

Specific comments: Methods – Line 113: IUPAC has done away with ‘equivalents’, alkalinites are now reported in moles.

Thanks for catching this. It is now in  $\mu\text{mol kg}^{-1}$ .

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.

We thank the reviewer for point out the interesting discussion about  $K_1$  and  $K_2$  of Millero (2010) in Orr et al. (2015). Using the constants of Cai and Wang (1998) leads to calculated DIC that ranged from being 0.23% lower, to 0.09% higher than those calculated from Millero (2010), with an average of 0.09% lower. Nevertheless, we have chosen to use Cai and Wang (1998) to calculate DIC.

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  $\text{pCO}_2$  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.

TALK was not corrected for silicate and phosphate. As we state in Lines 127-130: “The measured TALK and  $\text{pCO}_2$  from SharkTREx 2 were used to calculate DIC using CO2SYS (Pierrot et al., 2006) and the dissociation constants of (Millero, 2010), and the results were  $1.3 \pm 1.1\%$  (range: -2.4 to +4.4%) higher than the measured DIC, possibly indicating a slight contribution (ca. 1%) to TALK from organic or particulate material, as the samples were not filtered.”

The fact that the calculated DIC agree well with the measured DIC means that the contribution from organic alkalinity was minimal (ca. 1%), assuming that the dissociations constants used to calculate DIC are correct.

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

The TOC analyzer was standardized using 10 and 50 ppm of potassium hydrogen phthalate (KHP), with reagent water as a blank. The analytical precision based on replicates of KHP is ca.  $\pm 0.3$  ppm. We have added this information to the manuscript.

Lines 144-145: What was the reproducibility of the  $\delta^{13}\text{C}$  measurements?

Reproducibility was 0.2 ‰ as determined by repeated analysis of internal DIC standards. We have added this information to the manuscript.

Line 154: What were the  $\delta^{13}\text{C}$  standards?

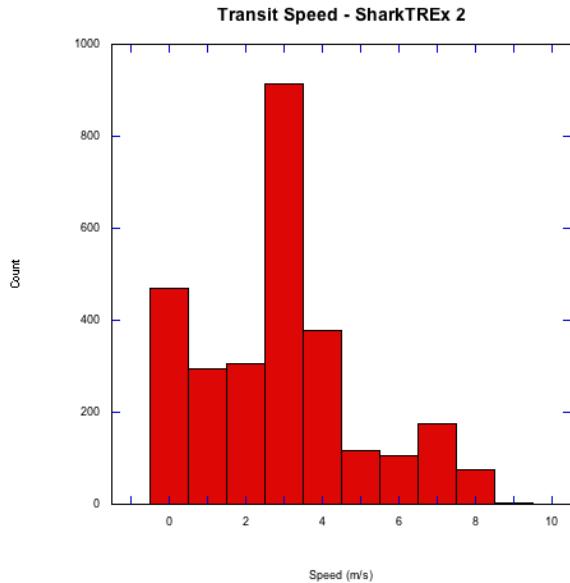
In order to measure the different isotopic ranges within the collected samples, an isotopic calibration was based on two external standards of potassium hydrogen phthalate (KHP - 29.8‰, OI-Analytical) and glutamine (-11.45‰, Fisher) with a concentration range of 0–25 ppm. These standards were prepared in synthetic seawater to match the sample matrix's salinity. The isotope values of these two standards were determined by using an elemental analyzer isotope ratio mass spectrometer (EA-IRMS). We have added this information to the manuscript

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.

See next response.

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?

The stated response time of the galvanic sensor is <10 s to reach 90% of final value, and <16 s to reach 95% of final value. As the reviewer states, the time constant of the optode is longer than the galvanic sensor. It has a stated response time of <25 s to reach 63% of final value. The boat speed during the experiments was typically ca. 3 m/s (ca. 6 knots) (see figure below). The other measurements such as the underway SF<sub>6</sub> and pCO<sub>2</sub> measurements also have their associated delay between when the water is taken into the SF<sub>6</sub> extraction system or pCO<sub>2</sub> equilibrator and then the gases finally reach the GC/ECD or NDIR analyzer for analysis. This delay is built-in to the LABVIEW program that assigns GPS position information to the individual measurements based on tests done on the delay in the laboratory. If the delayed response were not corrected, this would lead to a typical offset in location of ca. 50-100 m (less than 1% of the length of the river). Furthermore, most of the measurements are referenced to salinity instead of GPS position, making the exact position less important. Finally, the calculated difference between the effects of conservative mixing and estuarine input on DO in this manuscript were based on relative differences in oxygen, so accuracy of the DO measurements will not significantly affect the results.



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.

We have added brief descriptions of the underway SF<sub>6</sub> system.

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.

The gas transfer velocities are affected by both wind and currents, and we have added that to the manuscript. On Lines 191-193, we stated: “ $k(600)$  for SharkTREx 1 and 2, determined from the parameterization proposed in Ho et al. (2016), were  $3.5 \pm 1.0$  and  $4.2 \pm 1.8 \text{ cm h}^{-1}$ , respectively.” The details for gas exchange in Shark River is given in Ho, D. T., N. Coffineau, B. Hickman, N. Chow, T. Koffman, and P. Schlosser (2016), Influence of current velocity and wind speed on air-water gas exchange in a mangrove estuary, *Geophys. Res. Lett.*, 43, doi:10.1002/2016GL068727.

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 CO<sub>2</sub> generated by microbial degradation of dissolved or particulate organic matter in the sediment/karst.

Agreed. We now specify this in the text:

In the manuscript (lines 219-220), we wrote: "Groundwater in this region is likely to contain DIC from CaCO<sub>3</sub> dissolution that occurs when saltwater intrudes into the karst aquifer that underlies this region (Price et al., 2006)." We expanded on this with: "Groundwater in this region is likely to contain DIC from CaCO<sub>3</sub> dissolution that occurs when saltwater intrudes into the karst aquifer that underlies this region (Price et al., 2006), as well as DIC from sediment organic matter mineralization."

Line 234: As noted above, dissolution in saline groundwaters can only occur upon the addition metabolic CO<sub>2</sub> 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?

We assumed that all organic matter added in the estuary is from the mangroves.

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

The DIC from groundwater is assumed to be either from calcite dissolution or from microbial degradation of organic matter. As we specify in the text, the calculation of [DIC]<sub>dissolution</sub> from [TALK]<sub>estuary</sub> provides an upper-bound estimate of the contribution of dissolution to DIC as it does not take into account the contribution of other mineralization pathways to total alkalinity.

In mangrove sediments, aerobic respiration and sulfate reduction are generally the main organic matter degradation pathways, and in our case this is supported by Figure 6, which shows that the contributions of Fe and Mn reduction are likely small.

Also, Fe concentrations in Shark Slough sediments are very low (1.1 mg gdw<sup>-1</sup>; Chambers, R. M., and Pederson, K. A.: Variation in soil phosphorus, sulfur, and iron pools among south Florida wetlands, *Hydrobiologia*, 569, 63-70, 10.1007/s10750-006-0122-3, 2006), and Mn is expected to be similarly low in this carbonate/mangrove peat setting.

Furthermore, the agreement between measured and calculated DIC (discussed above) indicates that in this environment, the other sources of alkalinity are small, compared to carbonate alkalinity.

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

Groundwater added in the estuary is part of [DOC]<sub>estuary</sub>

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

We have removed this repetitive statement.

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

See reply above regarding measured DIC vs. DIC calculated from TALK and pCO<sub>2</sub>.

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

Because that is either considered to be calcite dissolution or microbial degradation of mangrove organic matter.

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?

Since we do not know whether isotopic exchange happens during dissolution and re-precipitation, we have removed this paragraph.

Lines 375, 382: Where and under what conditions is  $\text{CaCO}_3$  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  $\text{CaCO}_3$  precipitation in the anoxic sediments.

Dissolution/re-precipitation of  $\text{CaCO}_3$  is omnipresent in Florida. Unfortunately, this was not one of the processes examined during SharkTREx 1 and 2. However, surface waters in Florida show higher than expected Sr/Ca ratio. Sr/Ca released by dissolution is the same as seawater because aragonite Sr/Ca is the same as seawater Sr/Ca, but re-precipitation of calcite rejects Sr. Studies that have examined this process in Florida include: Stalker, J. C., R. M. Price, and P. K. Swart: Determining Spatial and Temporal Inputs of Freshwater, Including Submarine Groundwater Discharge, to a Subtropical Estuary Using Geochemical Tracers, Biscayne Bay, South Florida, *Estuar Coast*, 32, 694-708, doi:10.1007/s12237-009-9155-y, 2009.

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

We agree, and have removed this speculative sentence.

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

The ratio of TALK to DIC for calcite dissolution is 2, and that of sulfate reduction and aerobic respiration are 0.99 and -0.2, respectively. Hence, to achieve the observed ratios of TALK to DIC of 0.84, 0.92, and 0.90 for the three cases, and given the contribution of calcite dissolution of 30%, the contribution of sulfate reduction and aerobic respiration could be calculated using straightforward algebra (assuming no contribution from Fe and Mn reduction). We have stated this more explicitly in the manuscript.

Lines 394-396: The oxidation of these metabolites does not follow the same stoichiometry as aerobic oxidation of organic matter. In the case of  $\text{H}_2\text{S}$ , the redox reaction requires the exchange of 8 electrons (S(-II) to S(+VI), 2 in the case on  $\text{Mn}^{2+}$  (to  $\text{Mn}^{+IV}$ ) and one for  $\text{Fe}^{2+}$  (to  $\text{Fe}^{+III}$ )).

Here, we meant  $\text{O}_2$  to  $\text{CO}_2$  stoichiometry. Oxygen uptake due to the re-oxidation of reduced metabolites from sulfate, iron, and manganese reduction results in carbon to oxygen stoichiometry that is similar to aerobic respiration. For that reason, the uptake of oxygen is equivalent to total carbon mineralization if there is complete re-oxidation of metabolites and denitrification is negligible (see Canfield, 1993; Hulth et al. 1999;

Reimers et al., 1992). Therefore, the estimate can be considered as a lower-bound estimate of total carbon mineralization.

Canfield, D. E.: Organic Matter Oxidation in Marine Sediments, in: Interactions of C, N, P and S Biogeochemical Cycles and Global Change, edited by: Wollast, R., Mackenzie, F. T., and Chou, L., Springer Berlin Heidelberg, Berlin, Heidelberg, 333-363, 1993.

Hulth, S., Aller, R. C., and Gilbert, F.: Coupled anoxic nitrification/manganese reduction in marine sediments, *Geochim. Cosmochim. Acta*, 63, 49-66, 10.1016/S0016-7037(98)00285-3, 1999.

Reimers, C. E., Jahnke, R. A., and McCorkle, D. C.: Carbon fluxes and burial rates over the continental slope and rise off central California with implications for the global carbon cycle, *Glob. Biogeochem. Cycle*, 6, 199-224, 10.1029/92GB00105, 1992.

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

We thank the reviewer for catching this. This statement was a remnant from an early draft. Initial  $\delta^{13}\text{C}_{\text{DOC}}$  data did include salinity correction following the method detailed in Ya et al. (2015), where the standards were match to the salinity range of the samples with synthetic seawater mixtures, with a maxim salinity varying from 30 to 32 depending on the timing and reported salinities of the sampling period. In the revised  $\delta^{13}\text{C}_{\text{DOC}}$  data, the lowest observed values from SharkTREx 1 was  $-31.6 \pm 1.25 \text{‰}$ , as shown in Figure 4d. Previous studies of DOC from mangrove-dominated systems have reported values as low as  $-30.4 \text{‰}$  (Dittmar, et al, 2006), and some of the more depleted samples from SharkTREx 1 might have DOC sourced from algae associated with mangrove roots, which can have relatively depleted values (Kieckbusch et al, 2004).

Dittmar, T. , Hertkorn, N. , Kattner, G. and Lara, R. J.: Mangroves, a major source of dissolved organic carbon to the oceans , *Global biogeochemical cycles*, 20, GB1012. doi: 10.1029/2005GB002570, 2006.

Kieckbusch, D.K., Koch, M.S., Serafy, J.E., and Anderson, W.T.: Trophic linkages of primary producers and consumers in fringing mangroves of tropical lagoons: Bulletin of Marine Science, v. 74, no. 2, p. 271-285, 2004.

Ya, C., Anderson, W., and Jaffé, R.: Assessing dissolved organic matter dynamics and source strengths in a subtropical estuary: Application of stable carbon isotopes and optical properties, *Continental Shelf Research*, 92, 98-107, 10.1016/j.csr.2014.10.005, 2015.