution at this location. High and low chemical parameter values generally occurred during early morning (07:30) or late afternoon to evening (15:30 to 17:30) at all seagrass sites.

Greatest spatial variation at the Lower Tampa Bay site occurred at 07:30, concurrently with a slack tide during which pH, DO and  $\Omega\text{A}$  was 0.2 pH unit, 52% saturation and 1.1 lower, respectively, (and  $\text{pCO}_2$  and TA was 594  $\mu\text{atm}$  and 108  $\mu\text{mol kg}^{-1}$  higher, respectively) in the dense seagrass bed than in sand likely due to respiration throughout the night (Figure 3).

TA at the dense seagrass site in Lower Tampa Bay showed greater temporal variability than in Upper Tampa Bay possibly due to the higher percentage of carbonate sediments in the Lower Bay and the potential for carbonate sediment dissolution (that may buffer decreases in pH).

Our preliminary results indicate that seagrass beds in Tampa Bay can elevate pH and  $\Omega\text{A}$  over short (diurnal) time periods, and may provide a local buffer against ocean acidification. However, respiration in seagrass beds during dark hours may cause a decrease in pH and  $\Omega\text{A}$  relative to surrounding substrate. Longer term and larger scale (e.g. baywide) benefit from seagrass buffering of pH depends upon diurnal, seasonal and annual variability in carbonate system parameters, and the magnitude and balance of high and low pH exposure periods over seagrass growth cycles. The considerable gradients in chemical parameters over small spatial scales, and an increase in magnitude of variation with decreasing current velocity, indicates that direct benefit from seagrass buffering of pH also depends upon proximity to seagrass and hydrodynamic effects including water mass residence time and water flow direction. The relatively consistent occurrence of diurnal high and low carbonate parameter values during early morning and late afternoon can be used in combination with basic hydrodynamic information such as tidal stage to formulate a longer-term and larger scale ocean acidification monitoring program to more fully characterize ocean acidification buffering effects of seagrass in Tampa Bay.





**Figure 3.** Time series for pH, DO, aragonite saturation state ( $\Omega_A$ ), TA, DIC, and pCO<sub>2</sub> for each substrate type along sampling transects in Lower Tampa Bay. Black lines indicate dark and early morning hours. Gray lines indicate day light and evening hours.

## **ACKNOWLEDGEMENTS**

We would like to thank the Tampa Bay Estuary Program for funding this research, along with the U.S. Geological Survey Coastal and Marine Geology Program, Florida Fish and Wildlife Conservation Commission - Fish and Wildlife Research Institute, and ESA for financial and logistical support. Use of trade, firm or product names does not imply endorsement by the U.S. Government.

## REFERENCES

- Anthony, K.R.N., Kleypas, J.A., and Gattuso, J-P. 2011. Coral reefs modify their seawater carbon chemistry – implications for impacts of ocean acidification. *Global Change Biology* 17:3655-3666.
- Barton, A., Hales, B., Waldbusser, G.G., Langdon, C., and Feely, R.A. 2012. The Pacific oyster, *Crassostrea gigas*, shows negative correlation to naturally elevated carbon dioxide levels: Implications for near-term ocean acidification effects. *Limnology and Oceanography* 57(3):698-710.
- Dickson, A. G. 1990. Standard potential for the reaction:  $\text{AgCl(s)} + \frac{1}{2} \text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$ , and the standard acidity constant of the ion  $\text{HSO}_4^-$  in synthetic seawater from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* 22:113–127.
- Dickson, A. G. and Millero, J. J. 1987. A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Research* 34:1733–1743.
- Dickson, A.G., Sabine, C.L., and Christian, J.R. (Eds.). 2007. Guide to best practices for ocean acidification  $\text{CO}_2$  measurements. PICES Special Publication 3, 191pp.
- Edgar, E.T., Brooks, G., and Cronin, T.M. 2007. Location and surface sediment data for cores collected in Tampa Bay, 202 through 2006. U.S. Geological Survey [http://dl.cr.usgs.gov/tampa/prod\\_search\\_tampa.aspx?prodid=20147](http://dl.cr.usgs.gov/tampa/prod_search_tampa.aspx?prodid=20147).
- Fabry, V.J., Seibel, B.A., Feely, R.A., and Orr, J.C. 2008. Impacts of ocean acidification on marine fauna and ecosystem processes. *ICES Journal of Marine Science* 65:414-432.
- Gazeau, F., Quiblier, C., Jansen, J.M., Gattuso, J.-P., Middleburg, J.J., and Heip, C.H.R. 2007. Impact of elevated  $\text{CO}_2$  on shellfish calcification. *Geophysical Research Letters* 34, L07603, doi:10.1029/2006GL028554.
- Hendriks, I.E., Olsen, Y.S., Ramajo, L., Basso, L., Steckbauer, A., Moore, T.S., Howard, J., and Duarte, C.M. 2014. Photosynthetic activity buffers ocean acidification in seagrass meadows. *Biogeosciences* 11:333-346.
- IPCC. 2014. *Climate Change 2014: Impacts, Adaptation, and Vulnerability. Part A: Global and Sectoral Aspects. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* [Field, C.B., V.R. Barros, D.J. Dokken, K.J. Mach, M.D. Mastrandrea, T.E. Bilir, M. Chatterjee, K.L. Ebi, Y.O. Estrada, R.C. Genova, B. Girma, E.S. Kissel, A.N. Levy, S. MacCracken, P.R. Mastrandrea, and L.L. White (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Kleypas, J.A. and Yates, K.K. 2009. Coral reefs and ocean acidification. *Oceanography* 22(4):108-117.
- Kroecker, K.J., Kordas, R.L., Crim, R.N., and Singh, G.G. 2010. Meta-analysis reveals negative yet variable effects of ocean acidification on marine organisms. *Ecology Letters* 13:1419-1434.

- Kurihara, H. 2008. Effects of CO<sub>2</sub>-driven ocean acidification on the early developmental stages of invertebrates. *Marine Ecology Progress Series* 373:275-284.
- Manzello, D. P., Enochs, I. C., Melo, N., Gledhill, D. K., and Johns, E. M. 2012. Ocean acidification refugia of the Florida Reef Tract. *PLoS ONE* 7, e41715, doi:10.1371/journal.pone.0041715.
- Merbach, C., Culberson, C. H., Hawley, J. E., and Pytcowicz, R. M. 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, *Limnology and Oceanography* 18:897–907.
- Narita, D., Rehdanz, K., and Tol, R.S.J. 2012. Economic costs of ocean acidification: a look into the impacts on global shellfish production. *Climatic Change* 113:1049-1063.
- Pierrot, D.E., Lewis, E., Wallance, D.W.R. 2006. Ms Excel program developed for CO<sub>2</sub> system calculations. ORNL/CDIAC-105a, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee.
- Salm, R. V., Done, T., and Mcleod, E. 2006. Marine protected area planning in a changing climate, in: *Coral Reefs and Climate Change: Science and Management*, American Geophysical Union, Washington, DC, pp. 207-221.
- Semesi, I.S., Beer, S., and Bjork, M. 2009. Seagrass photosynthesis controls rates of calcification and photosynthesis of calcareous macroalgae in a tropical seagrass meadow. *Marine Ecology Progress Series* 382:41-47.
- Sherwood, E.T., Greening, H.S., Janicki, A.J., and Karlen, D.J. 2016. Tampa Bay estuary: monitoring long-term recovery through regional partnerships. *Regional Studies in Marine Science* 4:1.11.
- Tomasko, D., Crooks, S., and Robison, D. in press. Refining carbon sequestration estimates of seagrass meadows in Tampa Bay. *BASIS 6 Proceedings*, pp. 259-272.
- Waldbusser, G.G., Voigt, E.P., Bergschneider, H., Green, M.A., and Newell, R.I.E. 2011. Biocalcification in the Eastern Oyster (*Crassostrea virginica*) in relation to long-term trends in Chesapeake Bay pH. *Estuaries and Coasts* 34:221-231.
- Yao, W. and Byrne, R.H. 1998. Simplified seawater alkalinity analysis: use of linear array spectrometers. *Deep-Sea Research Part 1* 45:1383-1392.
- Zhang, H. and Byrne, R.H. 1996. Spectrophotometric pH measurements of surface seawater at in-situ conditions: absorbance and protonation behavior of thymol blue. *Marine Chemistry* 52:17-25.