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Interactive comment on “Dissolved carbon biogeochemistry and export in mangrove-dominated rivers of the Florida Everglades” *by* David T. Ho et al.

Anonymous Referee #1

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The authors investigated the dissolved carbon source-sink dynamics in two rivers in order to integrate and estimate the export of carbon from a large mangrove forest, “the largest contiguous mangrove forest in North America”. First of all, I must note that it is refreshing to read a manuscript that is written in proper English. I review about one manuscript per week and would put this one in the top 10% in terms of readability. I commend the authors for it. Nevertheless, I did make a number of editorial recommendations in the annotated manuscript that accompanies this review. On the other hand, whereas the paper addresses a relevant scientific question, the paper lacks scientific rigor, the methodologies are only sparsely described, the data processing is questionable if not inadequate and, consequently, the discussion is weak and interpretations

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are often speculative given the lack of supporting data. The manuscript is clearly not suitable for publication in its present state. Specific comments: Methods – Line 113: IUPAC has done away with ‘equivalents’, alkalinities are now reported in moles.

Lines 116, 128, 212: The Millero (2010) constants are not particularly dependable. Perhaps better to use the constants of Cai and Wang (1998). See: Orr, J. C., Epitalon, J. M., and Gattuso, J. P. (2015). Comparison of ten packages that compute ocean carbonate chemistry. Biogeosciences 12(5), 1483–1510.

Lines 127-128: Was TAlk corrected for silicate and phosphate contributions? What about the contributions of organic alkalinity? The latter can be very significant in the case of estuaries draining marshes and organic-rich soils, often accounting for the circum-neutral or even acidic nature of these waters. Uncorrected TAlk values, combined with pCO2 measurements, would generate erroneous DIC values. The authors note that DOC makes up about 20% of the DIC, it surely has a large (negative) contribution to Talk.

Lines 135-136: How were the DOC measurements calibrated and what was their reproducibility and accuracy?

Lines 144-145: What was the reproducibility of the δ13C measurements?

Line 154: What were the δ13C standards?

Lines 158-159: What was the time constant of the probe? These probes have a slow response and do not provide real-time measurements. The quality of the measurements will depend on the cruising speed of the boat or current velocity. Hence, these measurements may carry a spatial (and temporal) uncertainty.

Line 160: The time constant of the optode is even larger than the galvanic sensor. Although the optode response does not drift as much as the galvanic sensor, the precision of the optode is significantly worse than the galvanic sensor. What is the uncertainty on these two measurement methods?

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Lines 163-164: Even if the authors refer the reader to detailed descriptions in other papers, they should briefly describe the method and its uncertainties.

Lines 200, 206: Are the gas transfer velocities scaled for wind velocity or turbulence generated by flow in the shallow estuary? The authors should provide the estimated value of the gas transfer velocity in the study setting.

Lines 219-220: The seawater that intrudes at these shallow depths is likely to be supersaturated with respect to calcite and aragonite, but could become undersaturated by accumulating metabolic CO2 generated by microbial degradation of dissolved or particulate organic matter in the sediment/karst.

Line 234: As noted above, dissolution in saline groundwaters can only occur upon the addition metabolic CO2 to the groundwaters from microbial degradation of organic matter. Hence, how would the authors distinguish this contribution of 13C-depleted DIC from that of the mangrove-derived organic matter?

Line 256: Again, what about the metabolic DIC contribution from groundwaters? Mn and Fe oxide reduction will also generate alkalinity.

Line 265, Eqn. (9), 270-271: What about groundwater contributions?

Results and Discussion - Lines 311-312: Somewhat repetitive. Any statistics on this correlation?

Line 326: Very large and surely contributes to the titration alkalinity.

Lines 366-368: I noted this earlier. Why not include it in the mass balance equations?

Line 371: Under what conditions would this occur? Any evidence that aragonite and high Mg-calcites are being dissolved and replaced by low Mg-calcite?

Lines 375, 382: Where and under what conditions is CaCO3 being dissolved? In organic-rich sediments, anaerobic respiration leads to alkalinity production (as indicated earlier), and likely a flux of alkalinity and DIC to the overlying waters. The fluxes would be modulated by neutralization of alkalinity as it diffuses through the oxic sediment layer and by CaCO3 precipitation in the anoxic sediments.

Line 384: See previous comment. This is speculative in the absence of evidence that this dissolution-precipitation process is active.

Lines 386-388: The authors need to show how these estimates were derived as sulfate reduction does not appear in the mass balance equations.

Lines 394-396: The oxidation of these metabolites does not follow the same stoichiometry as aerobic oxidation of organic matter. In the case of H2S, the redox reaction requires the exchange of 8 electrons (S(-II) to S(+VI), 2 in the case on Mn2+ (to Mn(+IV)) and one for Fe2+ (to Fe(+III)).

Lines 405:-406: This statement makes little sense, unless the preferential degradation of 13C-enriched OM took place before respiration in the mangrove forest.

Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/bg-2017-6/bg-2017-6-RC1-supplement.pdf

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