

# Tampa Bay Ocean Acidification and the Influence of Dissolved Organic Carbon on Accurate Carbonate System Measurements

Miranda Conley<sup>1</sup>, Robert T. Masserini Jr<sup>1</sup>, Kim Yates<sup>2</sup>, Amy McKenna<sup>3</sup>

<sup>1</sup>The University of Tampa, <sup>2</sup>United States Geological Survey, <sup>3</sup>National High Magnetic Field Laboratory

## Purpose

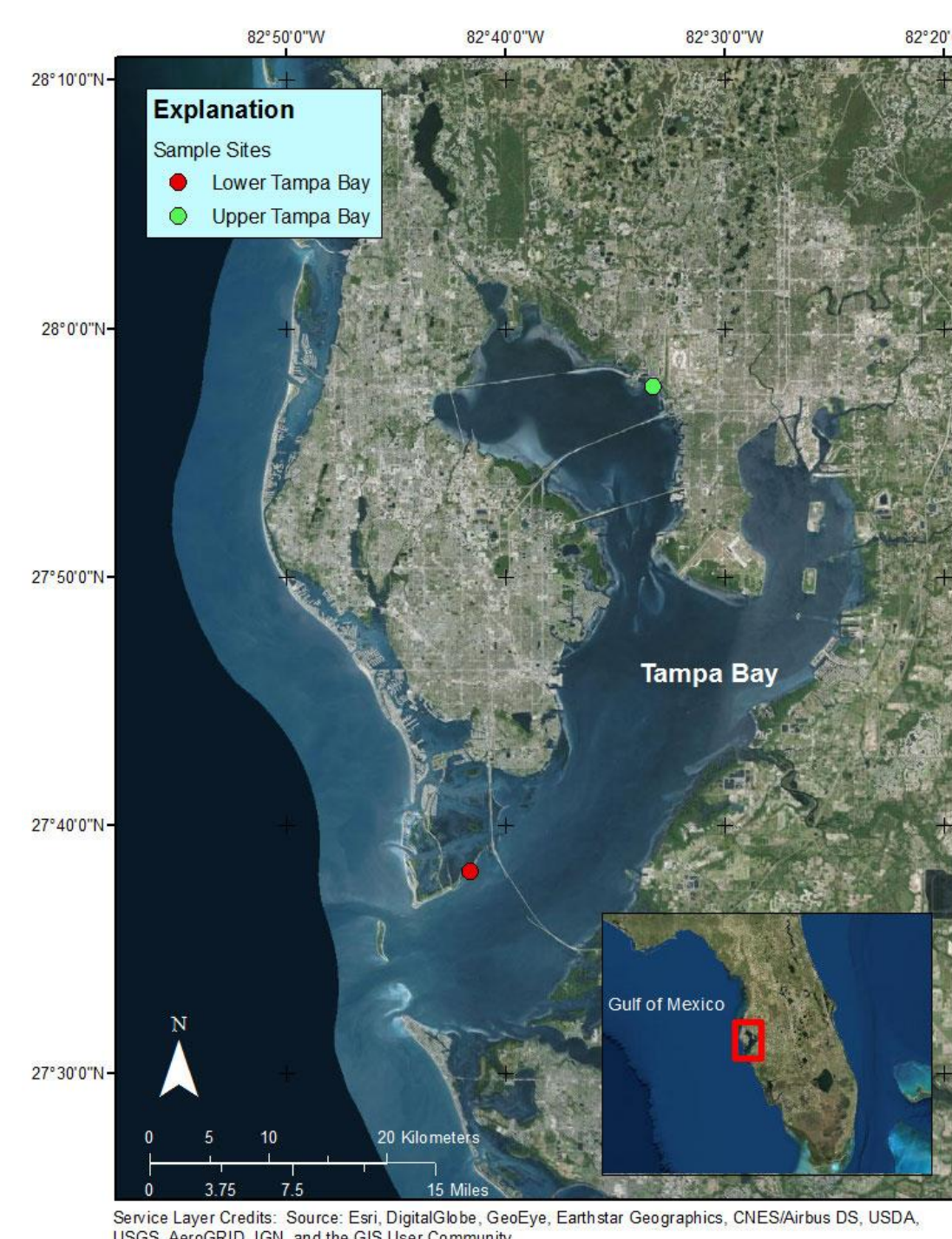
- In this study, we sought to determine if organic alkalinity from dissolved organic carbon (DOC) could be responsible for the difference between measured and calculated total alkalinity (TA), and if so, what the predominate forms of organic matter present were.

## Introduction

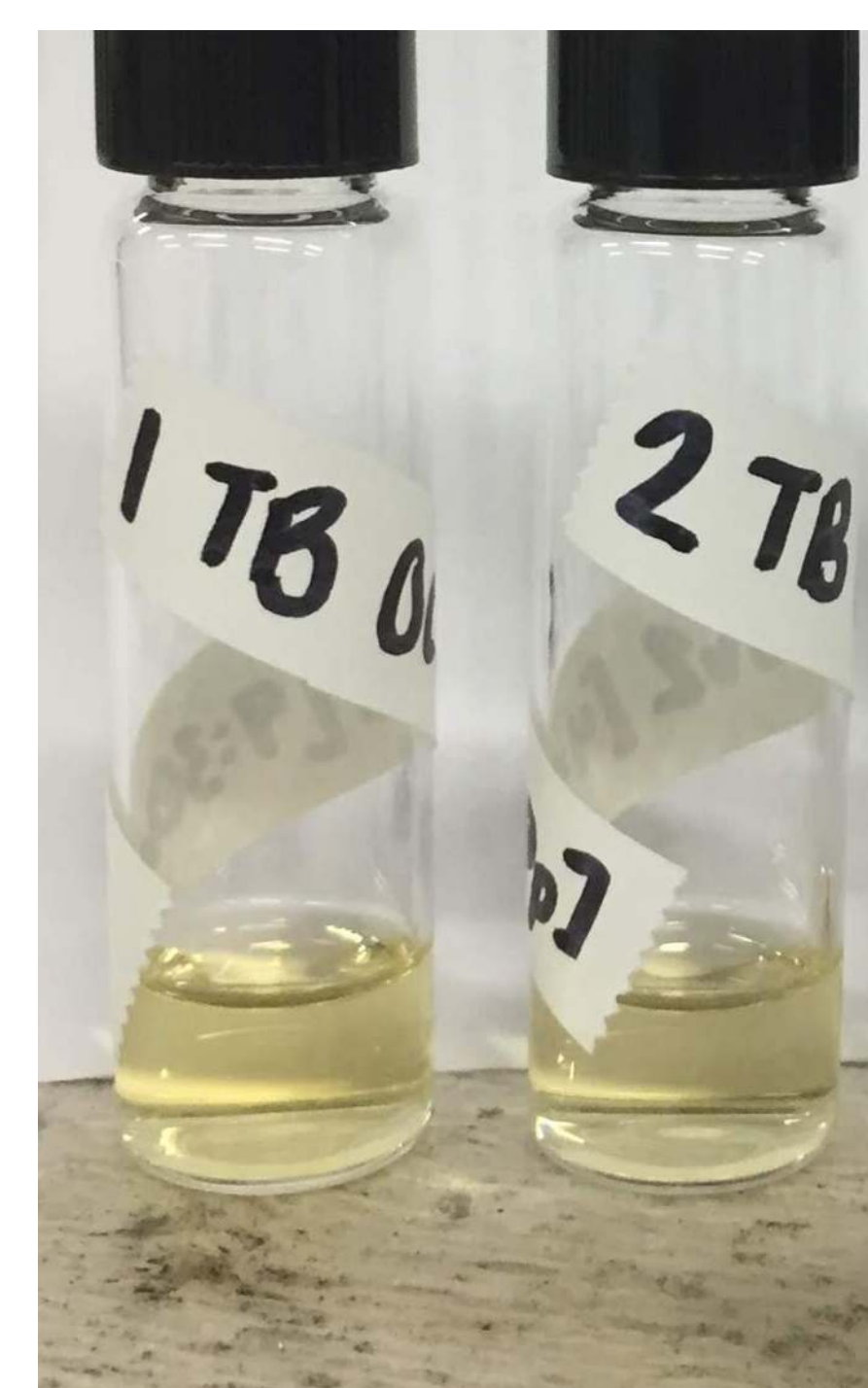
- Ocean acidification is a global process caused by the absorption of atmospheric carbon dioxide (CO<sub>2</sub>) by seawater resulting in a decrease in pH.
- Once carbon dioxide dissolves into solution, the carbon is distributed between aqueous carbon dioxide, carbonic acid, bicarbonate ion, and carbonate ion.
- Seagrasses are projected to benefit from elevated atmospheric CO<sub>2</sub><sup>1</sup> and are therefore 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<sup>2,3,4,5</sup>.
- Preliminary results from the Tampa Bay Ocean acidification monitoring program indicate that measured total alkalinity is higher than calculated total alkalinity after accounting for contribution from nutrients and suggests that organic alkalinity has a significant effect on total alkalinity measurements.

## Methods

- Collection of samples:** One-liter DOC samples were collected using a peristaltic pump and silicon tubing. Sample bottles were stored for field collection with 100 mL of 0.01 M hydrochloric acid, this acid was emptied just before the filtrate was collected.
- Composition analysis:** Solid Phase Extraction (SPE) was performed utilizing the methods detailed in Dittmar et al.<sup>6</sup> Samples were then analyzed using Fourier Transformation Ion Cyclotron Resonance Mass Spectrometry (FT-ICRMS) at 9.4T at the National High Magnetic Field Laboratory in Tallahassee, Florida.
- Carbonate system analysis:** pH was measured using the methods of Douglas and Byrne<sup>7</sup> while TCO<sub>2</sub> was measured using the methods of Dickson et al.<sup>8</sup> Carbonate system calculations were performed following the protocols of Pierrot et al.<sup>9</sup>
- Nutrient analysis:** Samples were collected and frozen in 30mL high density polyethylene bottles. The nutrient concentration of phosphate and silica were determined using the methods of Gordon et al.<sup>10</sup>

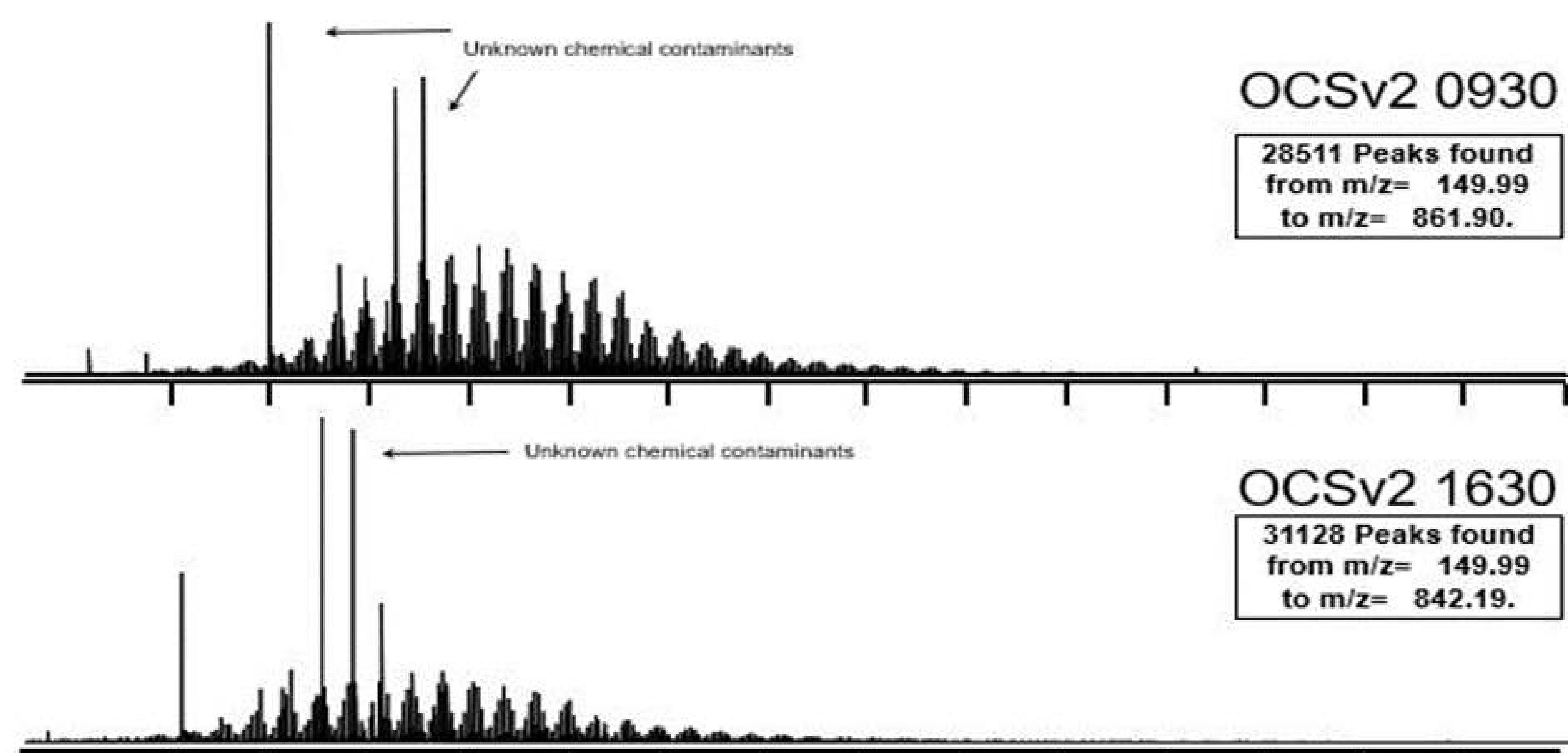


**Figure 1:** Two samples were taken from the OCSv2 site at 9:30am during low tide and the other at 4:30pm during high tide. Both samples were collected on April 24, 2018.

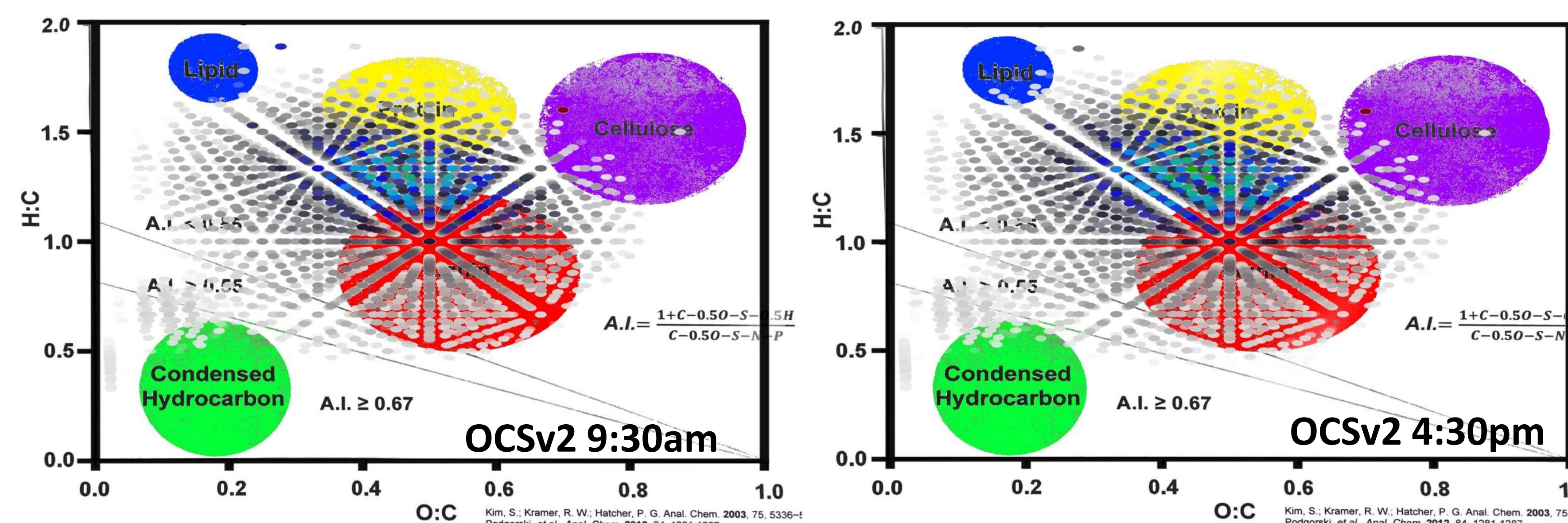


**Figure 2:** DOM was extracted using SPE following the methods of Dittmar et al.<sup>6</sup> On the left is OCS V2 DOM 09:30am and on the right is OCS V2 DOM 4:30pm.

## Results



**Figure 3:** Negative-ion electrospray ionization (ESI) FT-ICR mass spectra at 9.4T. More than 28,000 unique elemental compositions were assigned for each sample that correspond to mass spectral peaks with signal magnitude greater than six times the baseline noise level. This data was used to determine the source of material via van Krevelen transformation.



**Figure 4:** van Krevelen diagrams illustrating the sources of the organic compounds. Most of the organic components were primarily proteinaceous and ligninaceous.

**Table 1:** Total alkalinity results, including the difference per  $\mu\text{mol}$  and titratable carboxylic acid.

Sample	Calculated TA ( $\mu\text{mol}/\text{kg}$ )	Measured TA ( $\mu\text{mol}/\text{kg}$ )	Difference per $\mu\text{mol}$	Titratable Carboxylic Acid ( $\mu\text{mol}/\text{kg}$ )
OCSv2 9:30am (low tide)	2473	2503	30	9
OCSv2 4:30pm (high tide)	2488	2497	10	7

**Table 2:** Nutrient data for the OCSv2 samples.

Sample	DOC (mg/L)	DOC ( $\mu\text{mol}/\text{kg}$ )	Phosphate ( $\mu\text{mol}/\text{kg}$ )	Silicate ( $\mu\text{mol}/\text{kg}$ )	P Alkalinity in ( $\mu\text{mol}/\text{kgSW}$ )	Si Alkalinity in ( $\mu\text{mol}/\text{kgSW}$ )
OCSv2 9:30am (low tide)	3.75	139	1.32	5.64	1.47	0.2
OCSv2 4:30pm (high tide)	3.10	115	1.43	5.61	1.59	0.2

## Conclusions

- Measured TA was on average 20  $\mu\text{mol}/\text{kg}$  greater than the calculated TA.
- Nutrient analysis indicated that although silicic acid and phosphate are present in Tampa Bay, these nutrients contributed approximately 2  $\mu\text{mol}/\text{kg}$  to TA. This is on the order of the precision of the alkalinity measurements.
- The contribution of DOC suggested that organic compounds could be responsible for 8  $\mu\text{mol}/\text{kg}$  of the TA of alkalinity.
- At low tide, titratable carboxylic acid is 30% of the difference between calculated and measured TA, and 70% at high tide. Therefore, at low tide, something else (not organic alkalinity) must be contributing to the TA.
- The average mass to charge ratio of the organic milieu was 350, with most compounds ranging from 200-500, and van Krevelen analysis indicates that most organic compounds were proteinaceous and ligninaceous.

## Acknowledgements

- This project was funded by The University of Tampa Office of Undergraduate Research and Inquiry Grant, The University of Tampa Student Travel Award, and the NSF DMR-1644779.
- This project was supported by the United States Geological Survey, the National High Magnetic Field Laboratory-Tallahassee, and the University of Tampa.

## References

- Kleyvas, J.A., Yates, K.K., 2009. Coral reefs and ocean acidification. *Oceanography* 22, 108–117. <https://doi.org/10.5670/oceanog.2009.101>.
- Anthony, K.R.N., A. Kleyvas, J., Gattuso, J.P., 2011. Coral reefs modify their seawater carbon chemistry - implications for buffers of ocean acidification. *Glob. Chang. Biol.* 17, 3655–3666. <https://doi.org/10.1111/j.1365-2486.2011.02510.x>
- Hendriks, I.E., Olsen, Y.S., Ramajo, L., Basso, L., Steckbauer, A., Moore, T.S., Howard, J., Duarte, C.M., 2014. Photosynthetic activity impacts ocean acidification in seagrass meadows. *Biogeosciences* 11, 333–346. <https://doi.org/10.5194/bg-11-333-2014>
- Manzello, D.P., Enochs, I.C., Melo, N., Gledhill, D.K., Johns, E.M., 2012. Ocean acidification refugia of the Florida reef tract. *PLoS One* 7, 1–10. <https://doi.org/10.1371/journal.pone.0041715>
- Semesi, I.S., Beer, S., Björk, M., 2009. Seagrass photosynthesis controls rates of calcification and photosynthesis of calcareous macroalgae in a tropical seagrass meadow. *Mar. Ecol. Prog. Ser.* 382, 41–47. <https://doi.org/10.3354/meps07973>
- Dittmar, T., Koch, B., Hertkorn, N., Kattner, G., 2008. OCEANOGRAPHY : METHODS A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater 230–235.
- Dickson, A.G., Sabine, C.L., Christian, J.R. (Eds.), 2007. Guide to best practices for ocean CO<sub>2</sub> measurements, PICES Special Publication 3.
- Douglas, N.K., Byrne, R.H., 2017. Spectrophotometric pH measurements from river to sea: Calibration of mCP for 0 ≤ S ≤ 40 and 278.15 ≤ T ≤ 308.15 K. *Mar. Chem.* 197, 64–69. <https://doi.org/10.1016/j.marchem.2017.10.001>
- Pierrot, D.E., Lewis, E., Wallace, D.W.R., 2006. MS Excel Program Developed For CO<sub>2</sub> System Calculations.
- Gordon, L.I., Jennings, J.C., Ross, A. a, Krest, J.M., 1993. A Suggested Protocol for Continuous Flow Automated Analysis of Seawater Nutrients (Phosphate, Nitrate, Nitrite and Silicic Acid) in the WOCE Hydrographic Program and the Joint Global Ocean Fluxes Study. *Coll. Ocean. Atmos. Sci. Oregon State Univ.* 1–55.