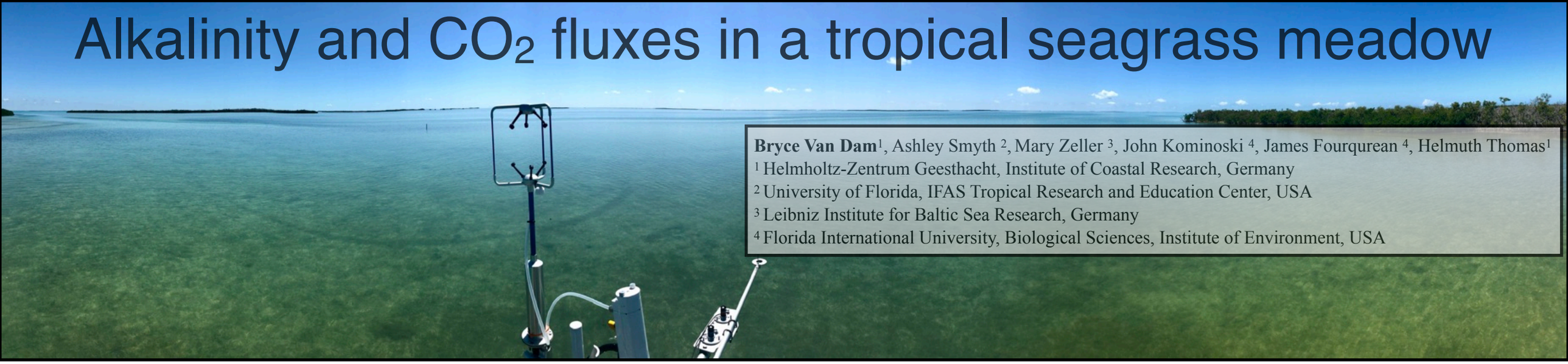
Alkalinity and CO_2 fluxes in a tropical seagrass meadow

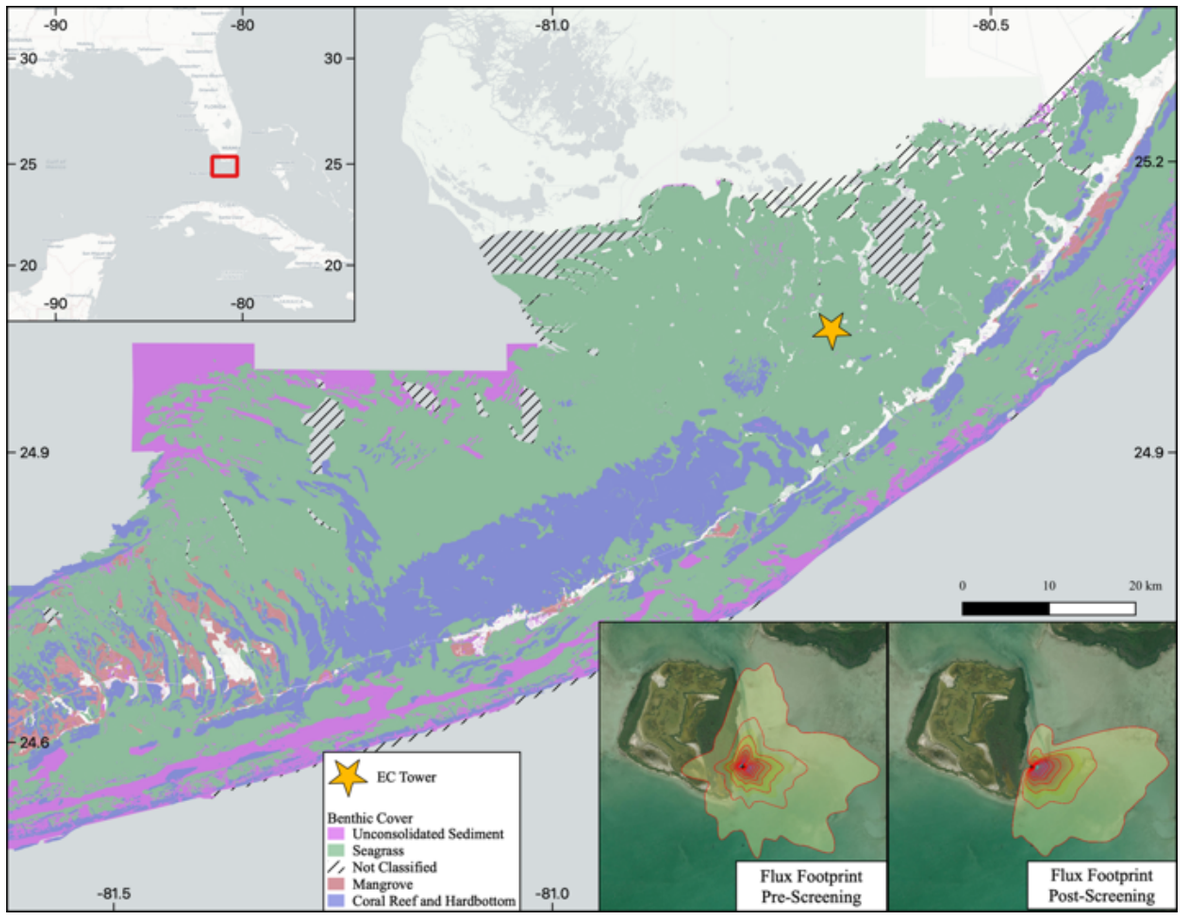


Bryce Van Dam[1], Ashley Smyth [2], Mary Zeller [3], John Kominoski [4], James Fourqurean [4], Helmuth Thomas[1]
[1] Helmholtz-Zentrum Geesthacht, Institute of Coastal Research, Germany
[2] University of Florida, IFAS Tropical Research and Education Center, USA
[3] Leibniz Institute for Baltic Sea Research, Germany
[4] Florida International University, Biological Sciences, Institute of Environment, USA

Introduction:

Total alkalinity (TA) production in vegetated coastal systems is considered a putative sink for atmospheric CO_2, due to the increase in the seawater buffer capacity when TA is produced in excess of DIC. This TA is often generated by denitrification and Fe reduction, although in oligotrophic tropical waters with carbonate sediments, these sources of TA may be minimal.

We quantified carbon fluxes across both sediment-water and air-water interfaces in a tropical seagrass meadow, Florida Bay, USA, which overlies sediments composed of biogenically-precipitated $CaCO_3$. We measured sediment-water fluxes of N_2, TA, and DIC, and placed these measurements into the context of water-air CO_2 exchange, which was measured by atmospheric eddy covariance.



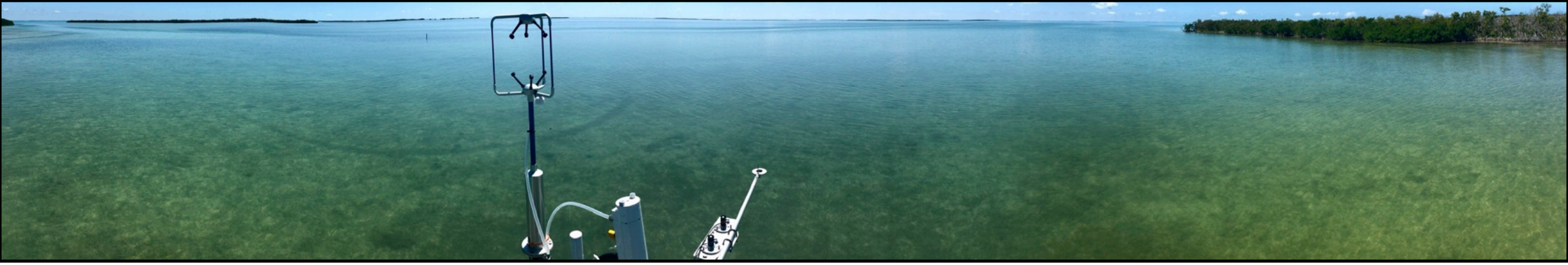
Helmholtz-Zentrum Geesthacht
Zentrum für Material- und Küstenforschung

Leibniz-Institut für Ostseeforschung Warnemünde

FIU Institute of Water and Environment

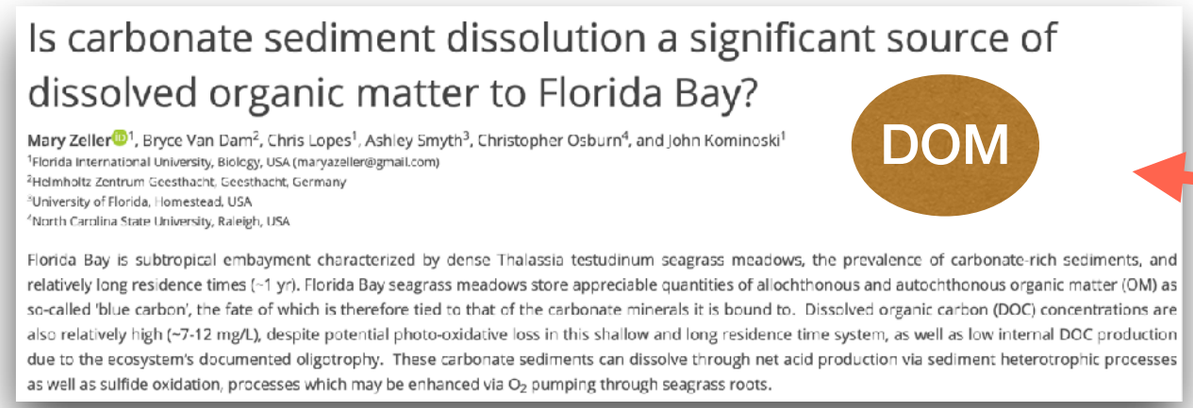
UF IFAS University of Florida

National MAGLAB



Specific Scientific Questions:

1. *Are sediments net sources or sinks of DIC and TA, and how much can be explained by denitrification and calcification?* Seagrass meadows are considered as 'blue carbon' ecosystems due to high rates of organic carbon burial. However, this carbon sink may be counteracted by CO_2 generated via calcification and net heterotrophy in sediments. Still, the production of alkalinity in underlying sediments (via reduction of NO_3, SO_4, Fe) may constitute a related carbon sink by buffering the carbonate chemistry of overlying waters.
2. *What is the combined effect of sediment biogeochemical processes on CO_2 emission/uptake at the air-water interface?* The subject of air-water CO_2 exchange over seagrasses has received much attention in recent years, related to their capacity as coastal 'blue carbon' sinks, and the growing recognition of calcification as a potential confounding factor. Understanding air-water CO_2 exchange above seagrass meadows is key to their importance in global carbon budgets, yet few studies have measured CO_2 fluxes (FCO_2) over seagrasses, essentially none in the tropics.
3. *Are carbonate sediments a significant source of organic matter?* Organic matter can be masked in carbonate sediments in intracrystalline networks from the point of biogenesis, and acidic organic matter can be adsorbed following carbonate mineral dissolution/recrystallization. How much DOM is then released upon eventual sediment dissolution, and what impact does this have on the water column DOM signature? We used sediment extractions and FT-ICR-MS to find out! Check out our findings related to DOM dynamics here: https://doi.org/10.5194/egusphere-egu2020-812



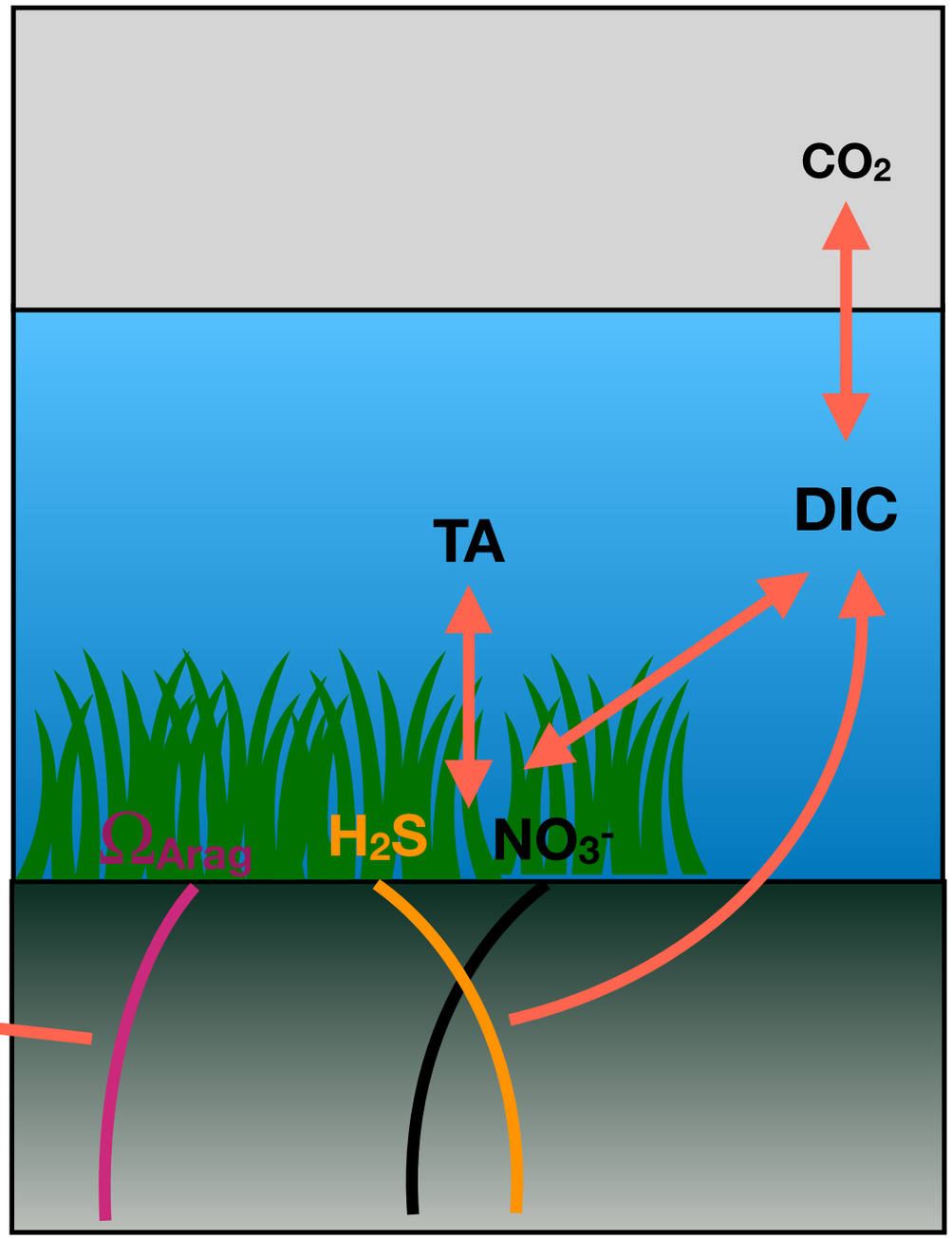
Is carbonate sediment dissolution a significant source of dissolved organic matter to Florida Bay?

Mary Zeller[1], Bryce Van Dam[2], Chris Lopes[1], Ashley Smyth[3], Christopher Osburn[4], and John Kominoski[1]
[1]Florida International University, Biology, USA (maryazeller@gmail.com)
[2]Helmholtz Zentrum Geesthacht, Geesthacht, Germany
[3]University of Florida, Homestead, USA
[4]North Carolina State University, Raleigh, USA

Florida Bay is subtropical embayment characterized by dense Thalassia testudinum seagrass meadows, the prevalence of carbonate-rich sediments, and relatively long residence times (~1 yr). Florida Bay seagrass meadows store appreciable quantities of allochthonous and autochthonous organic matter (OM) as so-called 'blue carbon', the fate of which is therefore tied to that of the carbonate minerals it is bound to. Dissolved organic carbon (DOC) concentrations are also relatively high (~7-12 mg/L), despite potential photo-oxidative loss in this shallow and long residence time system, as well as low internal DOC production due to the ecosystem's documented oligotrophy. These carbonate sediments can dissolve through net acid production via sediment heterotrophic processes as well as sulfide oxidation, processes which may be enhanced via O_2 pumping through seagrass roots.

DOM

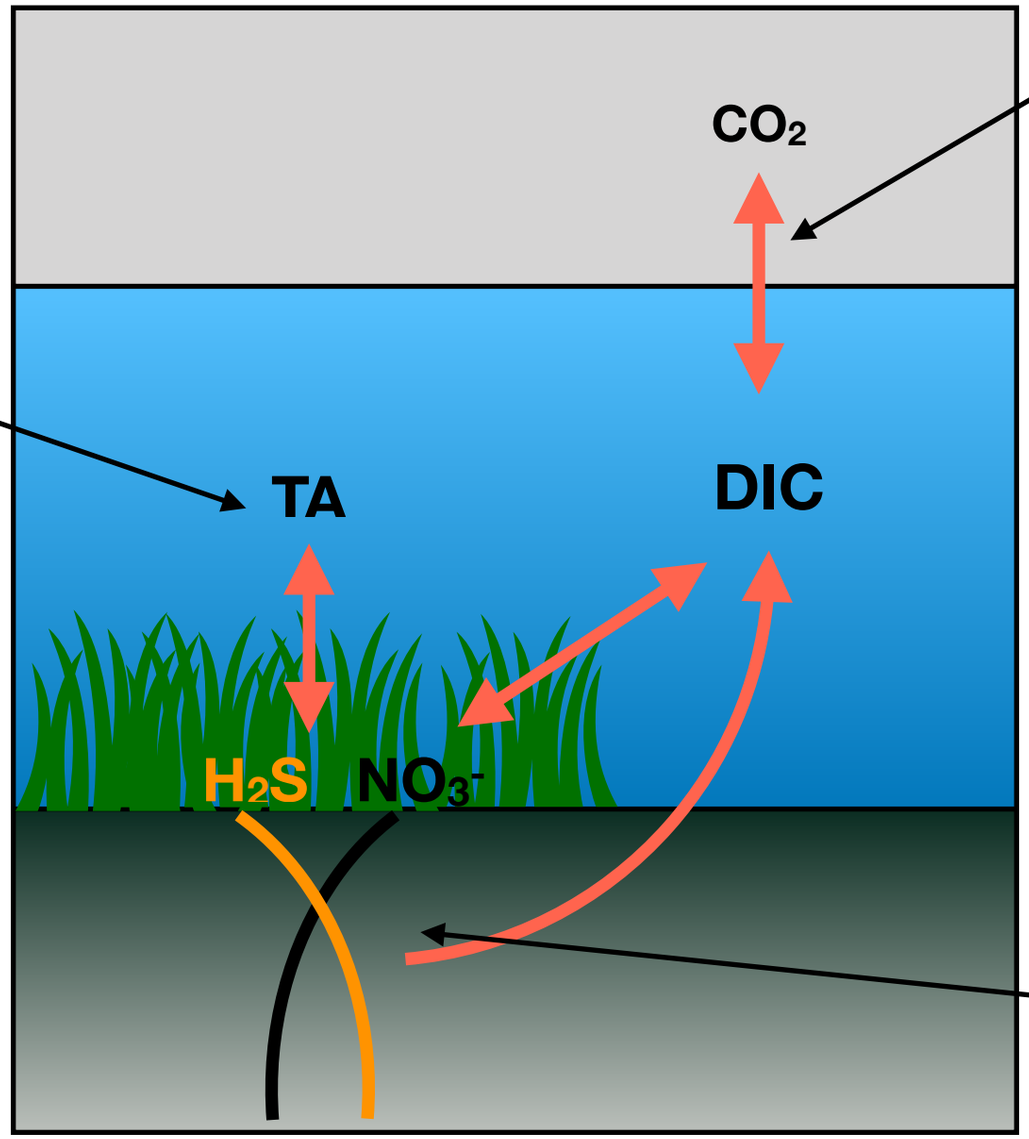
?



Methods

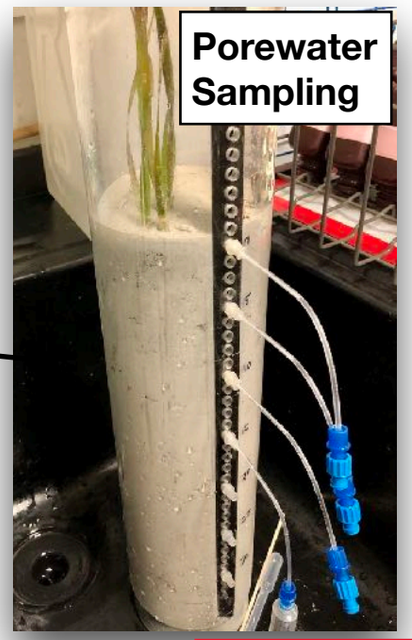
1. This study took place during a ~4 day period in November 2019, representing conditions typical of South Florida's wet season.
2. We used a flow-through experimental setup with in-tact sediment cores to measure sediment-water fluxes of dissolved constituents.
3. Rhizons™ were used to sample pore-waters for geochemical analysis
4. An eddy covariance tower provided direct measurements of air-water CO_2 exchange, such that the flux footprint roughly overlapped with the seagrass meadow under study (see footprint analysis on first slide)

A flow-through setup was used to directly measure sediment-water fluxes of TA, DIC, N_2 (net denitrification), etc.

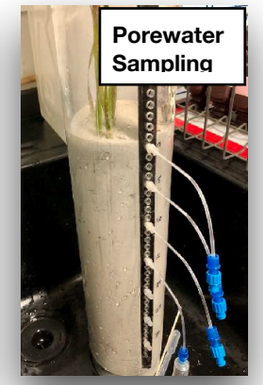


Atmospheric eddy covariance platform used to quantify rates of air-water CO_2 exchange

Pore-water sampling for geochemical parameters (H_2S, SO_4^{2-}, ^{13}C-DIC, etc). These samples have not yet been analyzed, due to the current pandemic situation

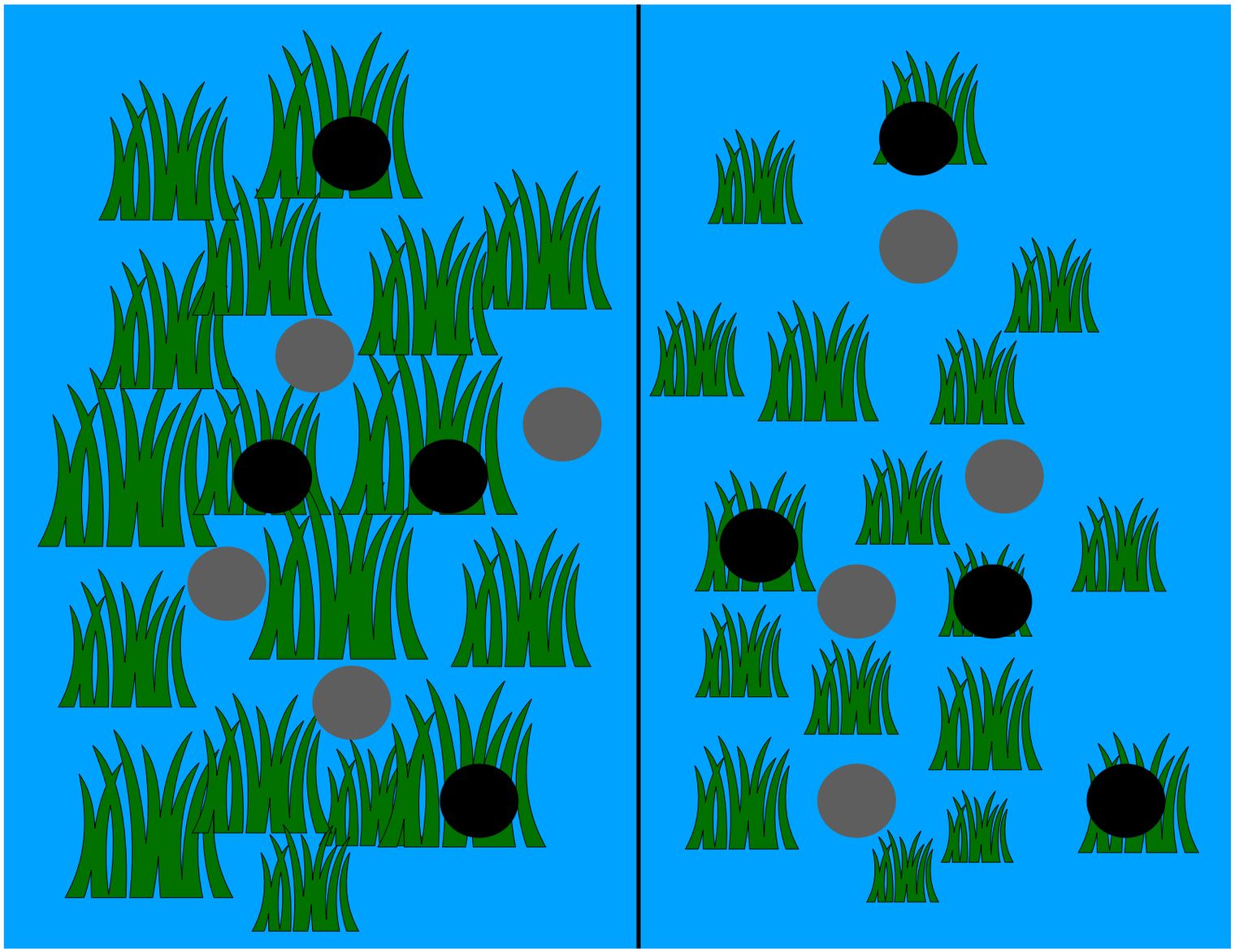


Methods



Seagrass included in sediment core

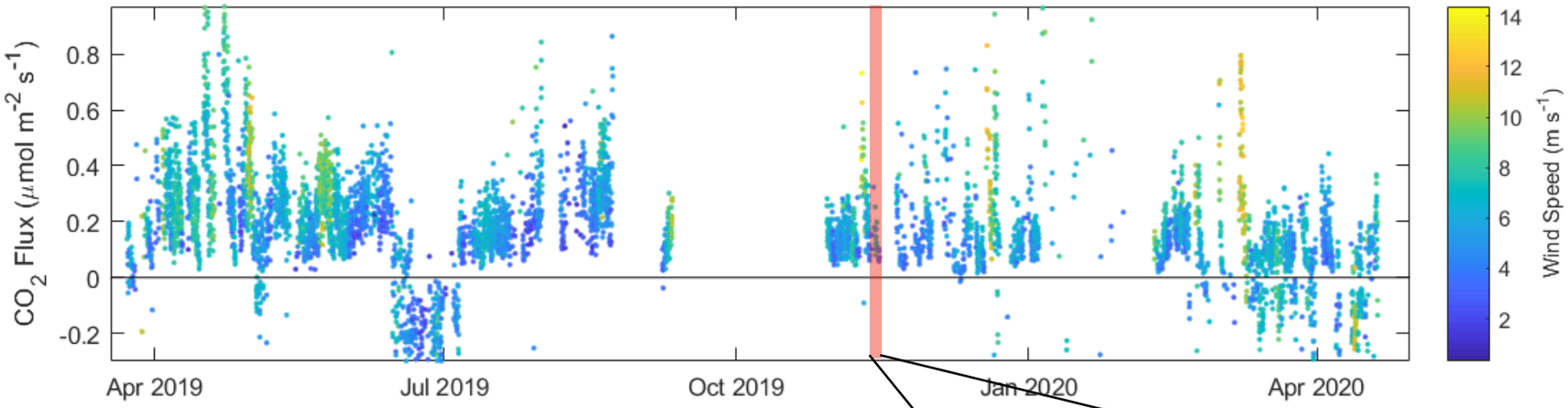
Seagrass absent from sediment core



1. In an attempt to capture the spatial heterogeneity in the seagrass meadow, we collected 24 sediment cores in two regions where seagrass biomass was relatively high and low.
2. Half of the cores included aboveground biomass, and half were still in the meadow, but excluded aboveground biomass (as in the picture to the left).

Results

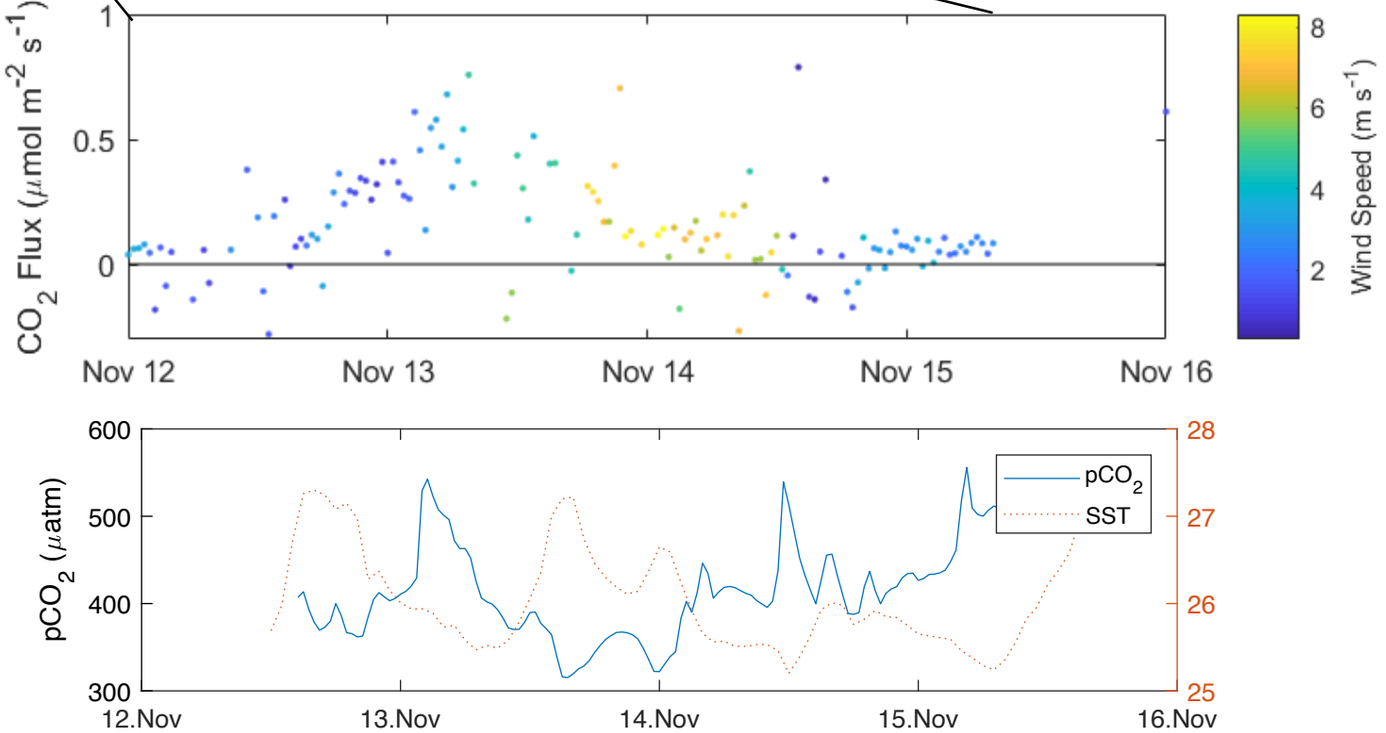
Air-water CO_2 exchange for the entire period of record at this site



1. Air-water CO_2 exchange was small and variable, reflecting the highly-buffered seawater chemistry and oligotrophic nature of this seagrass meadow.

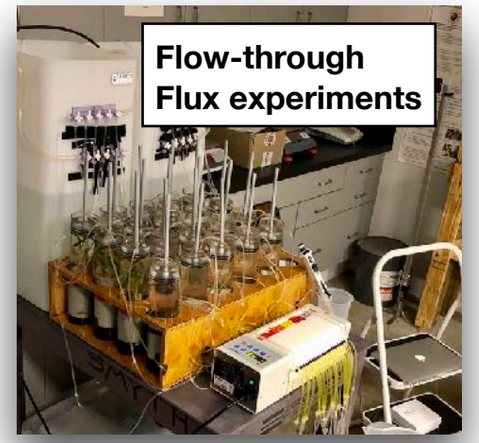
2. As is typical for this site (above figure), the seagrass meadow was a small CO_2 source to the atmosphere during the study period (bottom figure). On average, CO_2 flux was 0.078 μmol m^{-2} sec^{-1} or 0.28 ± 0.23 mmol m^{-2} hr^{-1}.

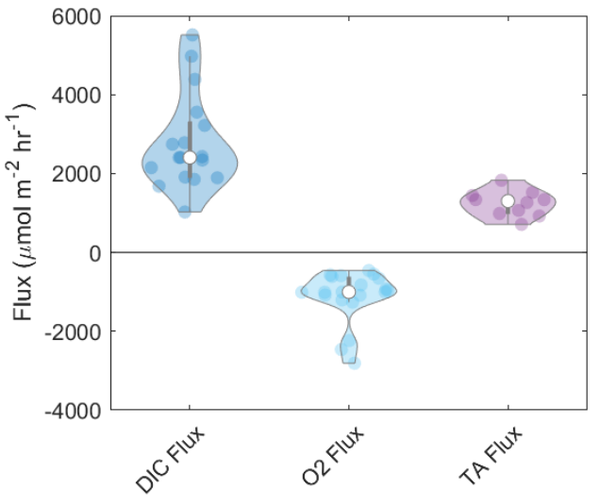
3. CO_2 flux does not always coincide with greater wind speed. This is consistent with prior findings at this site, which suggest water-side convective forcing as a dominant physical driver of gas transfer, not simply wind-driven turbulence (Van Dam et al., under review).

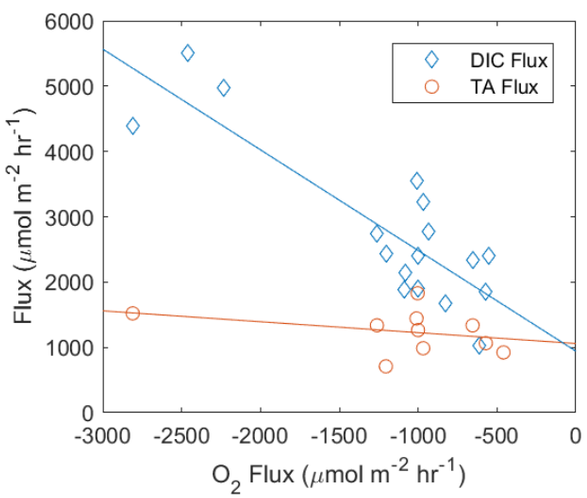


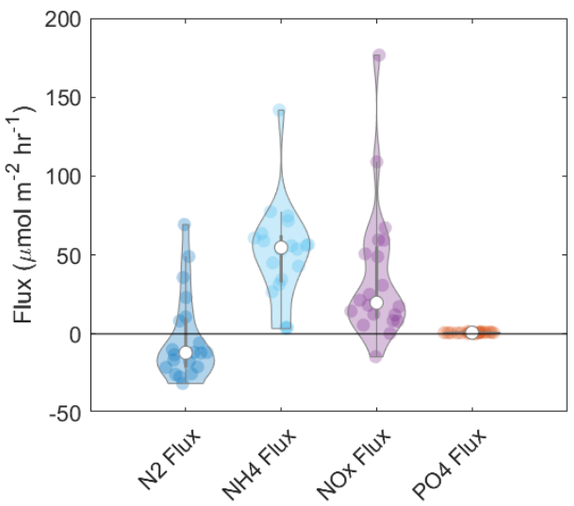
CO_2 Flux (top) and pCO_2 (bottom) for this study period in Fall 2019

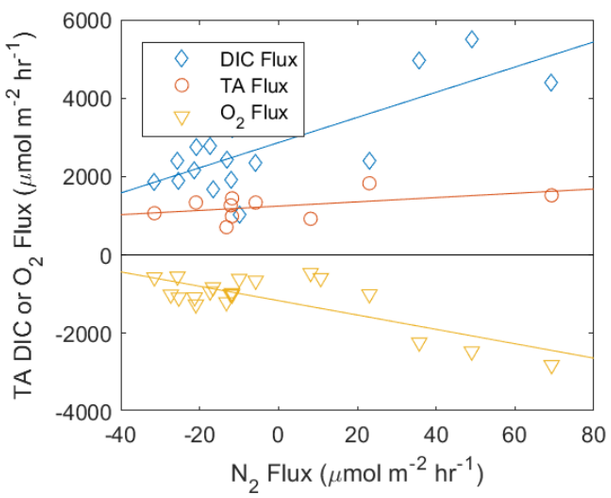
Results







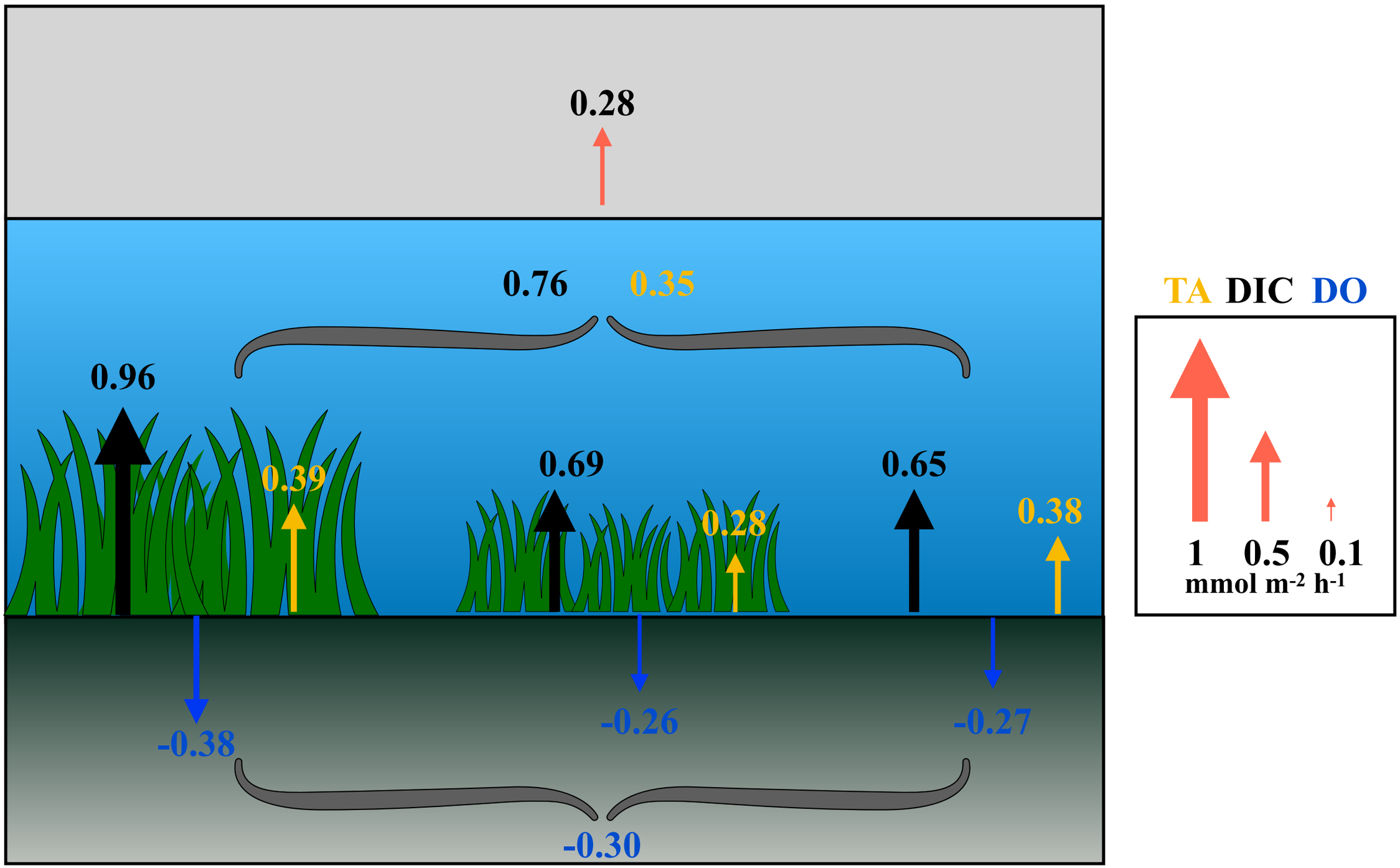


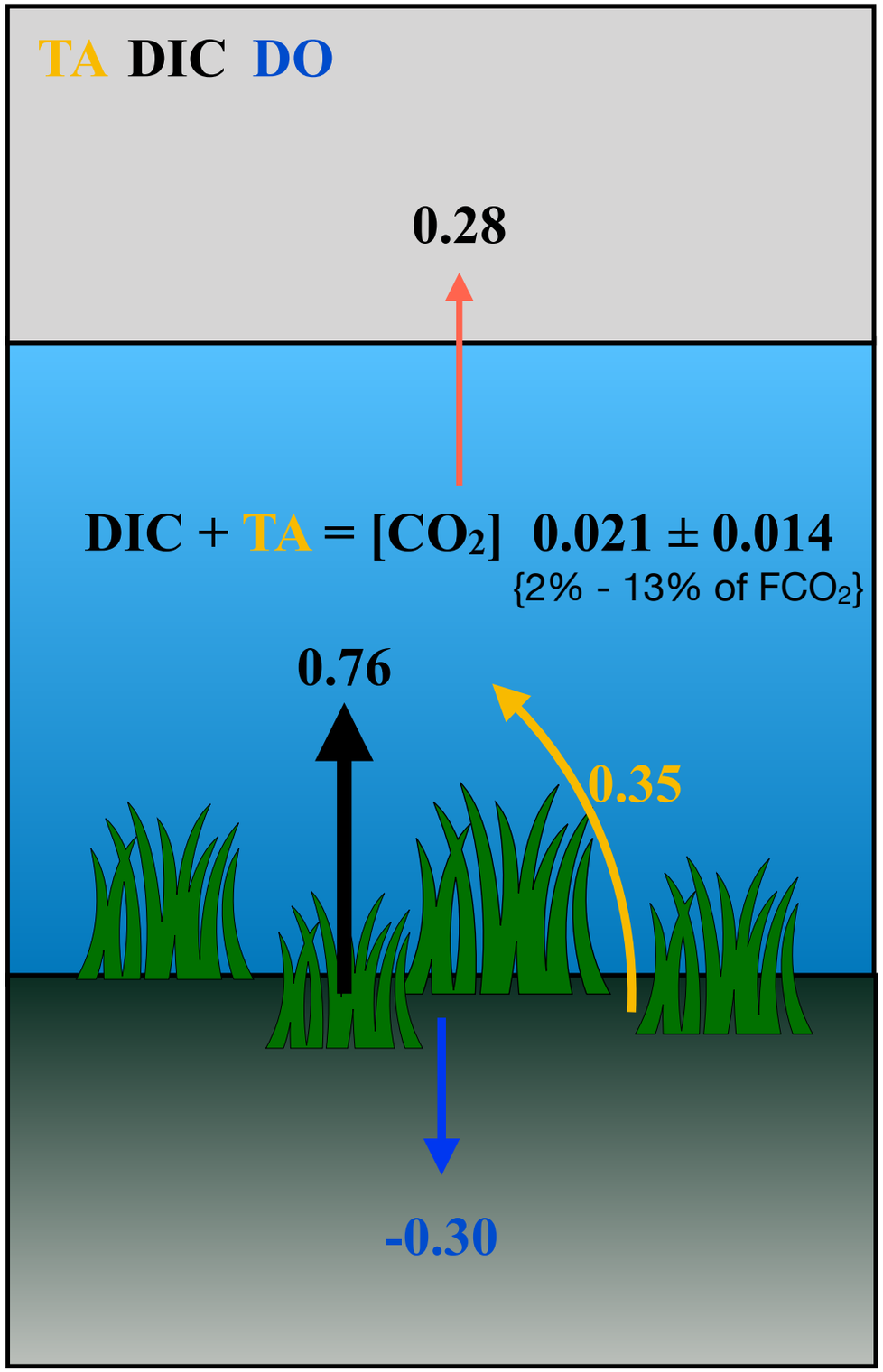


1. Net O_2 consumption was observed in all cores, although sediment O2 demand was greater and more variable in cores with seagrass biomass included. Note that this experiment was conducted in a relatively dark room (picture above), so as to avoid bubble formation.
2. Likewise, all cores were net sources of DIC. However, DIC release was ~2-3x greater than O_2 uptake, suggesting that carbonate dissolution and anaerobic respiration were significant sources of DIC, in excess of aerobic respiration.
3. Net N_2 fluxes were near 0 and variable, indicating that denitrification was in close balance with N Fixation. This is consistent with the sulfide inhibition of DNF, which has been observed previously in Florida Bay (Gardner and McCarthy 2009).
4. Nevertheless, net DNF was observed in cores which included seagrass biomass, indicating that seagrasses here may enhance DNF.
5. All cores were also TA sources, but the correlation between TA flux and net N_2 flux was not significant. Therefore, it appears that sediment-water TA fluxes were dominated by the combined effect of SO_4 reduction, H_2S oxidation, and carbonate dissolution/precipitation.
6. Concentrations of solid-phase Fe and Mn are very low at this site (not shown), indicating that metal reduction is not likely an important TA source here.

Summary

1. We construct a simple carbon budget, by combining measurements of fluxes across the sediment-water and air-water interface.
2. Sediments are large sources of DIC (mean = 0.76 mmol m^{-2} hr^{-1}), exceeding O_2 consumption (0.3 mmol m^{-2} hr^{-1}) by a factor of > 2x.
3. However, DIC fluxes were accompanied by substantial TA release (mean = 0.35 mmol m^{-2} hr^{-1}), muting the effect of benthic respiration on the pCO_2 of overlying water.





Summary

Summary:

1. Given overlying water TA and DIC of 2860 and 2436 µmol kg^{-1}, and a salinity and temperature of 36.5 and 26 respectively, we can estimate that these combined TA an DIC fluxes would have caused dissolved CO_2 concentrations to increase at a rate of ~0.021 mmol m^{-2} hr^{-1}.
2. This can only explain 2-13% of the air-water CO_2 exchange.
3. So, where is the remaining CO_2 coming from?

Missing Fluxes:

A. Water column metabolism
- Unlikely, given the shallow water depth (<2 m) and very low chl-a (<1 µg L^{-1}) and bacterial productivity (1 µg L^{-1} d^{-1}, or 0.04 mg m^{-2} hr^{-1}) - Boyer et al 2006.

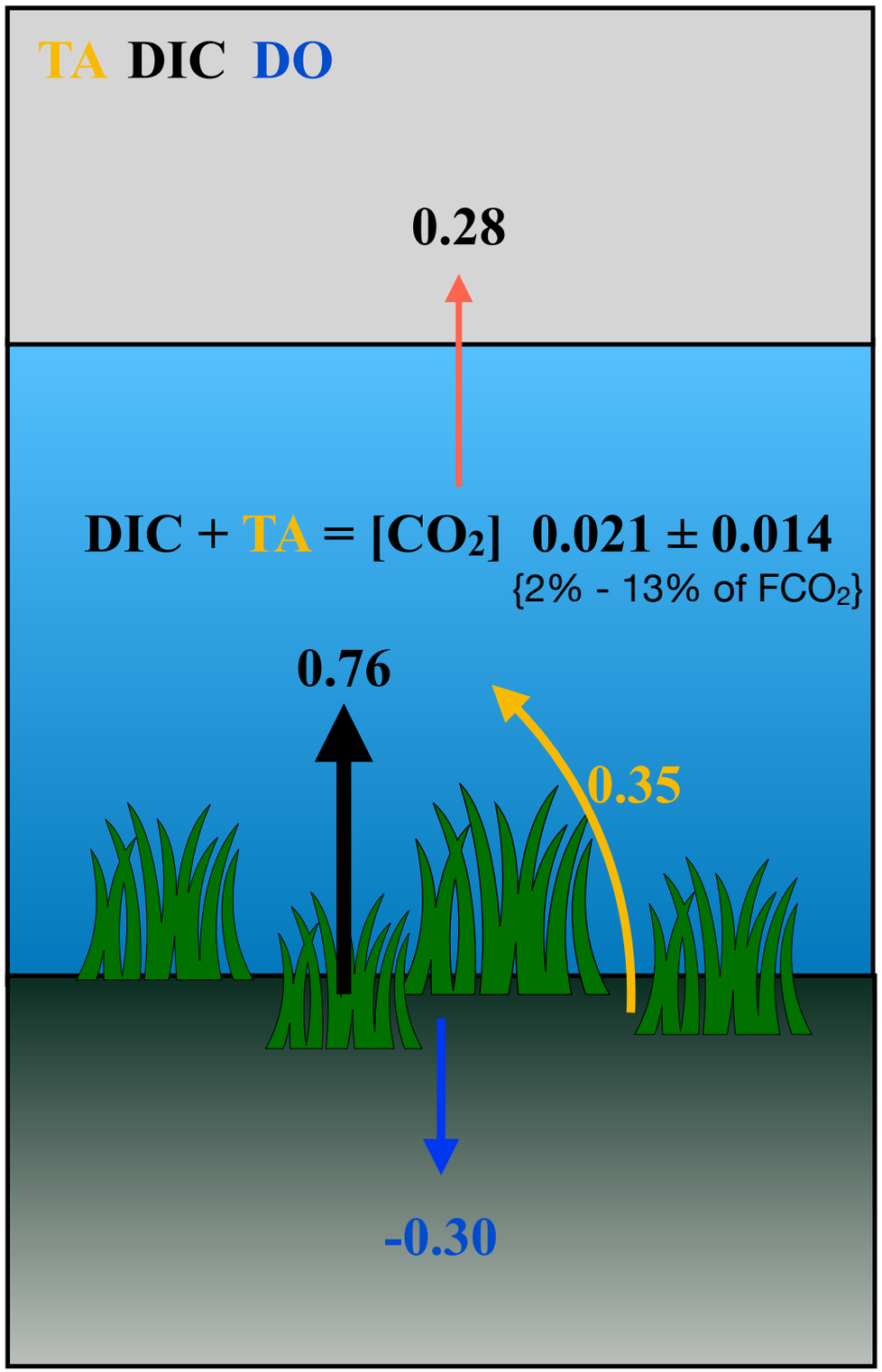
B. Calcification
- We conducted these flux experiments in the dark, likely underestimating the calcification that accompanies photosynthetic primary production here.
- Prior studies show calcification/dissolution elsewhere in Florida Bay is highly variable, between -5 to 5 mmol m^{-2} hr^{-1} (Van Dam et al 2019)

C. Lateral DIC input from adjacent mangrove forests

D. Photodegradation of DOC
- Please visit our related EGU 2020 presentation on DOM dynamics in Florida Bay here: https://doi.org/10.5194/egusphere-egu2020-812

Take a step back…

1. We can assume that the rate of organic ('blue carbon') burial here is close to a global average of ~ -0.47 mmol C m^{-2} hr^{-1}.
2. In the present study, this 'blue carbon' burial is entirely offset by DIC release from the sediments (0.76 mmol C m^{-2} hr^{-1})
3. However, the ultimate fate of this C is important, which may be released to the atmosphere as CO_2, or remain in solution as DIC. This depends on the buffering capacity (Revelle Factor) of the overlying water.
4. While this site was a net CO_2 source to the atmosphere, CO_2 emissions would have been much larger if not for the appreciable sediment-water TA fluxes, which acted to buffer the accompanying benthic DIC flux.



Next Steps

1. Finish analytical work delayed by pandemic
    1. Pore-water
        1. H_2S, SO_4^{2-}, ^{13}C-DIC, Fe^{2+}, Nutrients, etc
    2. Sediment physical properties (XRD, SEM)
    3. DOC
        1. DOC fluxes and ^{13}C-DOC
        2. DOM photolability study
        3. FT-ICR-MS
2. Continue with dry-season sampling this summer

Helmholtz-Zentrum Geesthacht
Zentrum für Material- und Küstenforschung

Leibniz-Institut für Ostseeforschung Warnemünde
iow

FIU Institute of Water and Environment

UF IFAS University of Florida

National MAGLAB

References

Boyer, J. N., S. K. Dailey, P. J. Gibson, M. T. Rogers, and D. Mir-Gonzalez. 2006. The role of dissolved organic matter bioavailability in promoting phytoplankton blooms in Florida Bay. Hydrobiologia **569**: 71–85. doi:10.1007/s10750-006-0123-2

Gardner, W., & McCarthy, M. 2009. Nitrogen Dynamics at the Sediment-Water Interface in Shallow, Sub-Tropical Florida Bay: Why Denitrification Efficiency May Decrease with Increased Eutrophication. Biogeochemistry. ***95.*** 185-198.

Van Dam, B. R., C. Lopes, C. L. Osburn, and J. W. Fourqurean. 2019. Net heterotrophy and carbonate dissolution in two subtropical seagrass meadows. Biogeosciences **16**: 4411–4428. doi:10.5194/bg-16-4411-2019

Van Dam, B. R., C. Lopes, C. L., Polsenaere, P., Price, R.M., Rutgersson, A., Fourqurean, J. W. Under Review. Water temperature control on CO_2 flux and evaporation over a subtropical seagrass meadow revealed by atmospheric Eddy Covariance. Limnology and Oceanography.