



NATIONAL HIGH
MMAGNETIC
FIELD LABORATORY



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

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FUNDING

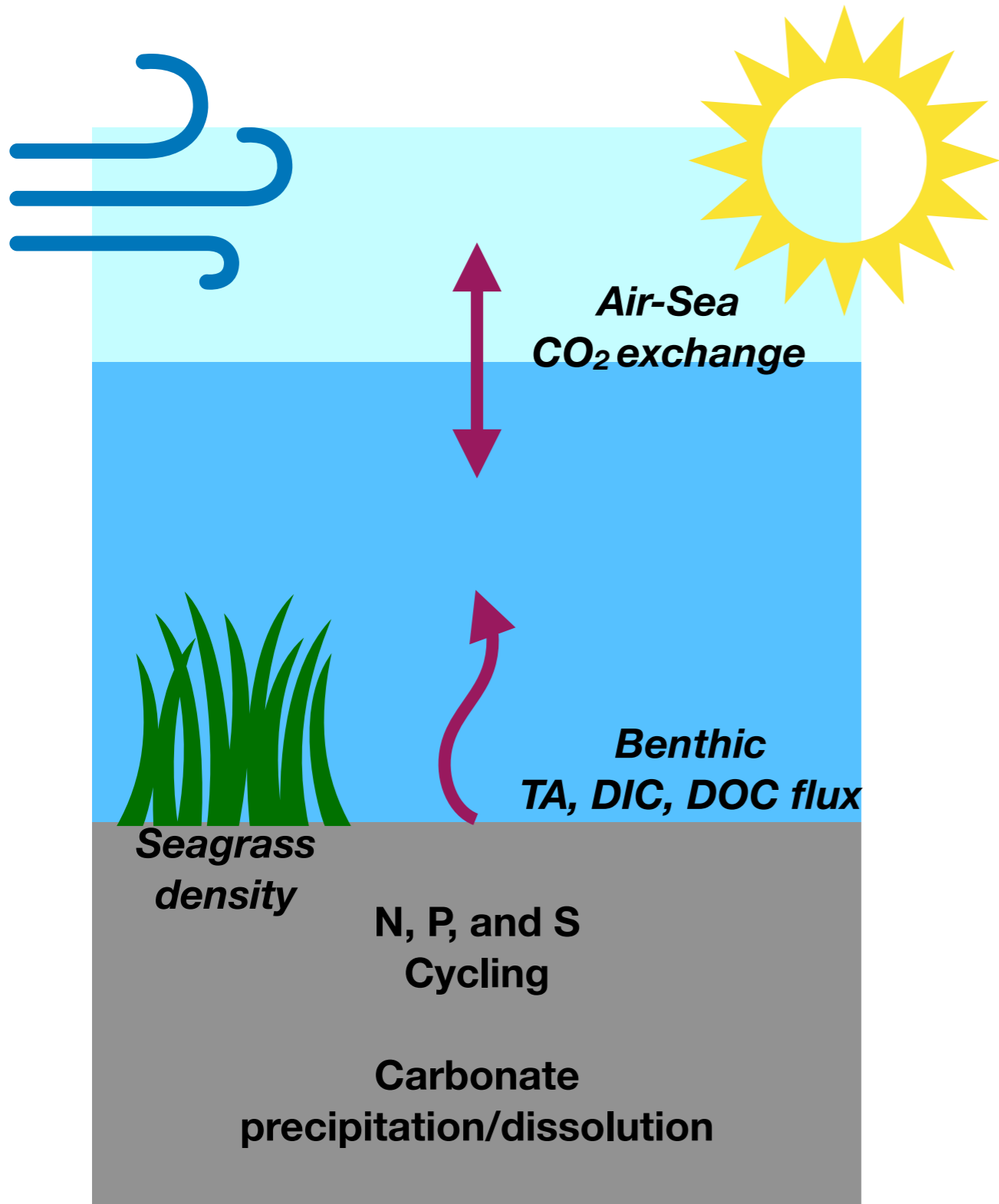
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Introduction



Broader collaborative study:

- Are seagrasses in carbonate sediments sinks or sources of carbon?
- Interplay of seagrass density, sediment biogeochemistry, and air-sea CO₂ exchange
- Week-long study in November 2019

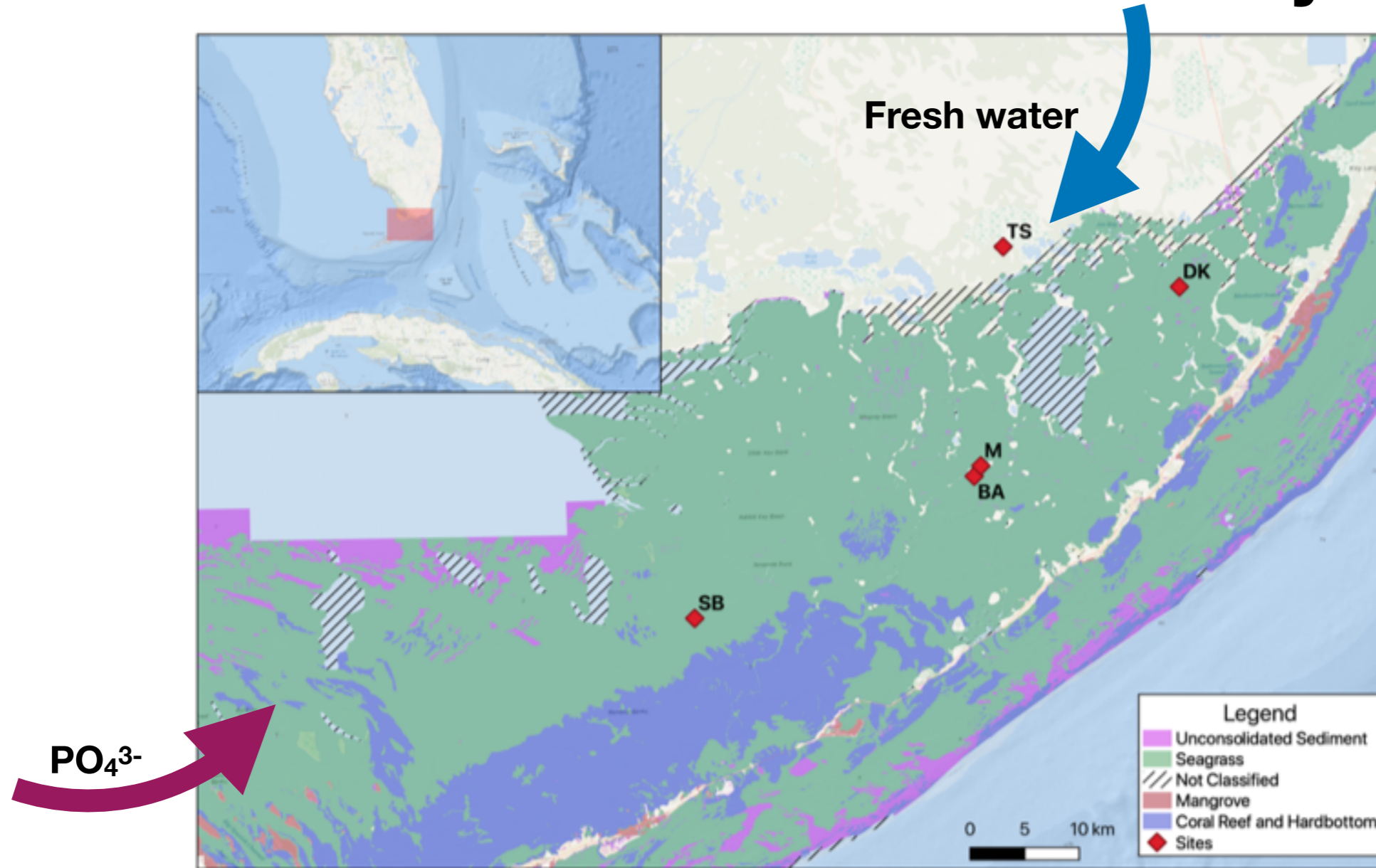
This work:

- Does carbonate dissolution release organic matter and how important is this process in the OM cycle?
- Interplay of seagrass density, sediment dissolution, and benthic OM flux

Collaborator's presentation:

- Air-sea CO₂ exchange and TA story
- [BG4.1/OS2.13, D661](#)
- Wed, 06 May, 14:00-15:45

An Introduction to Florida Bay



Florida Bay: a “reverse estuary”, where fresh water dilutes nutrients delivered from the Gulf of Mexico





Sediments: 80-95% carbonate
Very low Fe (sulfidic)
Carbonates associate a lot of limited PO₄³⁻

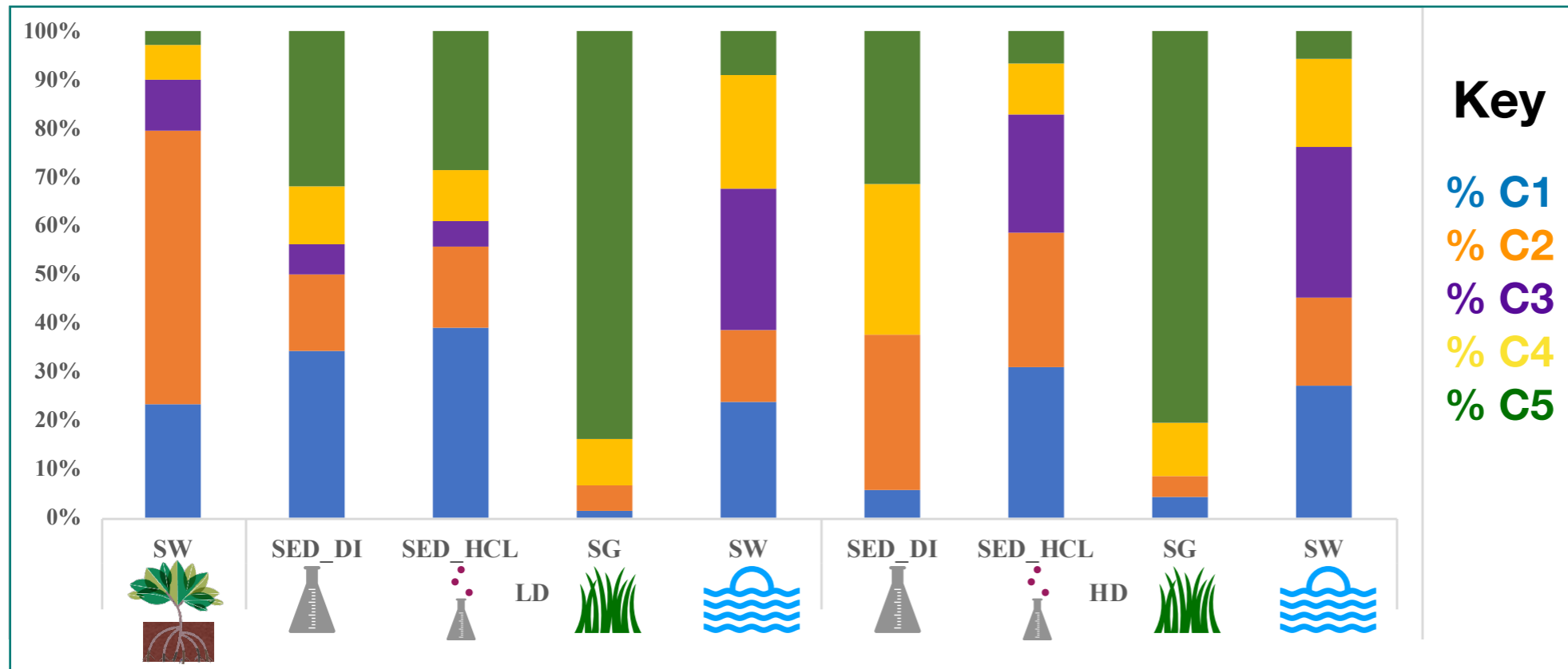
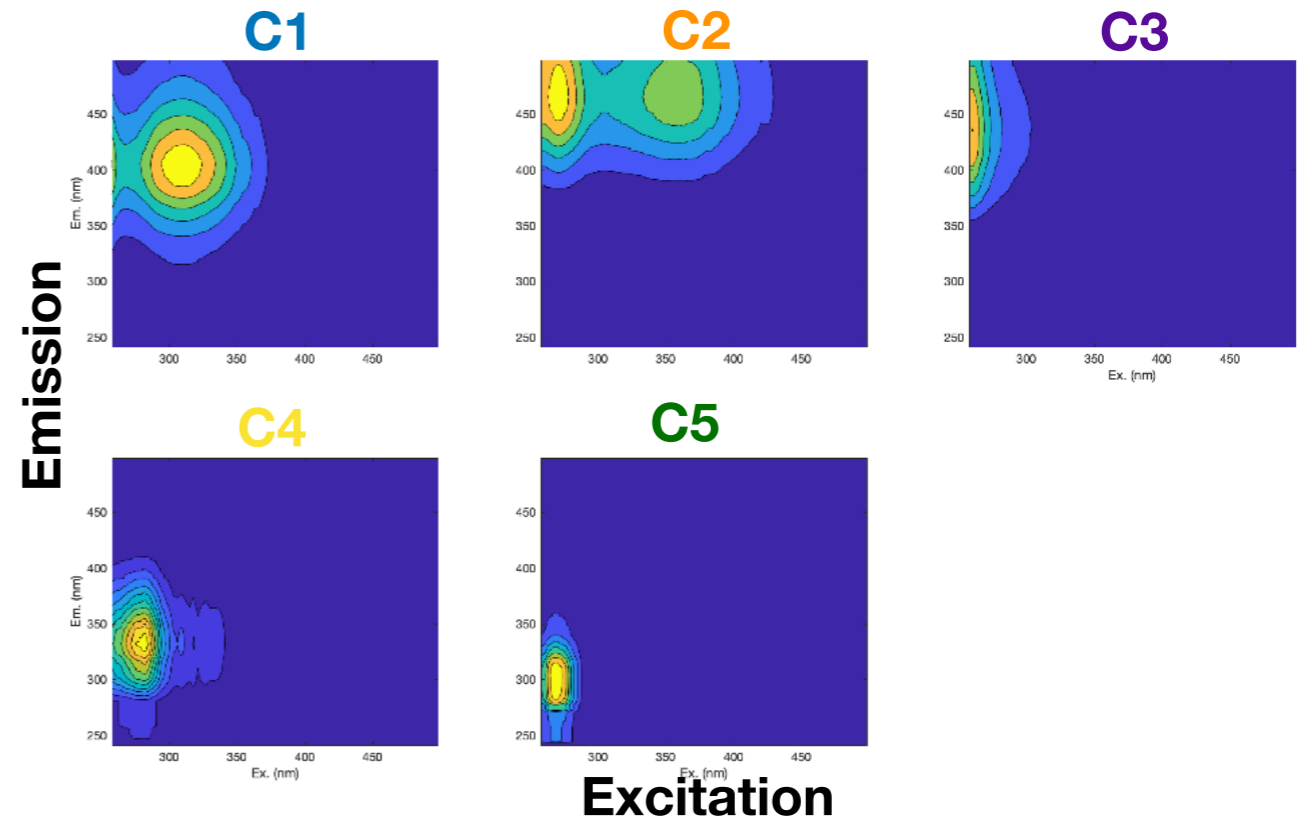
Seagrasses: Strategies for obtaining PO₄³⁻ from sediments via carbonate dissolution: O₂ pumping and organic acid production in roots

Our question: Does carbonate dissolution release carbonate associated OM as well?

Background: Prior Work

Early leachate fDOM experiment:

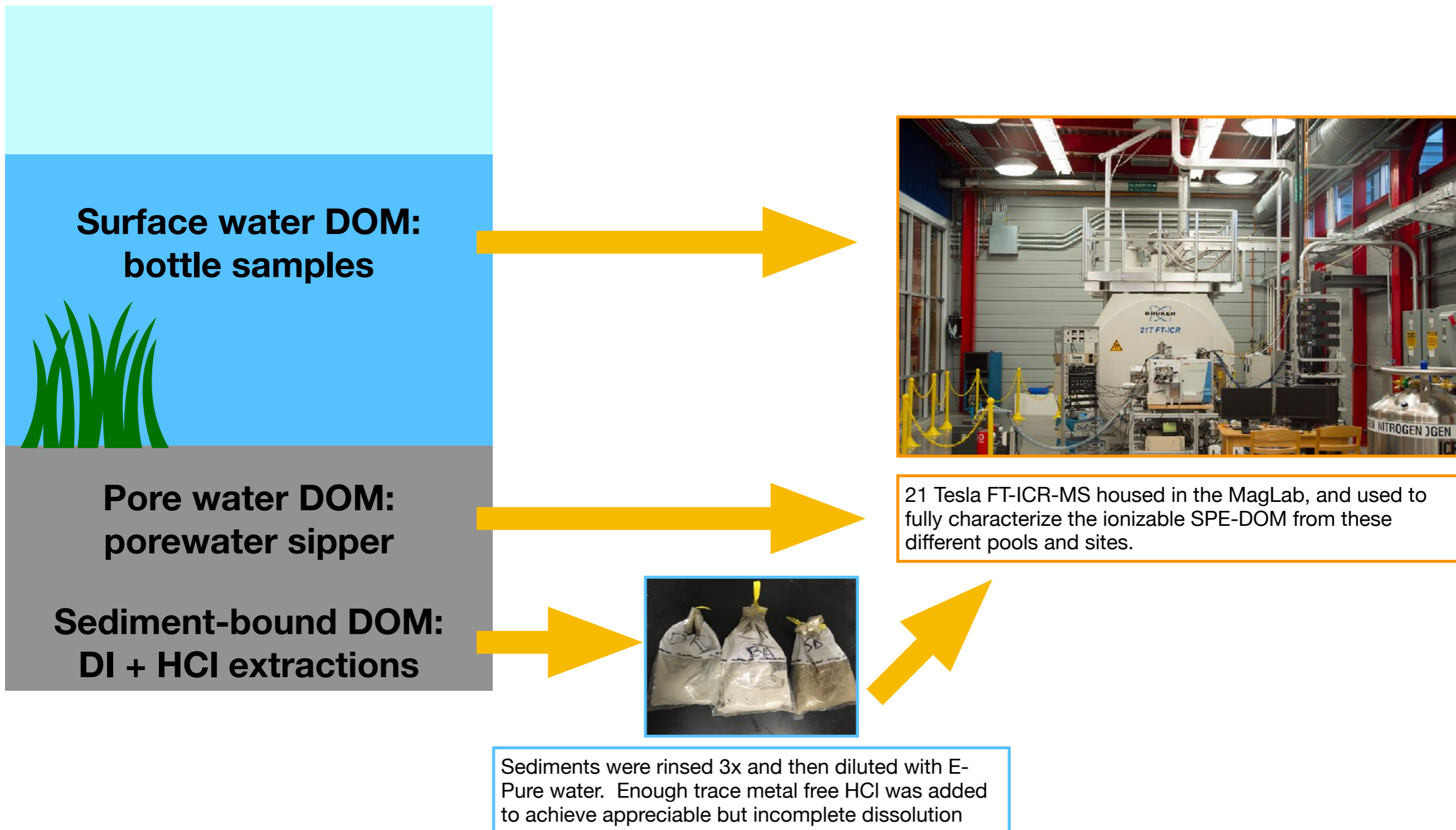
 Seagrass Leaves leached with DI
 Mangrove Surface Water
 Carbonate sediment leachate
 DI and HCl + DI
 HD (high density) and LD (low density)
 seagrass meadow surface water



Main Finding:
 fDOM of Florida Bay
 seagrass meadow
 surface waters most
 resemble the fDOM of
 their sediment HCl
 extracts (mimicking
 carbonate sediment
 dissolution)

Experimental Design

Step 1: Fully characterize DOC from potential sources and pools from multiple sites throughout Florida Bay



Experimental Design

Step 2: Fully characterize biogeochemical processes at one focused site

At BA (central Florida Bay) :



Continuous:

CO₂ Flux
H₂O Flux
PAR, Temp, Salinity

Study period:

pCO₂, pH



Pore water:

¹³C DIC
HS⁻ (³⁴S)
SO₄²⁻ (³⁴S)

Sediments:

Total metals
(incl. Fe and Mn)
XRD, SEM
TOC, TP, TN



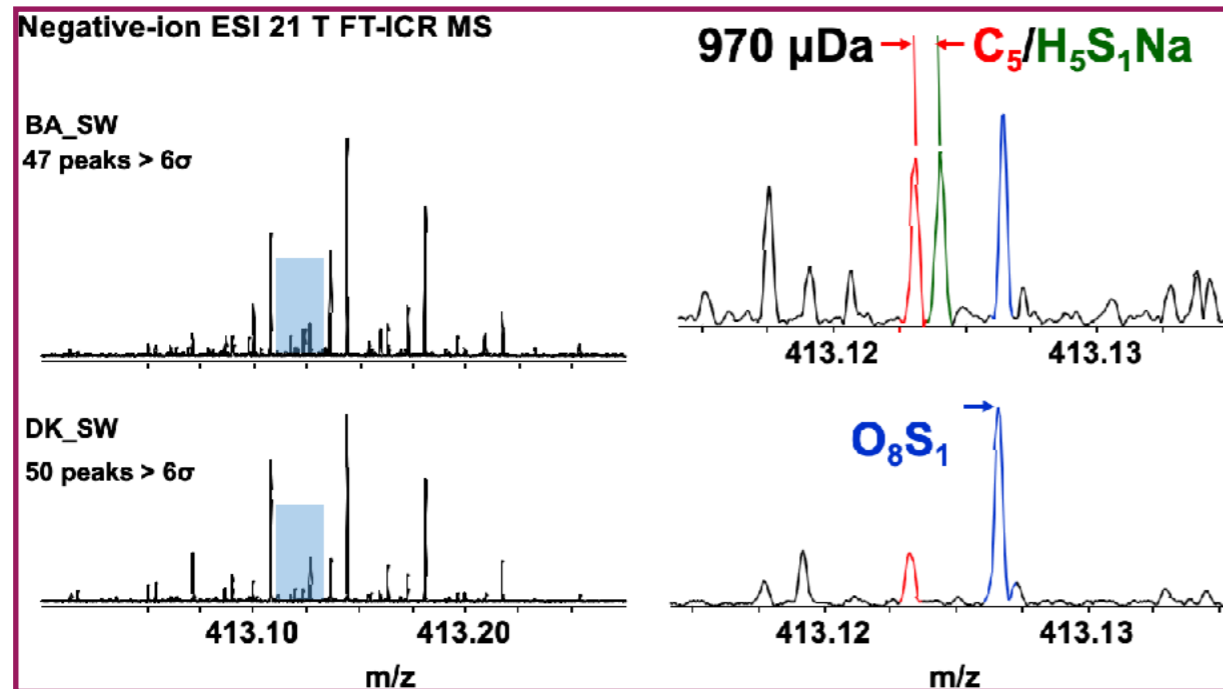
5 hour flow through flux:

N₂, O₂
NH₄⁺, PO₄³⁻, NO_x
¹³C DIC
Tot Alk
¹³C DOC
EEMs
FT-ICR-MS

Many pieces are still incomplete, in part due to the Coronavirus limiting the ability to analyze samples, and in part due to the sheer quantity of interconnected parts, so this presentation focuses on Step 1

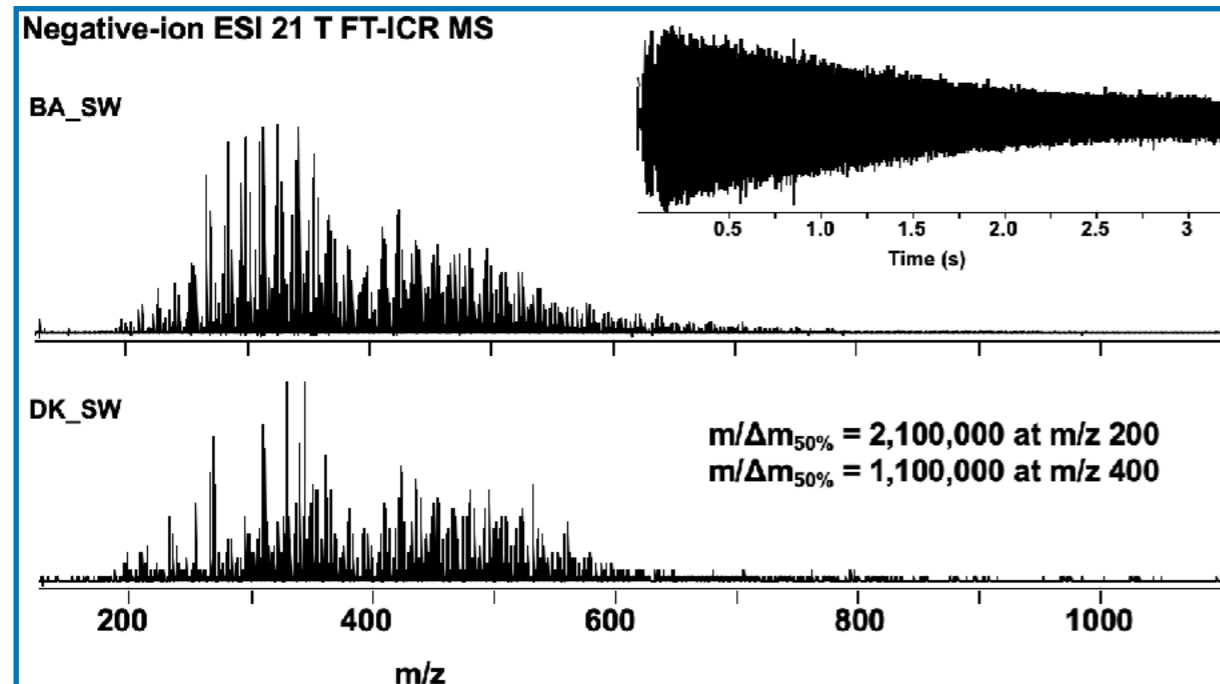
FT-ICR-MS : Resolution

Ultra high resolution mass spectrometry:



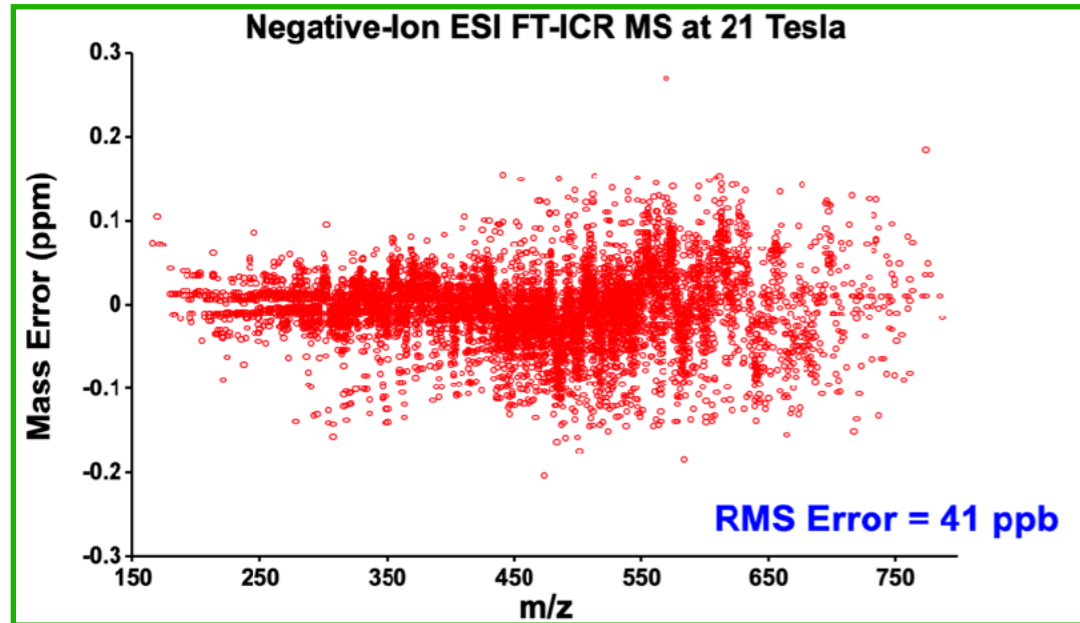
(Left) Mass spectral zoom insets from m/z 413-413.30 are shown for BA_SW (top) and DK_SW (bottom) to highlight the compositional complexity and the requirement for ultrahigh resolution mass spectrometry. In this figure, more than 50 mass spectral peaks are resolved at 6 times the signal-to-noise ratio baseline root-mean-square (rms) noise across the mass range for the DK_SW compared to 47 peaks in BA_SW across the same mass range. (Right) Mass scale zoom insets for each samples across m/z 413.10-413.15 highlight the compositional complexity between these two samples by highlighting the sulfur-containing compounds. For DW_SW, the most abundant mass spectral peak (blue) corresponds to a compound with the elemental composition [C₁₉H₂₅O₈S₁]⁻. The same mass spectral peak is also observed for the BA_SW sample, but also contains two additional sulfur-containing compounds at nearly equal relative abundance: [C₂₂H₂₁O₈]⁻ (red) and [C₁₇H₂₆O₈S₁Na]⁻ (green). These compounds differ in elemental composition by C₅ and H₅S₁Na, which is an exact mass difference of 970 μDa and is less than the mass of two electrons.

Resolving power of 21 Tesla FT-ICR-MS:



Broadband 21 T negative-ion electrospray ionization mass spectra for two water samples (BA_SW and DK_SW) collected on a 21 T hybrid linear ion trap FT-ICR mass spectrometer at the National High Magnetic Field Laboratory in Tallahassee, FL, USA. All samples were collected with spray conditions of -2.2-2.4 kV at a flow rate of 0.5 mL/min and optimized instrumentation parameters for complex mixtures as previously reported (*J. Am. Soc. Mass Spectr.*, 26, 9, 1626-1632 (2015); *Anal. Chem.*, 90, 3, 2041-2047 (2018)). The molecular weight distribution for each sample was first verified by LTQ analysis to ensure the validity of the molecular weight distribution based on FT-ICR MS. For each magnitude mode data set, the achieved resolving power ($m/\Delta m_{50\%}$) was 1,100,000 at m/z 400 (2,100,000 at m/z 200).

FT-ICR-MS : Peak Assignment



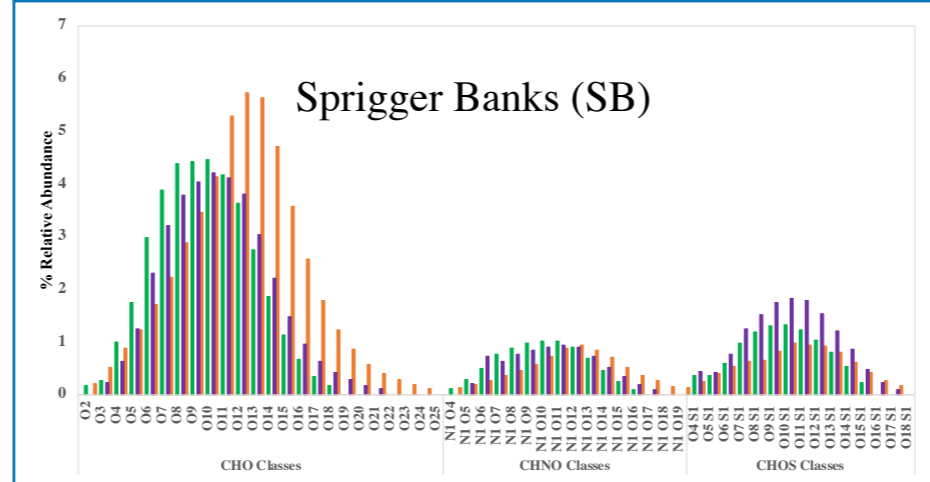
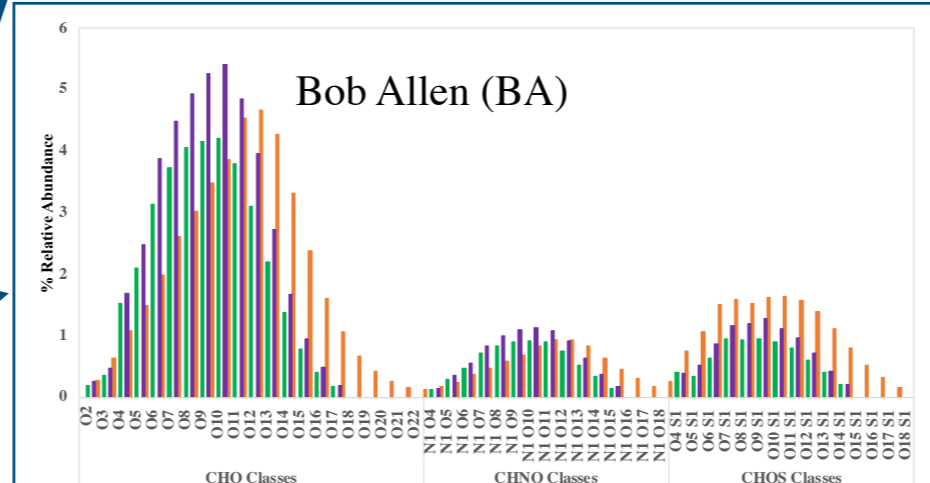
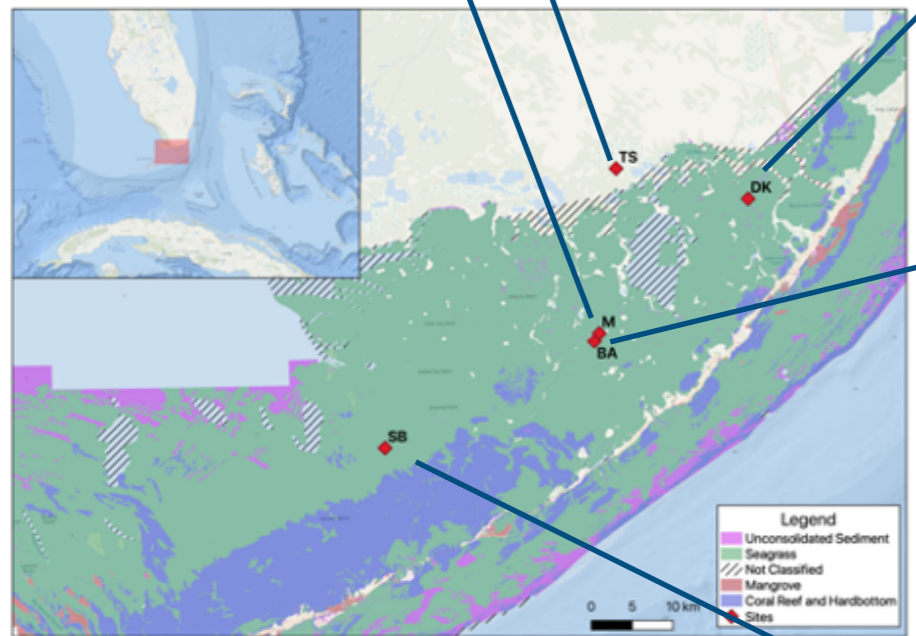
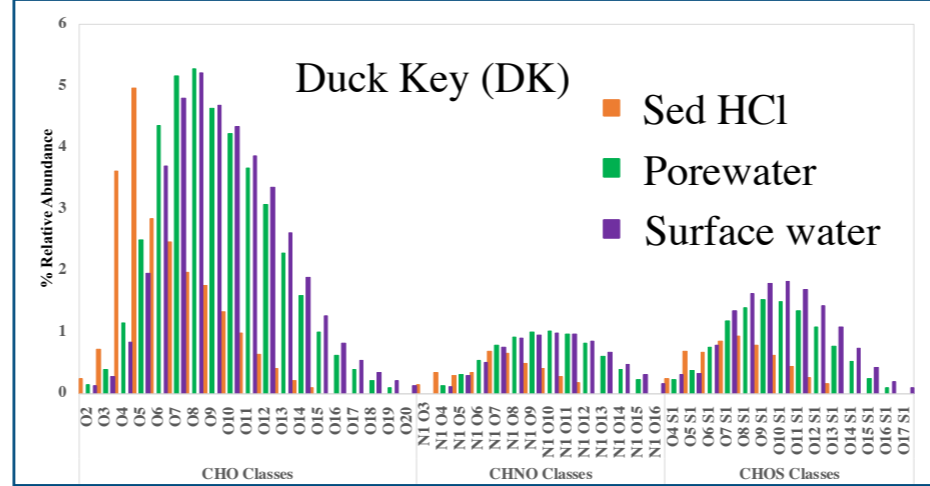
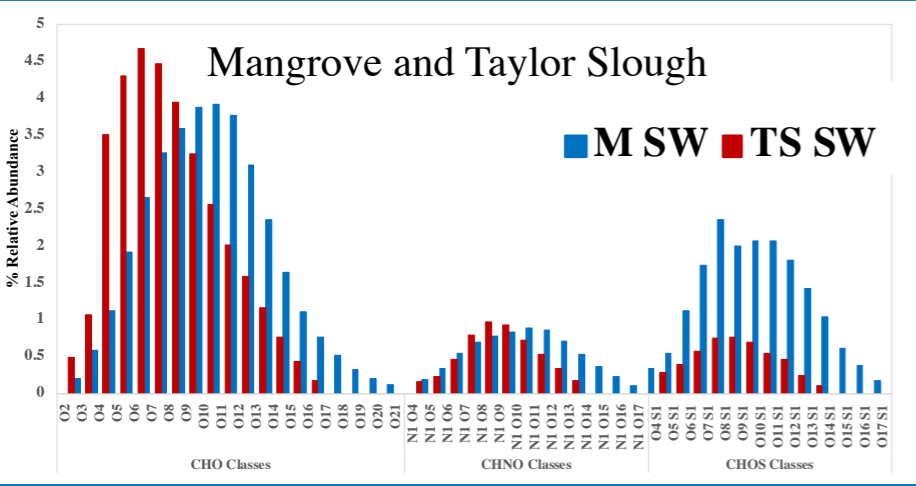
Mass error distribution for peaks assigned above six times the baseline rms noise level for a negative ion ESI 21T FT-ICR mass spectrum of BA_SW. The root-mean-square error for all peaks with signal magnitude greater than 0.1% relative abundance is 41 ppb.

Formulae were assigned conservatively, $C_{2-100}H_{4-200}N_{0-2}O_{2-50}S_{0-2}$, sorted by homologous series and Kendrick mass difference, and screened for large breaks in carbon number, DBE, or sudden increases in RMS error. Only classes with >0.1% RA are used for analyses.

	BA SW	BA PW	BA SED HCL	DK SW	DK PW	DK SED HCL	SB SW	SB PW	SB SED HCL	TS SW	M SW
Peaks assigned	6958	6779	13072	10215	8656	4637	11397	8501	11104	6073	12681
RMS Error (ppb)	42	48	45	48	46.5	59	49	50	55.5	50.5	50.5
%No Hits*	32	45	25.5	31	34.5	53	30.5	35.5	28.4	39	28.5
%RA SO₃ class**	2.41	1.93	0.99	0.75	2.19	14.15	3.07	2.46	1.91	14.86	2.58

* % No Hits includes all peaks below 0.1% relative abundance as well as an ¹³C peaks, and isolated peaks. ** %RA SO₃ indicates the degree of highly ionizable soap impurities, which can skew some of other class %RA. This is especially true for DK SED HCL and TS SW.

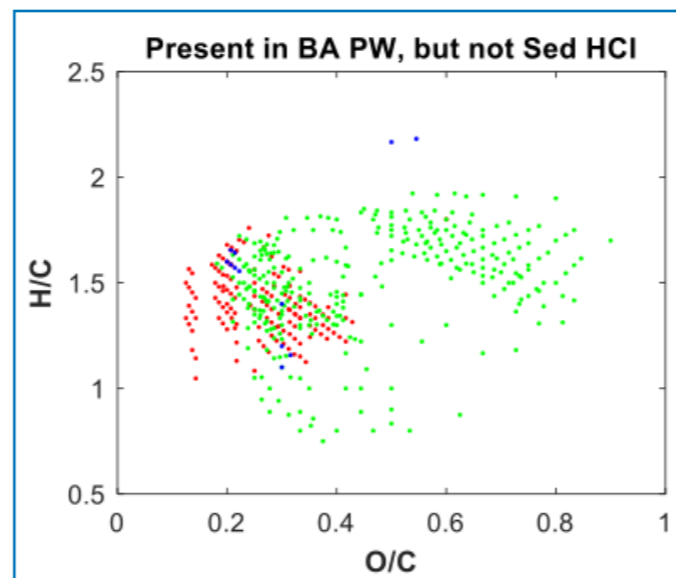
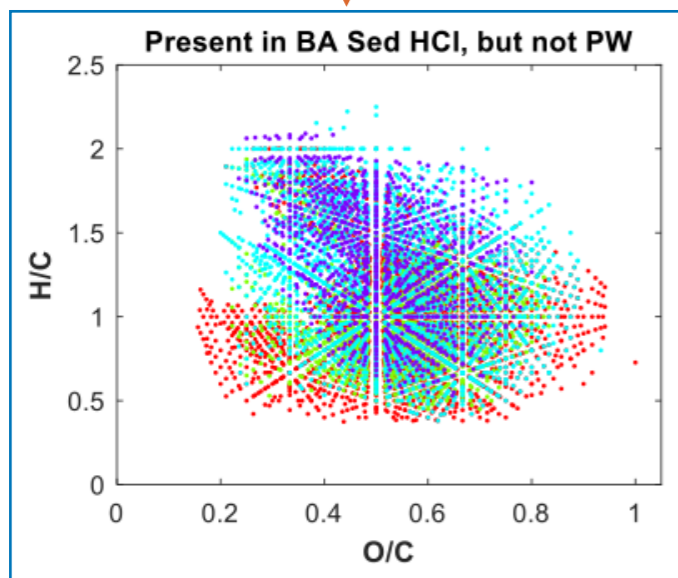
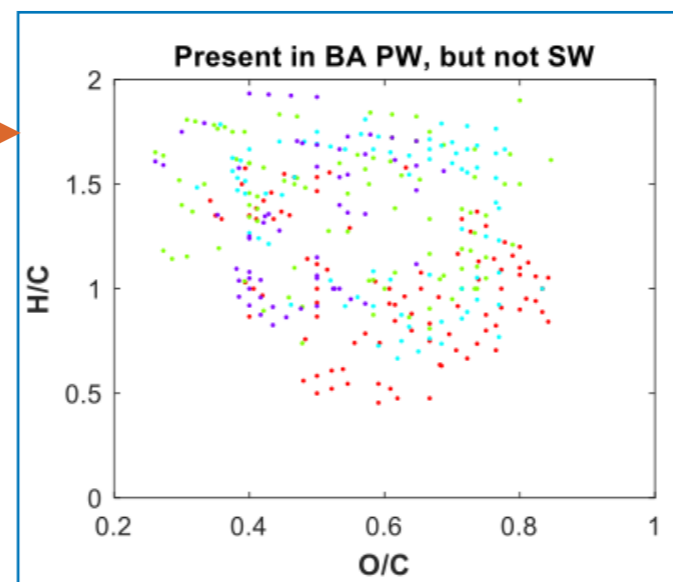
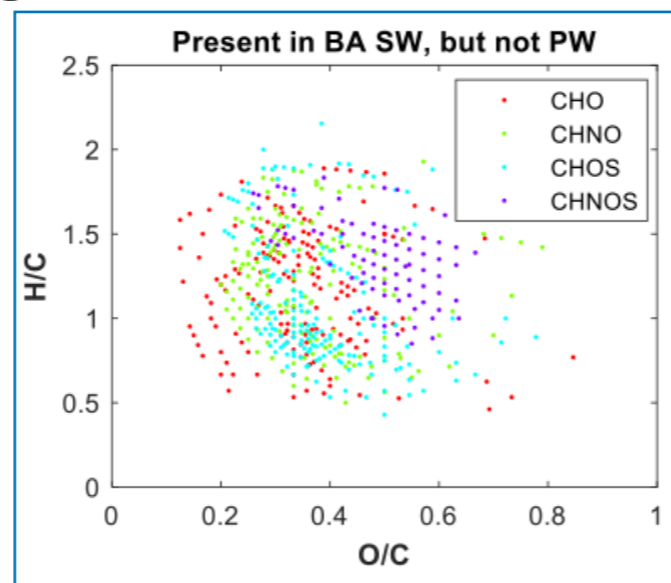
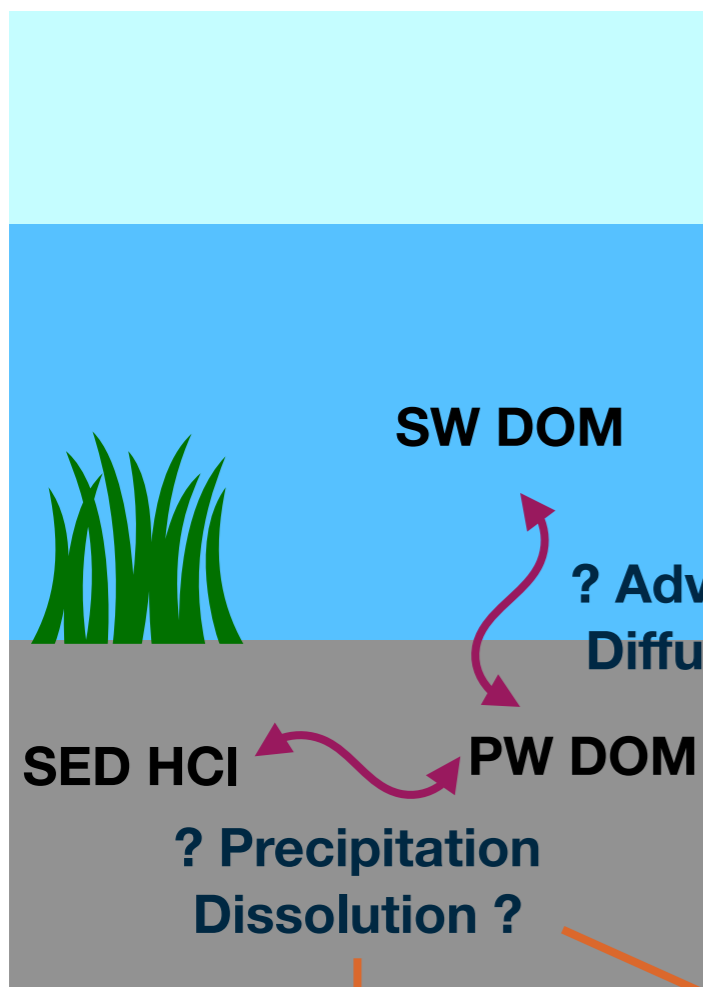
Results: Spatial survey of Florida Bay



Class distribution histograms:

- 1) Porewater (green bars) mirrors trends in Surface water (purple) for all sites
- 2) Sed HCl-leachates (orange) tend to have higher CHO_x classes, and potentially more CHOS (esp. at BA)
- 3) DK Sed HCl and TS SW are potentially skewed by soap impurities (see table on previous slide)

Results: Zooming in on BA (central Florida Bay)



Presence/Absence comparison plots:

Each point in these figures represents a molecular formula that is present in one sample but not in another (see titles).

Main Findings:

- 1) PW and SW have very similar formulae. Very few formulae are not shared between them. This suggests dynamic exchange.
- 2) PW has quite a lot of CHNO formula that were not present in Sed HCl
- 3) Sed HCL has much more diverse formula than PW, especially in the CHOS and CHNOS classes. This could potentially be due to alteration in sulfidic sediments.

Summary and Next Steps

Our question: Is carbonate sediment dissolution an important source of DOM in seagrass meadows?

Our main findings:

We do not yet know the quantity or rates of DOC released through sediment dissolution, but we have characterized the quality of DOM from pore waters, surface waters, and carbonate-associated DOM.

- 1) Prior work with EEMs suggests similarities between carbonate-associated DOM and surface water DOM in Florida Bay seagrass meadows.
- 2) This FT-ICR-MS study shows greater molecular complexity in carbonate-associated DOM, as compared to pore waters or surface waters. This highlights the need for high resolution techniques in low fluorescence waters.
- 3) Our work suggests exchange between pore waters and surface waters, as seen by the similarity between DOM class distributions and formula assignments of these two pools.
- 4) Sediment dissolution could be a mechanism for increasing the molecular diversity of pore water DOM (and thereby surface water DOM). We hope to quantify these exchanges (i.e. natural sediment dissolution and benthic DOM flux) as part of our next steps.

Next steps: Place results into a biogeochemical context.

As part of our experimental design, we have already collected the samples that would allow us to:

- 1) Understand the extent of carbonate dissolution at BA, including impact of seagrass density
- 2) Measure and characterize the DOM flux directly
- 3) Relate these measurements to biogeochemical processes assessed during this study (denitrification, sulfate reduction, sulfide oxidation)

Future work:

We hope to repeat this study during the peak of seagrass productivity, in late July or early August.