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

We thank the reviewer for catching this. It is now in $\mu$mol kg$^{-1}$.


We thank the reviewer for pointing 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. That is, the difference is pretty insignificant. Nevertheless, we have chosen to use Cai and Wang (1998) to calculate DIC.

Lines 127-128: Was TA 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 TA 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.

TA was not corrected for silicate and phosphate. As we state in Lines 127-130: “The measured TA and 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 ± 1.1% (range: -2.4 to +4.4%) higher than the measured DIC, possibly indicating a slight contribution (ca. 1%) to TA 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. ±0.3 ppm. We have added this information to the manuscript.

Lines 144-145: What was the reproducibility of the $\delta^{13}$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 $\delta^{13}$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$_6$ and pCO$_2$ measurements also have their associated delay between when the water is taken into the SF$_6$ extraction system or pCO$_2$ 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 SF₆ 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 ± 1.0 and 4.2 ± 1.8 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, Geophy. 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\(_2\) 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\(_3\) 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\(_3\) 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 $\text{CO}_2$ to the groundwaters from microbial degradation of organic matter. Hence, how would the authors distinguish this contribution of $^{13}$C-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 $[\text{DIC}]_{\text{dissolution}}$ from $[\text{TAlk}]_{\text{estuary}}$ 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$^{-1}$; 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 $[\text{DOC}]_{\text{estuary}}$

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 $p\text{CO}_2$.

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 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.

Dissolution/re-precipitation of CaCO3 is omnipresent in Florida, but this was not one of the processes examined during SharkTREx 1 and 2. Previous studies (e.g., Stalker et al, 2009) have shown that, surface waters in Florida show higher Sr/Ca ratio than expected from seawater. Even though Sr/Ca released by dissolution is the same as seawater because aragonite Sr/Ca is the same as seawater Sr/Ca, re-precipitation of calcite rejects Sr, which elevates the Sr/Ca ratio.


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 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)).

Here, we meant O2 to CO2 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

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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.


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

We thank the reviewer for catching this, and have revised the statement. This statement was a remnant from an early draft. Initial δ13CDOC 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 δ13CDOC data, the lowest observed values from SharkTREx 1 was -31.6 ± 1.25 ‰, as shown in Figure 4d. Previous studies of DOC from mangrove-dominated systems have reported values as low as -30.4‰ (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).


Reply to Reviewer 2

Major comments

The technique by which the authors quantify gas fluxes is clear and robust, though error estimates would be helpful. It’s the longitudinal fluxes, as the authors call them, that cause confusion. As the authors use the term, the longitudinal flux is averaged over the time period of the tracer release and hence accounts for tidal dispersion as well as the net downstream advective transport. The problem is that the authors use the term too broadly and in ways that defy notions of mass conservation. I specifically take issue with a longitudinal flux due to a certain source, such as freshwater wetlands, mangroves, calcium carbonate, or the ocean (lines 18-21); or due to a certain process, such as estuarine or non-estuarine (lines 289-290 and Table 4), and respiration or dissolution (lines 217-218). A longitudinal flux is due to movement of water and nothing else. It’s a term in the mass conservation equation that is separate from internal sources and sinks. The two should not be mixed up.

It is true that longitudinal water flux would be due solely to movement of water. However, longitudinal carbon flux is due to movement of water and the concentration of dissolved carbon in the water. When we talk about contributions, we are not talking about the contribution of the freshwater marsh, mangroves, or carbonate to the water movement, but to the dissolved carbon concentration.

We have clarified this in the revised manuscript. For example, we have changed this sentence in the abstract:

“Approximately 80% of the total dissolved carbon flux from all sources (i.e., freshwater wetlands, mangrove, carbonate dissolution, and marine input) out of the Shark and Harney Rivers during these experiments was as inorganic carbon, either via air-water CO₂ exchange or longitudinal flux of inorganic carbon to the coastal ocean.”

To:

“Approximately 80% of the total dissolved carbon flux out of the Shark and Harney Rivers during these experiments was in the form of inorganic carbon, either via air-water CO₂ exchange or longitudinal flux of dissolved inorganic carbon (DIC) to the coastal ocean..”

In the methods section, we have changed:

“As with the inventory calculations, longitudinal fluxes were separated into estuarine and non-estuarine contributions.”

To:

“In addition, using the estuarine and non-estuarine fractions of the inventories in equation (12) allowed the estuarine and non-estuarine proportions of the longitudinal carbon fluxes to be quantified.”

Also confusing is the alternation between approaches based on inventories and approaches based
on fluxes. My suggestion is to focus on a budget approach because this paper is basically about the carbon balance of two estuaries. The final budget is shown in a key figure towards the end of the paper (Figure 5), which clearly shows the control volume approach I am recommending. Remarkably, there is not a single budget equation in the paper. And the method for determining the freshwater wetlands flux shown in this figure should be detailed in the methods, not the figure caption. In the paper, the authors should start with a budget equation and then use inventory equations, such as Equations 2 and 9, as needed to support the budget approach. Budget equations should be shown for DOC, DIC, oxygen, and (perhaps) alkalinity.

We recognize that what the reviewer is suggesting is one valid approach, but we have taken what we feel is an equally valid approach. Determining the carbon balance in the estuaries was not our main goal, although in determining the main sources and sinks, we do eventually arrive there.

Our goal is to determine the export (fluxes to the coastal ocean and across the air-water interface) of mangrove derived carbon from the estuary. We took the approach: Flux = Inventory/Residence Time, where residence times were determined from the tracer release experiments. Hence, in order to determine mangrove derived DIC and DOC fluxes, we needed to find out how much DIC and DOC were in the rivers (i.e., the inventory), and also the sources of this carbon (mangrove vs. calcite dissolution). Then, we needed to determine the fate of the mangrove-derived carbon in the river (i.e., lost to the atmosphere vs. lost to the coastal ocean).

We are not alternating between an inventory and flux approach. We are systematically using the inventory to determine the flux.

A process that appears to be missing in the paper is organic mineralization inside the estuary. The very low DO suggests quite significant net heterotrophy. The authors lump organic mineralization inside the estuary with mangrove root respiration and call it a mangrove source of DIC. Those seem like two very different sources to me, which could perhaps be distinguished using the isotopes. Figure 5 is remarkable in that it does not show any in situ production or consumption. The net organic matter remineralization should be revealed in the DO budget of the individual terms. The “Evidence from DO” section (3.3.3) should basically detail the DO budget: gas exchange, upstream input, downstream export, net in situ consumption, etc. And this budget could be nicely shown in an additional panel on Figure 5.

We consider all organic matter added in the estuary as mangrove derived, so the reviewer is correct that we consider DIC produced from organic mineralization inside the estuary as mangrove derived carbon. In the final budget, it does not matter whether the mineralization occurred in the mangrove sediments, or in the river.

Photosynthesis in the river is ignored, which may be reasonable, but the authors need to be more convincing (lines 228-231). Saying chlorophyll is low is not enough. They state that diurnal pCO₂ variations are small but provide no data to support that. Please be quantitative.

As we state in the manuscript, photosynthesis in the river is ignored because of low chl a and low phytoplankton biomass. With respect to day/night pCO₂ variations, we make continuous hourly measurements of pCO₂ from Shark River. The average difference in pCO₂ during the night (6p to 5:59a local time) is 3% lower than during the day (6a to 5:59p local time), a small

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amount and not in the direction one might expect if photosynthesis were significant. We have added this quantification to the manuscript.

The choice of endmembers is not clear. How exactly are these chosen and what are the values?

We write in the manuscript that “the freshwater and marine end-members were assigned to the values measured at the lowest (Tarpon Bay) and highest salinities, respectively.” Basically, we went as far as up river and out to the Gulf of Mexico as we could with the boat that we had, and we chose those measurements as the end-members. As we state in the paper, “During SharkTREx 1, the salinity along the longitudinal transects ranged from 1.2 to 27.1, and the mean (± s.d.) water temperature was 23.4 ± 0.2 °C. During SharkTREx 2, salinity ranged from 0.6 to 27.1, and water temperatures averaged 22.7 ± 0.9 °C.”

The use of X +/- Y throughout the text (lines 192, 299, 319, 333, 343, 375, etc.) and tables (1, 2, and 3) is unclear. How are X and Y computed? Am I supposed to take Y as a standard deviation or a standard error? What is the sample size for computing X and Y.

Depending on the parameter, the error estimates are based on standard deviations of the measured parameters, or the propagated errors of variables used to calculate the parameter.

Some of the values that the reviewer questioned are quoted from other published papers (e.g., line 192), whereas we do specify that we are quoting the mean and standard deviation in others (e.g., line 299):

“During SharkTREx 1, the salinity along the longitudinal transects ranged from 1.2 to 27.1, and the mean (± s.d.) water temperature was 23.4 ± 0.2 °C. During SharkTREx 2, salinity ranged from 0.6 to 27.1, and water temperatures averaged 22.7 ± 0.9 °C.”

We have indicated the number of samples used to calculate mean ± s.d. in the appropriate places in the manuscript, and have specified in the caption to the tables how ± are calculated.

Minor comments

Line 25: I think the area referred to here in this flux is the forest area, but the authors should make it clear to remove any ambiguity.

Yes, we have added language that indicates that flux is from the forest.

Line 26: To be clear that you are not talking about the Everglades in general, I would replace “in this region” with “for the Shark and Harney Rivers”

Done

I was pleased to see that the authors recognize the likelihood of large seasonality in the carbon cycle of south Florida estuaries (Section 3.7). However, the authors give no indication as to why they chose to sample in November two years in a row instead of sampling once in the wet season and once in the dry season, which would have given them a sense of the importance of
seasonality. All I am asking for here is a few sentences in the intro or methods describing the rationale for the sampling periods chosen.

There was no good scientific reason for choosing to conduct the experiments in November, twice. SharkTREx 1 and 2 were piggy-backed on funded experiments that took the team from Hawaii to Florida, and these funded experiments had to be conducted in November. SharkTREx 1 was a pilot experiment, and focused on just the Shark River, had fewer stations, and where some important measurements were not made (e.g., DIC). SharkTREx 2 was a follow up to fill some of the gaps (i.e., more stations, Harney River, and high quality DIC measurements). Future studies will be conducted in the dry season.
Dissolved carbon biogeochemistry and export in mangrove-dominated rivers of the Florida Everglades

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Abstract. The Shark and Harney Rivers, located on the southwest coast of Florida, USA, originate in the freshwater, karstic marshes of the Everglades and flow through the largest contiguous mangrove forest in North America. In November 2010 and 2011, dissolved carbon source-sink dynamics were examined in these rivers during SF6 tracer release experiments. Approximately 80% of the total dissolved carbon flux out of the Shark and Harney Rivers during these experiments was in the form of inorganic carbon, either via air-water CO2 exchange or longitudinal flux of dissolved inorganic carbon (DIC) to the coastal ocean. Between 42 and 48% of the total mangrove-derived DIC flux into the rivers was emitted to the atmosphere, with the remaining being discharged to the coastal ocean. Dissolved organic carbon (DOC) represented ca. 10% of the total mangrove-derived dissolved carbon flux from the forests to the rivers. The sum of mangrove-derived DIC and DOC export from the forest to these rivers was estimated to be at least 18.9 to 24.5 mmol m-2 d-1, a rate lower than other independent estimates from Shark River and from other mangrove forests. Results from these experiments also suggest that in Shark and Harney Rivers, mangrove contribution to the estuarine flux of dissolved carbon to the ocean is less than 10%.
1 Introduction

In many tropical and sub-tropical regions, mangrove forests are a typical feature surrounding estuaries (Twilley et al., 1992; Bouillon et al., 2008a). Mangroves are thought to play an important role in tropical and subtropical coastal biogeochemical cycling and the global coastal carbon budget, due to their high productivity and rapid cycling of organic and inorganic carbon (Twilley et al., 1992; Jennerjahn and Ittekkot, 2002; Dittmar et al., 2006). However, there remain uncertainties regarding the fate of mangrove-fixed carbon and the amount of carbon exported to the coastal waters from these ecosystems (Bouillon et al., 2008a; Bouillon et al., 2008b; Kristensen et al., 2008).

Bouillon et al. (2008a) showed that over 50% of the carbon fixed by mangroves through photosynthesis could not be accounted for by growth in biomass, accumulation in soils, and export of organic carbon, and suggested that a large fraction of this missing organic carbon may be mineralized to dissolved inorganic carbon (DIC) and either lost to the atmosphere or exported to the surrounding waters. In fact, several studies have shown that the lateral advective transport of interstitial waters through tidal pumping represents a major carbon export pathway from mangroves into adjacent waters, both for DIC (Koné and Borges, 2008; Miyajima et al., 2009; Maher et al., 2013) and dissolved organic carbon (DOC) (Dittmar and Lara, 2001; Bouillon et al., 2007c). However, to date, lateral mangrove derived aquatic carbon fluxes (as a proportion of overall forest carbon mass balance) have only been estimated for short time periods and over limited spatial (e.g., plot) scales (e.g., Troxler et al., 2015). These studies also typically do not determine the fate of mangrove-derived carbon once it is exported from the forest through tidal pumping and drainage.

Additional measurements of the magnitude and fate of mangrove carbon export at the basin scale are needed to help quantify connections between inter-tidal, estuarine and coastal ocean carbon cycles.

Rates of lateral dissolved carbon export from tidal mangrove forest are heterogeneous over space and time due to variability in inundation patterns, forest structure, topography, and soil hydraulic properties. Direct, plot-scale measurements of dissolved carbon export therefore may not represent rates quantified at the basin-scale. However, mangrove-derived dissolved carbon fluxes may be estimated in some systems using information on the spatial distribution of carbon-related measurements in adjacent waters. For example, the carbon balance of tidal riverine systems adjacent to mangrove forests should integrate the spatial and temporal variability of these lateral fluxes.

The objective in the study is to quantify dissolved carbon source-sink dynamics in a subtropical estuary dominated by two tidal rivers, the Shark and Harney Rivers in Everglades National Park, Florida, USA. These rivers
are centrally-located within the largest contiguous mangrove forest in North America and they discharge to the Gulf of Mexico. The total dissolved carbon inventories and fluxes in these rivers are determined using a series of discrete and continuous measurements of carbon-related parameters along a salinity gradient, and the mangrove contribution separated using measurements of stable isotopic composition of dissolved organic and inorganic carbon. The results are then scaled by the area of mangrove forest that surrounds these rivers to express dissolved carbon fluxes on an aerial basis for comparison to independent measurements of dissolved carbon fluxes from this forest.

2 Methods

2.1 Study site

The tidal-dominated Shark and Harney Rivers (river and estuary are used interchangeably in this contribution) are surrounded by mangrove forests and located on the southwest coast of Florida (Fig. 1), within Everglades National Park. The subtropical climate in southern Florida is characterized by a May to October wet season, when approximately 60% of the annual precipitation occurs (Southeast Regional Climate Center, http://www.sercc.com). The Shark and Harney Rivers together discharge approximately 50% of the flow from the Shark River Slough (SRS), the primary drainage feature of Everglades National Park, to the Gulf of Mexico (GOM) (Levesque, 2004). Seasonal variation of the water discharge from SRS mostly follows the precipitation patterns (Saha et al., 2012), and influences the transport of nutrients to the mangrove ecotone (Rivera-Monroy et al., 2011). The Shark and Harney Rivers are each approximately 15 km long, and connected in Tarpon Bay (Fig. 1). The mean depths of Tarpon Bay, Shark River, and Harney River at mid tide are 1.4 ± 0.3, 2.8 ± 0.4, and 2.6 ± 0.4 m (Ho et al., 2014), respectively, and the surface areas are 1.48 x 10⁶, 2.54 x 10⁶, and 2.75 x 10⁶ m², respectively. The inter-tidal zones bordering the Shark and Harney Rivers are dominated by Rhizophora mangle (red mangrove), Avicennia germinans (black mangrove), Laguncularia racemosa (white mangrove), and Conocarpus erectus (buttonwood). Semi-diurnal tides in this region inundate the forest as often as twice a day. River discharge to the GOM is primarily influenced by tides, wind, and freshwater inflow from SRS (Levesque, 2004).

Discharges are determined by the US Geological Survey at stations near the midpoints of Shark River (USGS 252230081021300 Shark River) and Harney River (USGS 252551081050900 Harney River) (Fig. 1). Discharges are generally lower during March-May than the rest of the year. Hourly mean residual discharge values (i.e., filtered for tides) from March to May of the 5-year period from 2007 to 2011 ranged from -21.9 to 24.1 m³ s⁻¹, with a mean of 0. 

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m$^3$s$^{-1}$ for Shark River, and ranged from -28.9 to 38.5 m$^3$s$^{-1}$, with a mean of 4.4 m$^3$s$^{-1}$ for Harney River. Positive values indicate flow towards the GOM. For the rest of the year (i.e., June to February), these values ranged from -46.2 to 89.2 m$^3$s$^{-1}$, with a mean of 8.8 m$^3$s$^{-1}$ for Shark River, and -41.6 to 75.0 m$^3$s$^{-1}$, with a mean of 11.3 m$^3$s$^{-1}$ for Harney River.

2.2 Shark River Tracer Release Experiments

Two field studies were conducted as part of the Shark River Tracer Release Experiment (SharkTREx 1: 20 to 25 November 2010; SharkTREx 2: 10 to 15 November 2011; (Ho et al., 2014)). The mean residual discharges for Shark River were 6.9 (hourly range: -2 to 19.9) and 4.9 (hourly range: -18.9 to 34.8) m$^3$s$^{-1}$, during SharkTREx 1 and 2, respectively, and those for Harney River were 6.0 (hourly range: -1.6 to 22.8) and 1.9 (hourly range: -17.3 to 30.6) m$^3$s$^{-1}$, during SharkTREx 1 and 2, respectively (U.S. Geological Survey, 2016).

During both campaigns, an inert tracer (sulfur hexafluoride; SF$_6$) was injected in the river near the point where the rivers diverge just downstream of Tarpon Bay (25.4092, -81.0083) to determine the rates of longitudinal dispersion, and the water residence time. Each day, longitudinal surveys were made along the Shark and Harney Rivers from Tarpon Bay to the GOM, and included continuous underway measurements of temperature, salinity, SF$_6$, dissolved O$_2$(DO; µmol kg$^{-1}$), and partial pressure of CO$_2$ (pCO$_2$; µatm), and discrete measurements of total alkalinity (TAlk; µmol kg$^{-1}$), dissolved inorganic carbon (DIC; µmol kg$^{-1}$), dissolved organic carbon (DOC; µmol kg$^{-1}$), stable carbon isotopic composition of DIC and DOC ($\delta^{13}$C$_{DIC}$ and $\delta^{13}$C$_{DOC}$, respectively; ‰).

2.3 Discrete measurements

During SharkTREx 1, three to five surface water samples were collected daily in the Shark River with a 5-L Niskin bottle at ~0.5 m below the surface for the analysis of TAlk, DOC, $\delta^{13}$C$_{DIC}$, and $\delta^{13}$C$_{DOC}$. At each sampling site, vertical profiles of temperature, salinity, and DO were recorded using a conductivity, temperature, and depth sonde (Sea-Bird SBE 19plus V2) equipped with a Clark type polarographic O$_2$ sensor (SBE 43). These profiles showed that the water column was vertically well mixed. No discrete samples were collected in the Harney River during SharkTREx 1. During SharkTREx 2, discrete samples for DIC, TAlk, DOC, $\delta^{13}$C$_{DIC}$, and $\delta^{13}$C$_{DOC}$ were collected daily at 20 stations distributed within the Shark and Harney Rivers (Fig. 1).
2.3.1 Total alkalinity and dissolved inorganic carbon

During SharkTREx 1, samples for TAlk were collected in 250 mL HDPE bottles after passing through a 0.45 μm filter. They were stored on ice for transport to the laboratory at FIU, where TAlk was determined at room temperature using an automated titrator (Brinkman Titriso 751) with 0.1 N HCl to a pH of 2. TAlk was calculated from the volume of acid added at the inflection point closest to a pH of 4, and reported as meq L⁻¹ HCO₃⁻ since the original pH of the water samples was near neutral. The precision of the measurements was ±2% from replicate analysis (n = 5) with an accuracy of ±2% as determined by analysis of certified reference material (Dickson, 2010). DIC and pH were computed from TAlk and pCO₂ using the dissociation constants of Cai and Wang (1998) for estuarine waters.

During SharkTREx 2, samples for TAlk and DIC were collected in 550 mL borosilicate glass bottles, poisoned with HgCl₂, and sealed with hydrocarbon grease (Apiezon M). The samples were stored at room temperature in the dark for travel to the laboratory at NOAA/AOML. Samples for TAlk were measured in an open thermostated cell (25 °C) with an automated titrator (Metrohm 765 Dosimat) connected to a pH glass-reference electrode system (Orion), using 0.2 M HCl as a titrant, and determined from the equivalence point of the titration curve using a non-linear least-squares fit. For DIC analysis, water samples were first acidified to convert all the carbonate species to CO₂ in a DIC analyzer (Apollo SciTech), and then measured with a NDIR detector (LI-COR LI-7000). Calibrations for DIC and TAlk were performed using certified reference material (Dickson, 2010). The analytical uncertainty of the DIC and TAlk measurements based on replicate samples are 0.1 and 0.2%, respectively.

The measured TAlk and pCO₂ from SharkTREx 2 were used to calculate DIC using CO2SYS (Pierrot et al., 2006) and the dissociation constants of Cai and Wang (1998), and the results were 1.3 ± 1.1% (mean ± s.d.; n = 77; 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.

2.3.2 Dissolved organic carbon

The samples analyzed for DOC were filtered with pre-combusted 0.7 μm GF/F filters and collected in pre-cleaned, acid-washed, brown high-density polyethylene bottles (HDPE; Nalgene). Containers were rinsed three times before sample collection, transported on ice to the FIU SERC Nutrient Analysis Lab, and stored in a refrigerator until analyses within three weeks of collection. DOC was measured using the high-temperature catalytic combustion method on a total organic carbon analyzer (Shimadzu TOC-V), and 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. ±0.3 ppm.

2.3.3 Stable carbon isotopic composition

Samples for δ¹³C were collected in 40 ml glass bottles after passing the sample through a GF/F filter, and then poisoning with HgCl₂. In the laboratory at RSMAS, vials with 0.5 ml 103% H₃PO₄ were flushed for 60 s with He. Approximately 2 ml of sample were then injected into the vial, and after sonification the accumulated CO₂ was analyzed by a gas chromatograph (GC) coupled to an isotope ratio mass spectrometer (GC-IRMS; Thermo Delta V). The δ¹³C was calibrated using two standards of NH₄HCO₃ with differing δ¹³C values dissolved in H₂O whose isotopic compositions had been previously calibrated relative to NBS-19 using conventional dual inlet mass spectrometry (Finnigan-MAT 251). The δ¹³C values are reported relative to the Vienna Pee Dee Belemnite (VPDB) standard, and has a reproducibility of ±0.2 ‰ as determined by repeated analysis of internal DIC standards.

Samples for δ¹³C DOC were collected in 60 ml brown HDPE bottles and stored on ice until returned to the lab at FIU. δ¹³C DOC samples were filtered with GF/F (0.7 µm) filter, and then stored in pre-cleaned 40 ml bottles until analyses. Measurements for δ¹³C DOC were made using a total organic carbon (TOC) analyzer (Aurora 1030W, OI Analytical) coupled to a cavity ring-down spectroscopy system (CRDS; G1111-i, Picarro) following the approach of Ya et al. (2015). DIC was removed by adding H₃PO₄ and sparging with N₂. 1.5 ml of sample was chemically oxidized to CO₂ at a temperature of 98°C in the presence of sodium persulfate (Na₂S₂O₈). The CO₂ generated was detected by non-dispersive infrared absorption (NDIR) for determination of DOC. The CO₂ was collected in a gas-tight bag and then pulsed into the CRDS for the δ¹³C measurement. 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 salinity of the sample matrix. The isotope values of these two standards were determined by using an elemental analyzer isotope ratio mass spectrometer (EA-IRMS). Analytical precision based on replicated standards ranged from ±0.15 to ±1.52 ‰ for this study.

2.4 Underway measurements

Surface water was continuously pumped from an intake located near the bow of the boat at a water depth of approximately 1 m during tracer recovery operations. Water temperature and salinity were continuously recorded using a thermosalinograph (SBE 45 MicroTSG). During SharkTREx 1, DO was measured underway with a membrane covered galvanic sensor (WTW Cellox 325) calibrated with saturated air. During SharkTREx 2, DO was measured using an oxygen optode (Aanderaa 3835) calibrated against Winkler titration.

Underway measurements of atmospheric and waterside pCO₂ were made. Waterside pCO₂ were obtained with a showerhead type equilibrator coupled to a non-dispersive infrared (NDIR) analyzer (LI-COR 840A). Measurements of underway SF₆ were made with an automated SF₆ analysis system (Ho et al., 2002), which is...
comprised of gas extraction (membrane contactor), separation (molecular sieve 5A), and detection units (gas chromatograph equipped with an electron capture detector). Both the underway pCO$_2$ and SF$_6$ measurements are described in greater detail in Ho et al. (2014).

2.5 Inventories of DIC, DOC and DO

The inventories of DIC, DOC and DO were calculated in the same way that SF$_6$ inventories were determined in Ho et al. (2014). The river was divided into 100-m longitudinal sections, and the measured concentrations, corrected for tidal movement to slack before ebb for each day, were assigned to each section $i$ and then summed over the entire length of the river. For example, to calculate the inventory of DIC, denoted $\Sigma$[DIC]$_{\text{observed}}$ (mol):

$$\Sigma[\text{DIC}]_{\text{observed}} = \sum_{i=1}^{n} [\text{DIC}]_{i} \cdot V_{i},$$

(1)

where $[\text{DIC}]_{i}$ is the mean concentration (mol L$^{-1}$) in section $i$, $V_{i}$ is the volume of the river (L) in section $i$ at mid-tide, and $n$ is the number of sections in each river ($n = 273$ for Shark River and Tarpon Bay; $n = 152$ for Harney River). DOC and DO inventories were also calculated using Eq. (1), by substituting $[\text{DOC}]_{i}$ or $[\text{DO}]_{i}$ for $[\text{DIC}]_{i}$ accordingly. The inventories of DIC and DOC were separated into contributions from estuarine and non-estuarine sources, first by determining inventories for DIC assuming conservative mixing between the freshwater and marine end members and then subtracting these inventories from the total observed inventories. The estuarine DIC inventory, $\Sigma[\text{DIC}]_{\text{estuary}}$, representing the DIC from all estuarine sources, was calculated as follows:

$$\Sigma[\text{DIC}]_{\text{estuary}} = \Sigma[\text{DIC}]_{\text{observed}} - \Sigma[\text{DIC}]_{\text{conserv}} + \Sigma[\text{DIC}]_{\text{gaseous}}$$

(2)

where $\Sigma[\text{DIC}]_{\text{conserv}}$ is the inventory of DIC assuming conservative mixing between freshwater and marine end members (i.e., from non-estuarine sources), and $\Sigma[\text{DIC}]_{\text{gaseous}}$ is the inventory of DIC lost to air-water gas exchange from the estuary, due to pCO$_2$ in the water being above solubility equilibrium with the atmosphere (see section 2.6). The freshwater and marine end-members were assigned to the values measured at the lowest (Tarpon Bay) and highest salinities, respectively.

The total O$_2$ deficit in Shark River during the experiments was determined by examining the difference in O$_2$ inventories for conservative mixing and actual measurements, correcting for O$_2$ influx due to gas exchange using a formulation similar to Eq. (2) above (i.e., $\Sigma[\text{DO}]_{\text{deficit}} = \Sigma[\text{DO}]_{\text{conserv}} - \Sigma[\text{DO}]_{\text{observed}} + \Sigma[\text{DO}]_{\text{gaseous}}$).
2.6 Air-water O₂ and CO₂ fluxes

To enable comparison between different gases and different aquatic environments, it is customary to normalize gas transfer velocities to a Schmidt number (\(Sc\); kinematic viscosity of water divided by diffusion coefficient of gas in water) of 600, \(k(600)\), corresponding to that of CO₂ in freshwater at 20 °C. \(k(600)\) for SharkTREx 1 and 2, determined from the wind speed and current velocity parameterization proposed in Ho et al. (2016), were 3.5 ± 1.0 and 4.2 ± 1.8 cm h⁻¹, respectively. To determine \(k\) for CO₂ at the temperature and salinity measured in the rivers, the following equation was used, assuming a \(Sc^{1/2}\) scaling (Jähne et al., 1987):

\[
k_{\text{CO}_2} = k(600) \left( \frac{\rho(02)}{\rho(600)} \right)^{-1/2},
\]

where \(k\) and \(Sc\) of CO₂ could be substituted in Eq. (3) for O₂, and \(Sc\) for O₂ and CO₂ were calculated as a function of temperature and salinity using data compiled by Wanninkhof (2014).

Air-water O₂ fluxes (\(F_{O_2}\); mmol m⁻² d⁻¹) were calculated as follows:

\[
F_{O_2} = k_{O_2} \left( O_{02\text{eq}} - O_2 \right),
\]

where \(k_{O_2}\) (cm h⁻¹) is the gas transfer velocity for O₂, \(O_{02\text{eq}}\) (mmol m⁻³) is the equilibrium concentration of O₂ in the water at a given temperature and salinity (Garcia and Gordon, 1992), and \(O_2\) is the measured oxygen concentration in the water.

Similarly, air-water CO₂ fluxes (\(F_{CO_2}\); mmol m⁻² d⁻¹), which were used to determine changes in DIC due to gas exchange, were calculated as follows:

\[
F_{CO_2} = k_{CO_2} K_0 \Delta p_{CO_2},
\]

where \(k_{CO_2}\) (cm h⁻¹) is the gas transfer velocity for CO₂, \(K_0\) (mol atm⁻¹ m⁻³) is the aqueous-phase solubility of CO₂ (Weiss, 1974), and \(\Delta p_{CO_2}\) (µatm) is the difference between the measured pCO₂ in air equilibrated with water and atmospheric pCO₂.

As with the inventories, \(F_{CO_2}\) were separated into estuarine and non-estuarine contributions. Because of the non-linearity in the relationship between pCO₂ and other carbonate system parameters, the pCO₂ in the river expected from conservative mixing was calculated by assuming conservative mixing for DIC and TAlk, and then calculating pCO₂ using CO2SYS (Pierrot et al., 2006), with the dissociation constants of Cai and Wang (1998). Then, the non-estuarine \(F_{CO_2}\) was calculated as above with Eq. (5), and the \(F_{CO_2}\) attributed to estuarine sources was determined as the difference between total and non-estuarine \(F_{CO_2}\).

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2.7 Estuarine and mangrove contributions to DIC

DIC in the Shark and Harney Rivers may originate from several sources in addition to input from the freshwater marsh upstream and the coastal ocean, including: 1) mangrove root respiration; 2) organic matter mineralization in sediments or in river water; 3) dissolution of CaCO$_3$ in sediments or in river water; and 4) groundwater discharge. Groundwater in this region is likely to contain DIC from CaCO$_3$ 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. In this setting, the combination of #1 and #2 represents the mangrove source of DIC ([DIC]$_{mangrove}$), and the combination of #3 and #4 represents the CaCO$_3$ dissolution source ([DIC]$_{dissolution}$) to estuarine [DIC]:

$$[\text{DIC}]_{\text{estuary}} = [\text{DIC}]_{\text{observed}} - [\text{DIC}]_{\text{conserv}} + [\text{DIC}]_{\text{gasex}} = [\text{DIC}]_{\text{mangrove}} + [\text{DIC}]_{\text{dissolution}} \quad (6)$$

where [DIC]$_{observed}$ is the observed DIC concentration, [DIC]$_{conserv}$ is the DIC concentration expected by conservative mixing of the two end-members, and [DIC]$_{gasex}$ is the correction for change in [DIC]$_{observed}$ due to loss through air-water gas exchange as the water transits through the estuary. [DIC]$_{conserv}$ was determined from $F_{CO_2}$ and the residence time of water during each experiment (Ho et al., 2016).

Measurements of $\delta^{13}$C$_{DIC}$ and estuarine DIC/TAlk ratios were used to determine the mangrove sources to estuarine DIC. Fixation of CO$_2$ through photosynthesis is neglected in both models as these rivers are characterized by low chlorophyll-$a$ concentration and low phytoplankton biomass (Boyer et al., 1997). During SharkTREx 1 and 2, there was a negligible difference between pCO$_2$ measured during the day and night (ca. 3%).

2.7.1 Determining mangrove contribution from $\delta^{13}$C$_{DIC}$

Processes 1 through 4 listed above influence $\delta^{13}$C$_{DIC}$ in the estuary differently due to the differences in the $\delta^{13}$C values originating from respiration of mangrove-derived organic matter, and CaCO$_3$ dissolution. The isotopic fractionation during respiration of organic matter is small, and the $\delta^{13}$C$_{DIC}$ values produced via this pathway should be approximately equivalent to the $\delta^{13}$C of the organic matter respired (DeNiro and Epstein, 1978). The isotopic fractionation during dissolution/re-precipitation of CaCO$_3$ is also considered to be negligible (Salomons and Mook, 1986).

The expected $\delta^{13}$C values of DIC in the rivers as a result of conservative mixing ($\delta^{13}$C$_{conserv}$) of the marine and freshwater end-members of the Shark and Harney Rivers were calculated as follows (Mook and Tan, 1991):
where $[\text{DIC}]$ is the observed DIC concentration, $S$ is the measured salinity, and $M$ and $F$ subscripts refer to the marine and freshwater end-members, respectively.

An estimate of the maximum contribution of $[\text{DIC}]_{\text{mangrove}}$ and $[\text{DIC}]_{\text{dissolution}}$ to $[\text{DIC}]_{\text{estuary}}$ can be obtained by solving Equations 6 and 8:

\[
\delta^{13}C_{\text{conserv}} = \frac{S([\text{DIC}]_{\text{est}} - [\text{DIC}]_{\text{mangrove}} - [\text{DIC}]_{\text{dissolution}})}{([\text{DIC}]_{\text{est}} - [\text{DIC}]_{\text{mangrove}} - [\text{DIC}]_{\text{dissolution}}) + S[\text{DIC}]_{\text{est}}}, 
\]

(7)

\[
\delta^{13}C_{\text{DIC}} \times [\text{DIC}]_{\text{observed}} = \delta^{13}C_{\text{conserv}} \times [\text{DIC}]_{\text{est}} + \delta^{13}C_{\text{mangrove}} \times [\text{DIC}]_{\text{mangrove}} + \delta^{13}C_{\text{dissolution}} \times [\text{DIC}]_{\text{dissolution}} + \varepsilon_{\text{DIC-CO}_2} \times [\text{DIC}]_{\text{air}}. 
\]

(8)

where the $\delta^{13}C_{\text{conserv}}$ value is the DIC isotopic composition expected for conservative mixing (Mook and Tan, 1991), $\delta^{13}C_{\text{mangrove}}$ is the isotopic composition for mangrove-derived material (~30‰; Mancera-Pineda et al., 2009), the $\delta^{13}C_{\text{dissolution}}$ value is the $\delta^{13}C$ composition of calcite (~1‰), and $\varepsilon_{\text{DIC-CO}_2}$ is the equilibrium isotope fractionation between DIC and CO$_2$ gas (~8‰; Zhang et al., 1995).

2.7.2 Determining mangrove contribution from TAlk/DIC

An independent approach to separate the mangrove contribution from CaCO$_3$ dissolution is to use the co-variation of $[\text{DIC}]_{\text{est}}$ and $[\text{TAlk}]_{\text{est}}$ as an indicator of the biogeochemical processes affecting DIC dynamics (Borges et al., 2003; Bouillon et al., 2007c), as these processes have different effects on DIC and TAlk. Assuming that $[\text{TAlk}]_{\text{est}}$ is mainly produced by the dissolution of CaCO$_3$, $[\text{DIC}]_{\text{dissolution}}$ can be determined as $0.5 \times [\text{TAlk}]_{\text{est}}$, and then $[\text{DIC}]_{\text{mangrove}}$ can be calculated from Eq. (6). However, since sulfate reduction, a primary mineralization pathway in mangrove sediments, may also contribute to $[\text{TAlk}]$ (Alongi, 1998; Alongi et al., 2005) this calculation represents an upper bound estimate for $[\text{DIC}]_{\text{dissolution}}$ and a lower bound estimate for $[\text{DIC}]_{\text{mangrove}}$.

2.8 Determining mangrove contribution to DOC

In the Shark and Harney Rivers, dissolved organic matter may be derived from upstream freshwater wetland species such as periphyton and sawgrass, from seagrass communities and marine phytoplankton, or from mangrove vegetation inside the estuary (Jaffe et al., 2001). The estuarine contributions to DOC ($[\text{DOC}]_{\text{est}}$) in the rivers was determined in the same way as for DIC above using Eq. (6), by substituting DOC for DIC accordingly, without the correction for gas exchange:

\[
[\text{DOC}]_{\text{est}} = [\text{DOC}]_{\text{observed}} - [\text{DOC}]_{\text{conserv}}. 
\]

(9)
where \([\text{DOC}]_{\text{observed}}\) is the observed DOC concentration, \([\text{DOC}]_{\text{conserv}}\) is the DOC concentration expected from conservative mixing of the two end-members.

Then, measurements of \(\delta^{13}\text{C}_{\text{DOC}}\) were made to ascertain the mangrove source of DOC in the river, in order to determine the proportion of \([\text{DOC}]_{\text{conserv}}\) that is of mangrove origin. The expected \(\delta^{13}\text{C}\) values of DOC as a result of conservative mixing \((\delta^{13}\text{C}_{\text{conserv}})\) were calculated using Eq. (7), substituting DOC for DIC. Assuming that \([\text{DOC}]_{\text{conserv}}\) was entirely mangrove-derived, \([\text{DOC}]_{\text{mangrove}}\) should equal:

\[
[\text{DOC}]_{\text{mangrove}} = \frac{[\text{DOC}]_{\text{observed}} \delta^{13}\text{C}_{\text{DOC}} + [\text{DOC}]_{\text{conserv}} \delta^{13}\text{C}_{\text{conserv}}}{\delta^{13}\text{C}_{\text{mangrove}}}
\]

where \(\delta^{13}\text{C}_{\text{mangrove}}\) is the isotopic composition for mangrove-derived material (-30‰).

2.9 Longitudinal dispersion

The longitudinal \(\text{SF}_6\) distribution was corrected for tidal movement to slack water before ebb for each day using a method described in Ho et al. (2002). The absolute magnitudes of the average daily corrections were 2.0 and 2.7 km for SharkTREx 1 and 2, respectively, with a range for individual measurements of 0 to 5.8 km and 0 to 7.3 km for SharkTREx 1 and 2, respectively. Longitudinal dispersion coefficient \(K_x\) (m² s⁻¹) was calculated from the change of moment of the longitudinal \(\text{SF}_6\) distribution over time as follows (Fischer et al., 1979; Rutherford, 1994):

\[
K_x = \frac{1}{2\sigma^2_x}\left(\frac{\text{d} \sigma^2_x}{\text{d}t}\right)
\]

where \(\sigma^2_x\) is the second moment of the longitudinal \(\text{SF}_6\) distribution for each day.

2.10 Longitudinal fluxes to the Gulf of Mexico

The longitudinal fluxes of DIC and DOC from Shark and Harney Rivers to the Gulf of Mexico were calculated using the averaged DIC or DOC inventories, and the residence time of water \((\tau; \text{d})\), which was determined from the decrease in the inventory of \(\text{SF}_6\) after correcting for air-water gas exchange (Ho et al., 2016). For example, the longitudinal DIC flux \((F_{\text{DIC}}; \text{mol d}^{-1})\) can be calculated as follows:

\[
F_{\text{DIC}} = \frac{\Sigma[\text{DIC}]_{\text{observed}}}{\tau}
\]

Equation (12) can be used to calculate the fluxes of any other dissolved or suspended substance in the river by substituting its inventory in place of DIC. In addition, using the estuarine and non-estuarine fractions of the inventories in equation (12) allowed the estuarine and non-estuarine proportions of the longitudinal carbon fluxes to be quantified.

The advantage of this method to calculate longitudinal flux in a tidal river over a method that uses net discharge and constituent concentration is that the effect of tidal flushing is implicitly accounted for by the residence

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time, and therefore there is not a need to explicitly define the fraction of river water in the return flow during each flood tide.

3 Results and Discussion

3.1 Distribution patterns and carbon inventories

During SharkTREx 1, the salinity along the longitudinal transects ranged from 1.2 to 27.1, and the mean (± s.d.) water temperature was 23.4 ± 0.2 °C (n = 3767). During SharkTREx 2, salinity ranged from 0.6 to 27.1, and water temperatures averaged 22.7 ± 0.9 °C (n = 3818).

Both pCO$_2$ and DO showed large spatial variability within the Shark and Harney Rivers during SharkTREx 1 and 2 (Fig. 2). Measured pCO$_2$ values were well above atmospheric equilibrium along the entire salinity range, with values ranging from ca. 1000 to 6200 µatm. Maximum pCO$_2$ values were observed at intermediate salinities, decreasing towards both end-members, while DO showed the opposite pattern, with saturations ranging from 36 to 113%.

The patterns of TAlk and DIC along the salinity gradient followed the same trend as pCO$_2$ and were clearly non-conservative (Fig. 3a-f). TAlk varied between ca. 3400 and 5000 µmol kg$^{-1}$ during SharkTREx 1 and between ca. 3000 and 3900 µmol kg$^{-1}$ during SharkTREx 2. DIC ranged from ca. 3400 to 5100 µmol kg$^{-1}$ during SharkTREx 1, and ca. 2800 to 4000 µmol kg$^{-1}$ during SharkTREx 2. $\delta^{13}$C$_{DIC}$ values ranged from -10.3 to -6.6 ‰ and from -11.4 to -5.8 ‰ during SharkTREx 1 and 2, respectively. Higher DIC, TAlk and pCO$_2$ coincided with lower O$_2$ saturation, more depleted $\delta^{13}$C$_{DIC}$, and lower pH values (Fig. 3g-i), indicative of mineralization of mangrove-derived organic matter within the estuary.

During SharkTREx 1, the DOC concentrations in the freshwater end member were higher than SharkTREx 2 (Fig. 4). For both experiments, DOC concentrations followed a non-conservative pattern (see also Cawley et al., 2013), but this trend was less apparent during SharkTREx 1 compared to SharkTREx 2 (Fig. 4).

The inventories of DIC, DOC, DO, TAlk, and pCO$_2$ were relatively constant in the Shark and Harney Rivers, indicating quasi steady state conditions during SharkTREx 1 and 2. Under these conditions, carbon inputs and exports are balanced, and fluxes and concentrations may be examined interchangeably. $K_x$ during the experiments (16.4 ± 4.7 and 77.3 ± 6.5 m$^2$ s$^{-1}$ for Shark River during SharkTREx 1 and 2, respectively, and 136.1 ± 16.5 m$^2$ s$^{-1}$ for Harney...
River during SharkTREx 2) were relatively large, and suggest that any perturbations (such as export of DIC from mangroves) would be quickly mixed thoroughly in the estuary.

In the following, for brevity, fluxes and inventories are summarized as ranges, which cover the two rivers and two experiments so they reflect both temporal and spatial variability. The individual values are given in Tables 1 and 2.

DIC was the dominant form of dissolved carbon in both rivers and accounted for 79 to 82% of the total dissolved carbon in the rivers. The contribution of DOC to the total carbon pool varied between 18 and 21% (Table 1).

3.2 Air-water CO₂ fluxes

As shown by Ho et al. (2014), pCO₂ observed during SharkTREx 1 and 2 fall in the upper range of those reported in other estuarine (Borges, 2005) and mangrove-dominated systems (Bouillon et al., 2003; Bouillon et al., 2007a; Bouillon et al., 2007b; Koné and Borges, 2008; Call et al., 2015). The mean air-water CO₂ fluxes in Shark River for SharkTREx 1 and 2 were 105 ± 9 and 99 ± 6 mmol m⁻² d⁻¹ (Ho et al., 2016). The analysis is taken further here by including data from Harney River. The mean air-water CO₂ fluxes in Harney River were 150 ± 8 and 114 ± 21 mmol m⁻² d⁻¹ for SharkTREx 1 and 2, respectively.

Borges et al. (2003) summarized all available pCO₂ data from mangrove surrounding waters, and calculated CO₂ fluxes to the atmosphere that averaged 50 mmol m⁻² d⁻¹ (with a range of 4.6 to 113.5 mmol m⁻² d⁻¹), and Bouillon et al. (2008a) estimated a global CO₂ flux from mangroves of ca. 60 ± 45 mmol m⁻² d⁻¹. One reason that the fluxes from SharkTREx 1 and 2 are on the upper end of those estimates may be that the Shark and Harney Rivers receive a large input of DIC from the freshwater marsh upstream (Table 1), causing higher pCO₂ in the estuary compared to the global average.

Scaling the air-water CO₂ fluxes by the area of open water in the Shark and Harney Rivers, where Tarpon Bay is included with Shark River, suggests that the total carbon emissions to the atmosphere through air-water gas exchange in Shark River was 4.2 ± 0.4 x 10⁵ and 4.0 ± 0.2 x 10⁵ mol d⁻¹ during SharkTREx 1 and 2, respectively, and were 4.1 ± 0.2 x 10⁵ and 3.1 ± 0.6 x 10⁵ mol d⁻¹ from the Harney River during SharkTREx 1 and 2, respectively (Fig. 5), which is remarkably consistent, both spatially and temporally.

These fluxes were incorporated into the DIC mass balance of the Shark and Harney Rivers (Eq. 2) by calculating the total CO₂ degassed over the residence time of water in the rivers. Given the mean air-water CO₂ fluxes

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Table 2), the total CO\textsubscript{2} degassed in the Shark River represents approximately 13 and 21% of \(\Sigma [\text{DIC}]_{\text{observed}}\) during SharkTREx 1 and 2, respectively, and the CO\textsubscript{2} degassed from the Harney River during SharkTREx 2 represents 20% of \(\Sigma [\text{DIC}]_{\text{observed}}\), indicating that air-water CO\textsubscript{2} exchange removes a non-negligible fraction of the inorganic carbon in these rivers. Exclusion of \(\Sigma [\text{DIC}]_{\text{water}}\) from the mass balance in Eq. (2) would lead to an underestimation of \(\Sigma [\text{DIC}]_{\text{estuary}}\) of between 33 and 44%.

3.3 Mangrove contribution to DIC inventory

The highest DIC concentrations were correlated with low DO (Fig. 2) and characterized by \(^{13}\text{C}\)-depletion (Fig. 3j, k, l). Observations of elevated DIC and pCO\textsubscript{2} in the middle of the estuary, coupled with \(^{13}\text{C}\)\text{DIC} and O\textsubscript{2} depletion may indicate the importance, noted by other authors, of lateral transport of pore water from the peat-based mangrove forest into the river via tidal pumping (Bouillon et al., 2008a; Maher et al., 2013). However, as demonstrated below, the observed DIC and \(^{13}\text{C}\)\text{DIC} distributions in these rivers cannot be explained solely by mineralization of mangrove-derived organic carbon.

3.3.1 Evidence from \(^{13}\text{C}\)DIC

The distributions of DIC and \(^{13}\text{C}\)DIC cannot be explained solely by the addition of mangrove-derived DIC and air-water gas exchange. Solving Eq. (8) for \(^{13}\text{C}\)\text{DIC}, assuming that \([\text{DIC}]_{\text{dissolution}}\) is negligible and that the only source of DIC in the rivers is of mangrove origin, would result in \(^{13}\text{C}\) values significantly lower than those observed. The low pH in interstitial waters of mangrove sediments due to organic matter mineralization processes may be favorable to CaCO\textsubscript{3} dissolution in mangrove sediments, and this process could have an effect on estuarine \(^{13}\text{C}\)DIC.

Groundwater discharge could also influence DIC and \(^{13}\text{C}\)DIC. Inputs of DIC derived from CaCO\textsubscript{3} dissolution from either of these sources may explain the differences in observed \(^{13}\text{C}\)DIC and those expected if \([\text{DIC}]_{\text{estuary}}\) was entirely of mangrove origin.

Solving Equations 6 and 8, the mineralization of mangrove-derived organic matter is estimated to account for ca. 60 ± 6 % of \(\Sigma [\text{DIC}]_{\text{estuary}}\) (Table 3), with the remainder originating from the dissolution of CaCO\textsubscript{3}. This estimate is sensitive to the end member value chosen for \(^{13}\text{C}\)\text{mangrove} and \(^{13}\text{C}\)\text{dissolution}. For instance, if \(^{13}\text{C}\)\text{mangrove} were -29‰ instead of -30‰, the mangrove contribution would increase to 62%.
3.3.2 Evidence from DIC and TAlk

In the Shark and Harney Rivers, the high correlation \( r^2 = 0.99 \); Fig. 6) between \([\text{DIC}]_{\text{estuary}}\) and \([\text{TAlk}]_{\text{estuary}}\) indicates the same processes control the inputs of DIC and TAlk to these rivers. By examining the covariation of \([\text{DIC}]_{\text{estuary}}\) and \([\text{TAlk}]_{\text{estuary}}\), mangroves were found to contribute a minimum of 70 ± 3 % of \([\text{DIC}]_{\text{estuary}}\) (Table 3), with the remainder due to the dissolution of CaCO$_3$. These estimates are in reasonable agreement with those based on the carbon isotopic mass balance.

The \([\text{TAlk}]_{\text{estuary}}\) vs. \([\text{DIC}]_{\text{estuary}}\) ratios were 0.84 and 0.92 for Shark River during SharkTREx 1 and 2, and 0.90 for the Harney River during SharkTREx 2 (Fig. 6). The TAlk to DIC ratios for CaCO$_3$ dissolution, sulfate reduction, and aerobic respiration are -0.2, 0.99, and 2, respectively. Hence, in order to achieve the observed ratios, and given the estimated contribution of CaCO$_3$ dissolution to \([\text{DIC}]_{\text{estuary}}\) of ca. 30%, sulfate reduction and aerobic respiration were estimated to contribute 32 to 39% and 31 to 38%, respectively.

3.3.3 Evidence from DO

The deficit of O$_2$ in Shark River was found to be 2.7 ± 0.7 x 10$^6$ and 3.7 ± 0.3 x 10$^6$ mol during SharkTREx 1 and 2, respectively. Assuming a stoichiometric ratio of ca. 1.1 for O$_2$ to CO$_2$ during degradation/remineralization of terrestrial organic matter (Severinghaus, 1995; Keeling and Manning, 2014), the maximum contribution of aerobic respiration to the DIC added to the estuary was estimated to be 57 to 69%. However, O$_2$ may also be consumed during oxidation of reduced products from anaerobic metabolism, such as H$_2$S, Mn$^{2+}$ or Fe$^{2+}$, with similar O$_2$ to CO$_2$ stoichiometry as aerobic respiration. Hence, the numbers derived above represent an upper limit for aerobic respiration, and if there were complete re-oxidation of metabolites from anaerobic respiration, the O$_2$ deficit would represent total mineralization of terrestrial organic matter instead of just aerobic respiration. The mangrove contributions estimated from $\delta^{13}$C$_{\text{DIC}}$ (section 3.3.1) and TAlk/DIC (section 3.3.2) are consistent with this analysis of the O$_2$ deficit, which indicates that a minimum of 57-69% of \([\text{DIC}]_{\text{estuary}}\) derived from the mineralization of organic matter.

3.4 Mangrove contributions to DOC inventory

During both experiments, the $\delta^{13}$C$_{\text{DOC}}$ was highly depleted, indicative of contribution from higher plants, including mangroves. During SharkTREx 1, the lowest observed $\delta^{13}$C$_{\text{DOC}}$ value (31.6‰) was in the mid-estuary (i.e., from salinity of ca. 10 to 20) (Fig. 4d). Previous studies of DOC from mangrove-dominated systems have reported

Deleted: 33.8‰ was in the mid-estuary (i.e., from salinity of ca. 10 to 20) (Fig. 4d), and it was lower than mangrove-derived material, indicative of a highly reworked organic matter source, and perhaps preferential degradation of enriched compounds had resulted in further $^{13}$C depletion (Hayes, 1993).
values as low as -30.4‰ (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). The overall δ^{13}C_{DOC} depletion was less during SharkTREx 2, and the overall distribution was indicative of a stronger marine influence and/or mixing (Fig. 4e, f). The marine end member had a more enriched δ^{13}C_{DOC}, indicating a greater contribution of seagrass and/or marine phytoplankton derived organic matter to the marine DOC pool (Anderson and Fourqurean, 2003). These observations are consistent with the greater longitudinal dispersion observed during SharkTREx 2 compared to SharkTREx 1.

The calculations of mangrove contribution using δ^{13}C_{DOC} mass balances (Eq. 10) also suggest that the majority of [DOC]_{estuary}, but only a small percentage of the total DOC inventory, was derived from mangroves (7 and 5% in the Shark River during SharkTREx 1 and 2, and 7% in the Harney River during SharkTREx 2).

3.5 Longitudinal fluxes to the Gulf of Mexico and comparison with previous studies

Residence times of Shark River (including Tarpon Bay) for SharkTREx 1 and 2 were, 5.8 ± 0.4 and 8.1 ± 1.1 days, respectively (Ho et al., 2016), and that of Harney River was 4.7 ± 0.7 days for SharkTREx 2. The resulting longitudinal DIC fluxes to the Gulf of Mexico (15.8 to 33.6 x 10⁵ mol d⁻¹) were significantly larger than the longitudinal DOC fluxes (3.3 to 7.5 x 10⁵ mol d⁻¹) at salinity of ca. 27 (Fig. 5; Table 2).

There are no previously published DIC inventories or fluxes for the Shark and Harney Rivers, so comparison with previous studies is focused on the DOC results. The DOC flux from the Shark River to the coastal ocean in SharkTREx 1 (7.5 ± 0.2 x 10⁵ mol d⁻¹) is in very good agreement to that estimated by Bergamaschi et al. (2011) in an experiment conducted in the Shark River from 20-30 September 2010 (7.6 ± 0.5 x 10⁵ mol d⁻¹). However, the net discharge during the Bergamaschi et al. (2011) study was higher than SharkTREx 1 (mean ± s.d.: 9.1 ± 7.1 vs. 6.9 ± 5.3 m³ s⁻¹), which would lead to a shorter residence time of 4.6 days using a relationship presented in Ho et al. (2016). Using the DOC concentration data presented in Bergamaschi et al. (2011) yields an inventory that is ca. 3% higher than the DOC inventory in Shark River during SharkTREx 1. Calculations using the shorter residence time and higher DOC inventory yields a DOC flux of 9.7 ± 0.2 x 10⁵ mol d⁻¹, which is ca. 30% higher than the estimates of Bergamaschi et al. (2011).

The longitudinal flux of mangrove-derived DOC from Shark River during SharkTREx 1 (0.3 ± 0.2 x 10⁵ mol d⁻¹; Table 2) is in rough agreement with the estimate of Cawley et al. (2013) during the same period (0.2 x 10⁵ mol d⁻¹), but the value for Harney River (0.6 ± 0.6 x 10⁵ mol d⁻¹) is lower than their estimate (1.6 x 10⁵ mol d⁻¹).

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Mangroves contributed 4% to 6% of the total longitudinal DOC flux in the Shark River and 7% in the Harney River during SharkTREx 2 (Tables 1 and 4). Cawley et al. (2013), estimated a mangrove contribution to DOC flux of 3 ± 10% for Shark River and 21 ± 8% for the Harney River during November 2010, the same time period as SharkTREx 1. DOC measurements were not made in Harney River as part of SharkTREx 1. However, using the November 2010 DOC data from Harney River collected by Cawley et al. (2013) for inventory calculations, along with residence time derived from the tracers, a mangrove contribution of 19% to the total DOC longitudinal flux to the Gulf of Mexico was obtained.

3.6 Distribution of carbon fluxes

During SharkTREx 1 and 2, $\sum[DIC]_{estuary}$ made up 20-28% of the total DIC in the rivers, and $\sum[DOC]_{estuary}$ made up only 4 to 7% of the total DOC in the rivers. Mangroves are estimated to contribute 13 to 19% to the total DIC inventory. In all cases, the mangrove contribution to the DIC inventory is a factor of 3 greater than the mangrove contribution to the DOC inventory (Table 1).

During SharkTREx 1 and 2, the inventory of mangrove-derived DIC exceeded that of DOC by a factor of 15 to 17, which supports the idea that a large fraction of the carbon exported by mangroves to surrounding water is as DIC (Bouillon et al., 2008a), but is considerably larger than the estimates of ca. 3 to 10 compiled by Bouillon et al. (2008a) for mangroves at 5 sites in Asia and Africa.

The total dissolved carbon fluxes from all sources (i.e., freshwater wetland, mangrove, carbonate dissolution, and marine input) out of the Shark and Harney Rivers during SharkTREx 1 and 2 are dominated by inorganic carbon (82-83%; see Tables 2 and 4), either via air-water CO$_2$ exchange or longitudinal flux of DIC to the coastal ocean (Fig. 5). The remaining 17-18% of the export is as DOC. This proportioning is remarkably similar between SharkTREx 1 and 2, and between the Shark and Harney Rivers (Table 1). The estuarine contribution to these fluxes is relatively small (generally <15%), with the exception of air-water CO$_2$ flux, where the estuary contribution was 49 to 63% (Table 4).

In this study, the particulate organic carbon (POC) flux was not examined. However, He et al. (2014) estimated the mangrove-derived POC flux in Shark River by taking the total volume discharge from the five major rivers along the southwest coast of Everglades National Park from 2004 to 2008, and assuming that Shark River contributed 14% to the mean annual discharge. They then multiplied this discharge by the average POM concentration...
(5.20 ± 0.614 mg L\(^{-1}\)) in the middle of the estuary to yield an annual POM flux from Shark River. Based on analysis of organic matter biomarkers, He et al. (2014) estimated that mangrove-derived POM was 70–90% of the total POM pool in the Shark River. Using this contribution and further assuming that 58% of POM weight is POC (Howard, 1965), they estimated a POC flux of 1.0 to 2.2 x 10^4 mol d\(^{-1}\). Because this estimate was based on biomarker and POM data from the mid-estuary, where the POM concentration and the mangrove contribution to POM are both likely to be much higher than either toward the freshwater end member or the marine end member, it is likely an overestimate of the mangrove derived POC flux. Nevertheless, the mangrove-derived POC flux determined by He et al. (2014) is still only a small fraction (3 to 7%) of the mangrove-derived dissolved carbon fluxes in Shark River during SharkTREx 1 and 2.

3.7 Mangrove contributing area and estuary carbon balance

One of the challenges of relating the results reported here to other studies is to scale the results to a mangrove contributing area, and thereby relate the findings to mangrove forest carbon balance, typically expressed on an aerial basis. Estimates of forest carbon export derived here are compared with other investigations in this estuary. The entire area of mangroves surrounding the Shark and Harney Rivers region is ca. 111 km\(^2\), and the water area is ca. 17.5 km\(^2\) (Ho et al., 2014). Scaling the forest area by the water area of Shark River (2.5 km\(^2\)) yields an associated forest area of 15.9 km\(^2\). The forest area associated with Harney River (2.8 km\(^2\)) is 17.4 km\(^2\).

Using the total forest area associated with Shark River to scale estimates of total export of mangrove-derived carbon (the combination of longitudinal fluxes and air-water gas exchange) suggests an average dissolved carbon lateral export rate from the forest of 18.9 to 24.5 mmol m\(^{-2}\) d\(^{-1}\), including both DIC and DOC. However, since it is unknown what fraction of the total forest area associated with these rivers exported dissolved carbon through tidal pumping (a function of tidal height and duration), this is considered to be a minimum estimate. Average water levels at high tide during SharkTREx 1 and 2 at the USGS Shark River station were 88% and 95% of maximum wet season water levels reported at this site over the period from November 2007 to December 2012 (U.S. Geological Survey, 2016), and 12 inundation events occurred during both SharkTREx 1 and 2. Water levels in the main river channel at the USGS Shark River station were above an estimate of the average minimum ground surface elevation derived from nearby groundwater monitoring wells in the estuary (sites SH3 and SH4; http://sofia.usgs.gov/eden/stationlist.php) for 21% and 28% of the time during the SharkTREx 1 and 2 experimental periods, respectively. These values indicate the export of dissolved carbon from flooded portions of the forest during the discontinuous inundation periods should be

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significantly greater than the dissolved carbon lateral export rate derived above in order to produce the observed inventories of mangrove-derived dissolved carbon in the main channel.

Bergamaschi et al. (2011) proposed an annual total DOC export from the forest surrounding Shark River of 15.1 ± 1.1 mol m⁻² y⁻¹ and describe their method of calculating contributing area using a model based on the relationship between discharge volume and changes in water levels during tidal cycles. They do not provide a contributing area, but this can be calculated from their results. They determined longitudinal DOC fluxes of 7.6 ± 0.5 x 10⁵ and 1.3 ± 0.02 x 10⁵ mol d⁻¹ for the wet and dry seasons, respectively, and assumed that they are entirely of mangrove origin. Given the lengths of the wet and dry seasons, this would yield a mean annual DOC flux of 3.9 ± 0.2 x 10⁵ mol d⁻¹, and 9.4 ± 0.7 km² of mangrove forest contributing to carbon fluxes thru tidal flushing in this segment of Shark River. However, data from SharkTREx 1 and 2 indicate that ca. 5% of the total longitudinal DOC fluxes were of mangrove origin, with an average mangrove-derived DIC to DOC flux ratio of 10.5. Using this information, the Bergamaschi et al. (2011) results were recalculated to yield a wet season dissolved carbon lateral export rate of 46.5 ± 4.4 mmol m⁻² d⁻¹ (as DIC and DOC) from the forest.

Another method of estimating forest lateral carbon export utilizes the difference between measurements of net ecosystem-atmosphere CO₂ exchange (NEE) above the mangrove forest surrounding Shark River (267 ± 15 mmol m⁻² y⁻¹ in 2004; Barr et al., 2012) and corresponding measures of net ecosystem carbon balance (NECB; 227 ± 14 mmol m⁻² d⁻¹). NECB in 2004 can be estimated as the sum of carbon in litter fall (104 ± 8 mmol m⁻² d⁻¹), wood production (44 ± 3 mmol m⁻² d⁻¹) (Castañeda-Moya et al., 2013), root growth (47 ± 11 mmol m⁻² d⁻¹) (Castañeda-Moya et al., 2011) and soil carbon accumulation (31.7 mmol m⁻² d⁻¹) (Breithaupt et al., 2014) measured at the same location (FCE LTER site SRS6) in this forest. The difference between NEE and NECB (40 ± 17 mmol m⁻² d⁻¹) provides an estimate of the annual rate of forest carbon export to Shark River on a daily basis (Chapin et al., 2006).

The rate of mangrove-derived carbon exported to estuarine waters is likely to vary over space and time, as a result of factors that include tidal cycles, phenology, and forest and soil structural characteristics. For example, Bergamaschi et al. (2011) found that DOC fluxes were 6 times higher during the wet season (September) than the dry season (April), whereas Cawley et al. (2013) found that the DOC fluxes were 4 and 10 times higher during the wet vs. dry season (November vs. March) in the Shark and Harney Rivers, respectively. Barr et al. (2013) showed that forest respiration rates derived from NEE data are greater during the wet than dry seasons. Higher respiration rates combined with increased inundation during the wet seasons suggest that wet season DIC export will also be
greater than dry season values. For these reasons, the annual carbon export rates derived from the difference between NECB and NEE are expected to underestimate wet season values. If annual lateral carbon export rates are considered equivalent to a time-weighted sum of dry season (7 months) and wet season (5 months) values (after Bergamaschi et al. 2011), and wet season export is assumed to be, for example, 5 times greater than dry season values, the seasonal export rates (15 and 75 mmol m\(^{-2}\) d\(^{-1}\) for dry and wet seasons, respectively) that correspond with the difference between annual NECB and NEE can be calculated.

The discrepancies between the estimates of carbon export rates derived here, and those derived from Bergamaschi et al. (2011) and the difference between NEE and NECB point out the need for additional studies to reduce the uncertainty in the relationships between riverine carbon fluxes, forest carbon export, and estimates of contributing areas. For example, Bergamaschi et al. (2011) conducted an Eulerian study at a single location in the middle of the estuary, where the mangrove influence might be higher than the Lagrangian study conducted during SharkTREx 1 and 2, which covered the entire estuary. Also, the estimate of forest carbon export based on the difference between NEE and NECB is from a single location along Shark River (at FCE LTER site SRS6), and may not be representative of the entire forest. Furthermore, forest lateral carbon export rates and contributing areas should be considered dynamic, varying over semi-diurnal time scales with the extent and duration of inundation during individual tidal cycles. The correct interpretation of a single, static value for contributing area such as derived above is therefore uncertain, since the tracer-based results represent an integration of carbon sources and sinks calculated over the water residence time and expressed on daily time scales. To improve understanding of how mangrove forest carbon balance and export influence riverine carbon inventories and fluxes to the Gulf of Mexico in this system, wet and dry season measurements over multiple years, information on the relationships between forest structure, productivity and lateral carbon export rates, and independent estimates of forest inundation area in relation to tidal height are needed.

4 Conclusions

The SharkTREx 1 and 2 studies are the first to provide estimates of longitudinal DIC export, air-water CO\(_2\) fluxes, and mangrove-derived DIC inputs for the Shark and Harney Rivers. The results show that air-water CO\(_2\) exchange and longitudinal DIC fluxes account for ca. 90% of the mangrove-derived dissolved carbon export out of the Shark and Harney Rivers, with the remainder being exported as dissolved organic carbon.
The mangrove contribution to the total longitudinal flux was 6.5 to 8.9% for DIC and 4 to 18% for DOC. A lower bound estimate of the dissolved carbon export (DIC and DOC) from the forest surrounding Shark River during the wet season was 18.9 to 24.5 mmol m⁻² d⁻¹ with 15.9 km² of mangrove contributing area. This basin-scale estimate is somewhat lower by comparison than other independent estimates of lateral carbon export from this mangrove forest. However, mangrove forest carbon export rates on an aerial basis are expected to vary with the spatial and temporal scales over which they are calculated, and depend on factors such as tidal inundation frequency, distance from the riverbank and the coast, and forest and soil characteristics.

Future experiments should investigate the contribution of DIC from groundwater to the rivers, by making measurements of δ¹³C of groundwater, Sr and Ca concentrations in the river to quantify CaCO₃ dissolution and to separate carbonate alkalinity from TALK, radon to quantify groundwater discharge, ¹⁴C to separate input of DIC from remineralization of organic matter from dissolution of CaCO₃. Experiments should also examine the seasonal variability in the carbon dynamics and export, by conducting process-based studies like SharkTREx during both wet and dry seasons. Also, time series measurement of current velocities, wind speeds, pCO₂ and pH (to calculate DIC), DO, chromophoric dissolved organic matter (CDOM, as a proxy for DOC), and radon will also allow the temporal variability of the sources and sinks of DIC in these rivers to be examined.

Author contribution
D. Ho, S. Ferron, and V. Engel conceived and executed the experiment, interpreted the data, and prepared the manuscript with input from the other authors. W. Anderson measured the samples for δ¹³C of dissolved organic carbon, P. Swart measured the samples for δ¹³C of dissolved inorganic carbon, R. Price measured the total alkalinity samples for SharkTREx 1, and L. Barbero measured the total alkalinity and dissolved inorganic carbon samples for SharkTREx 2.

Data availability
The pCO₂ data collected during SharkTREx 1 and 2 are available from the SOCAT database <www.socat.info>. The other data may be obtained by contacting the corresponding author.

Acknowledgments
We thank J. Barr, T. Custer, L. Larsen, M. Reid, and M. Vázquez-Rodriguez for assistance in the field, A. Arik, N. Coffineau and J. Harlay for assistance with data analysis, R. Wanninkhof and R. Zeebe for helpful discussions and comments, M. Sukop for the use of his laboratory, P. Sullivan for analyzing the total alkalinity samples during SharkTREx.
SharkTREx 1. K. Kotun and Everglades National Park provided boats, fuel, and logistical support for the experiment. Shark River flow velocity data were obtained from USGS via the National Water Information System. Funding was provided by National Park Service through the Critical Ecosystem Studies Initiative (Cooperative Agreement H5284-08-0029) and by National Science Foundation through the Water Sustainability and Climate solicitation (EAR 1038855). R.M.P. was supported by the Florida Coastal Everglades Long-Term Ecological Research program under National Science Foundation Grant Nos. DBI-0620409 and DEB-1237517. This is SERC contribution number ####. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.


Borges, A. V.: Do we have enough pieces of the jigsaw to integrate CO$_2$ fluxes in the coastal ocean?, Estuaries, 28, 3-27, 10.1007/BF02732750, 2005.


Table 1. Inventories of DIC and DOC in Shark and Harney Rivers, as well as contributions from estuarine and non-estuarine sources.

<table>
<thead>
<tr>
<th></th>
<th>SharkTREx 1</th>
<th>Shark River</th>
<th>SharkTREx 2</th>
<th>Harney River</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shark River</td>
<td>Harney River</td>
<td></td>
<td></td>
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<tr>
<td></td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>Inventory 1</td>
<td>Inventory 2</td>
<td>Inventory 1</td>
<td>Inventory 2</td>
</tr>
<tr>
<td></td>
<td>(x10^6 mol)</td>
<td>(x10^6 mol)</td>
<td>(x10^6 mol)</td>
<td>(x10^6 mol)</td>
</tr>
<tr>
<td><strong>DIC</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Observed</td>
<td>19.5 ± 0.9</td>
<td>15.2 ± 1.3</td>
<td>7.4 ± 0.4</td>
<td>-</td>
</tr>
<tr>
<td>Gas Exchange</td>
<td>2.5 ± 0.2</td>
<td>3.2 ± 0.1</td>
<td>1.5 ± 0.3</td>
<td>17%</td>
</tr>
<tr>
<td>Non-estuarine</td>
<td>17.6 ± 0.7</td>
<td>13.6 ± 1.2</td>
<td>6.5 ± 0.4</td>
<td>72%</td>
</tr>
<tr>
<td>Estuarine</td>
<td>4.4 ± 1.1</td>
<td>4.8 ± 1.8</td>
<td>2.5 ± 0.6</td>
<td>28%</td>
</tr>
<tr>
<td>Mangrove</td>
<td>2.9 ± 0.8</td>
<td>3.1 ± 1.2</td>
<td>1.7 ± 0.4</td>
<td>19%</td>
</tr>
<tr>
<td><strong>DOC</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Observed</td>
<td>4.4 ± 0.1</td>
<td>4.1 ± 0.4</td>
<td>1.9 ± 0.1</td>
<td>-</td>
</tr>
<tr>
<td>Non-estuarine</td>
<td>4.2 ± 0.1</td>
<td>3.9 ± 0.4</td>
<td>1.8 ± 0.1</td>
<td>93%</td>
</tr>
<tr>
<td>Estuarine</td>
<td>0.2 ± 0.1</td>
<td>0.2 ± 0.6</td>
<td>0.1 ± 0.2</td>
<td>7%</td>
</tr>
</tbody>
</table>

The uncertainty in the observed and non-estuarine inventories are the standard deviations of the inventories for all the days of the experiment. The estuarine contribution is calculated from the observed and non-estuarine contribution, and the uncertainty is from propagating the errors of the two. The uncertainty in contribution from gas exchange is from propagating the uncertainty in CO₂ flux and the residence time. The uncertainty in mangrove contribution is calculated from propagating the error from the estuarine contribution.

The DIC inventory is relative to the total DIC (i.e., ∑[DIC] observed + ∑[DIC] gas ex.).
Proportion of each form of carbon (i.e., DIC, DOC) relative to the total mangrove-derived carbon pool.

Proportion of each form of carbon (i.e., DIC, DOC) relative to the total carbon pool.

Estuarine DOC is assumed to be entirely of mangrove origin.
Table 2. Longitudinal DIC and DOC fluxes, and air-water CO$_2$ fluxes for the Shark and Harney Rivers during SharkTREx 1 and 2.

<table>
<thead>
<tr>
<th></th>
<th>SharkTREx 1</th>
<th>SharkTREx 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shark River</td>
<td>Harney River</td>
</tr>
<tr>
<td></td>
<td>Shark River</td>
<td>Harney River</td>
</tr>
<tr>
<td>Total Longitudinal DIC Fluxes (x 10$^5$ mol d$^{-1}$)</td>
<td>33.6 ± 1.6</td>
<td>N/A</td>
</tr>
<tr>
<td>Non-estuarine contribution</td>
<td>30.3 ± 1.1</td>
<td>N/A</td>
</tr>
<tr>
<td>Estuarine Contribution</td>
<td>3.3 ± 1.9</td>
<td>N/A</td>
</tr>
<tr>
<td>Mangrove Contribution</td>
<td>2.2 ± 1.3</td>
<td>N/A</td>
</tr>
<tr>
<td>Air-Water CO$_2$ Fluxes (x 10$^5$ mol d$^{-1}$)$^c$</td>
<td>4.2 ± 0.4</td>
<td>4.1 ± 0.2</td>
</tr>
<tr>
<td>Non-estuarine contribution</td>
<td>2.1 ± 0.2</td>
<td>2.0 ± 0.1</td>
</tr>
<tr>
<td>Estuarine Contribution</td>
<td>2.1 ± 0.4</td>
<td>2.1 ± 0.3</td>
</tr>
<tr>
<td>Mangrove Contribution</td>
<td>1.4 ± 0.3</td>
<td>1.4 ± 0.2</td>
</tr>
<tr>
<td>Total Longitudinal DOC Fluxes (x 10$^5$ mol d$^{-1}$)$^b$</td>
<td>7.5 ± 0.2</td>
<td>3.3 ± 0.4</td>
</tr>
<tr>
<td>Non-estuarine contribution</td>
<td>7.2 ± 0.1</td>
<td>2.6 ± 0.3</td>
</tr>
<tr>
<td>Estuarine Contribution $^d$</td>
<td>0.3 ± 0.2</td>
<td>0.6 ± 0.6</td>
</tr>
</tbody>
</table>

$^a$ Uncertainty in total and non-estuarine fluxes are from propagating the error in total inventory and the residence time. The uncertainty in the estuarine fluxes are from propagating the errors in total and non-estuarine fluxes. The uncertainty in mangrove contribution is from propagating the errors in the estuarine contribution.

$^b$ Data for DOC concentration in Harney River during SharkTREx 1 taken from Cawley et al. (2013).

$^c$ Estuarine contribution to DOC is assumed to be entirely of mangrove origin.
Table 3. Mangrove contribution to $\sum$ [DIC]$_{\text{estuary}}$ determined from $\delta^{13}$C$_{\text{DIC}}$ mass balance and TA/alk/DIC ratios.

<table>
<thead>
<tr>
<th>River</th>
<th>Experiment</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shark River</td>
<td>SharkTREx 1</td>
<td>60 ± 6% 70 ± 3%</td>
</tr>
<tr>
<td></td>
<td>SharkTREx 2</td>
<td>61 ± 6% 70 ± 3%</td>
</tr>
<tr>
<td>Harney River</td>
<td>SharkTREx 1</td>
<td>- -</td>
</tr>
<tr>
<td></td>
<td>SharkTREx 2</td>
<td>61 ± 6% 70 ± 2%</td>
</tr>
</tbody>
</table>
Table 4. Distribution of total and mangrove fluxes of DIC and DOC for Shark and Harney Rivers during SharkTREx 1 and 2.

<table>
<thead>
<tr>
<th>SharkTREx Experiment #</th>
<th>Estuarine Contribution</th>
<th>Percent of Total Export Flux</th>
<th>Percent of Total Mangrove Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shark River</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Longitudinal DIC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>10%</td>
<td>74%</td>
<td>57%</td>
</tr>
<tr>
<td>2</td>
<td>11%</td>
<td>67%</td>
<td>45%</td>
</tr>
<tr>
<td>Harney River</td>
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<td>2</td>
<td>13%</td>
<td>68%</td>
<td>48%</td>
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<tr>
<td>Air-Water CO\textsubscript{2} Flux</td>
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<td>Shark River</td>
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<td>1</td>
<td>49%</td>
<td>9%</td>
<td>35%</td>
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<tr>
<td>2</td>
<td>52%</td>
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<td>Harney River</td>
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<tr>
<td>2</td>
<td>63%</td>
<td>14%</td>
<td>43%</td>
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<tr>
<td>All DIC Fluxes</td>
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<tr>
<td>Shark River</td>
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<td>2</td>
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<td>Harney River</td>
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<td>2</td>
<td>82%</td>
<td>91%</td>
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</table>

\textsuperscript{a} Estuarine contribution to the individual fluxes in each river during each experiment

\textsuperscript{b} Flux as a percentage of the total dissolved carbon flux (i.e., longitudinal DIC, DOC and air-water CO\textsubscript{2} fluxes)

\textsuperscript{c} Flux as a percentage of the total mangrove-derived dissolved carbon flux (i.e., longitudinal DIC, DOC and air-water CO\textsubscript{2} fluxes)
Figure 1. Map of the study area near the southern tip of Florida, USA, showing locations of Shark River, Harney River, and Tarpon Bay. The blue circles indicate the locations where discrete samples were taken, and the black stars denote the USGS gaging stations on both rivers. The green areas in the inset are part of the largest contiguous mangrove forest in North America. Indicated in the inset are the boundaries of Everglades National Park.
Figure 2. Distributions of $pCO_2$ (a-d) and dissolved $O_2$ (e-h) along the salinity gradient in the Shark and Harney Rivers during the 2010 (SharkTREx 1) and 2011 (SharkTREx 2) campaigns. Different symbols represent measurements made on different days.
Figure 3. Distribution of TAlk (a-c), DIC (d-f), pH (g-i) and δ^{13}C_{DIC} (j-l) along the salinity gradient in the Shark and Harney Rivers during the 2010 (SharkTREx 1) and 2011 (SharkTREx 2) campaigns. During SharkTREx 1, TAlk and pH were measured at FIU, and DIC was calculated using CO2SYS (Pierrot et al., 2006). During SharkTREx 2, DIC and TAlk were measured at NOAA/AOML, and pH was calculated using CO2SYS. The dashed lines indicate the distribution expected for conservative mixing.
Figure 4. Distribution of DOC and $\delta^{13}$C$_{\text{DOC}}$ along the salinity gradient in the Shark and Harney Rivers in samples collected during SharkTREx 1 and 2. The dashed lines indicate the distribution expected for conservative mixing.
Figure 5. Diagrams showing the main DIC fluxes (in $10^5 \text{ mol d}^{-1}$) entering and exiting the Shark and Harney Rivers during SharkTREx 1 and 2. Fluxes from the freshwater marsh were assumed to be fluxes estimated from the conservative DIC curves.
Figure 6. (a) Covariation of DIC<sub>estuary</sub> and TAlk<sub>estuary</sub>. Black squares are samples from the Shark River during SharkTREx 1, and black and gray circles are from the Shark and Harney Rivers, respectively, during SharkTREx 2. Dotted lines represent the theoretical covariation of DIC and TAlk for different biogeochemical processes: 1) aerobic respiration; 2) CO<sub>2</sub> emission, 3) sulfate reduction, 4) CaCO<sub>3</sub> dissolution, 5) manganese reduction, and 6) iron reduction.