

Thank you to both Referees for providing specific and constructive comments. They have helped improve this manuscript. Below, we respond to each comment from **Referee #1**, **Referee #2**, and the **Associate Editor**, in that order. Reviewer comments are in [blue](#). Quoted manuscript text is in *italics*, with new additions in [green](#). A marked-up manuscript that shows all changes made since the original submission follows our response.

Referee #1

1. General Comments:

[I am not yet convinced that air-sea flux has been given full consideration. The relationship between DICex and air-sea flux is still unclear to me even after reading through the appendix.](#)

We have addressed specific comments below, but in general the relationship between air-sea flux and DICex is shown in section 3.5 (formerly section 4.1). We do not have our own atmospheric pCO₂ data, so are limited to weekly or longer temporal scales for the air-sea flux. We (now) show the air-sea flux is small on weekly time scales. It is almost always negative, so accumulates to a large effect on annual time scales. Because we do not have the spatial data to fully close a DIC budget, we can only infer that over the annual cycle, local biology plus advective effects must balance the air-sea flux.

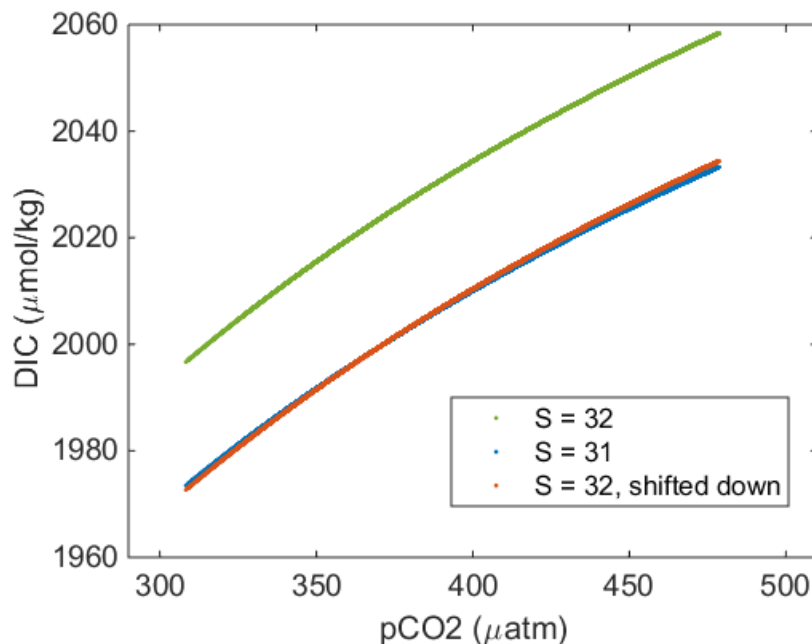
[With respect to data presentation, I recommend the abandonment of the rainbow colormap and the adoption of color schemes more true to the data and accessible to colorblind readers.](#)

Colormaps have been updated to perceptually uniform ones that are colorblind/greyscale friendly

2. Specific Comments:

- [• P3, l15: The tidally-estimated salinity has a much lower range than the measured salinity. How sensitive are your downstream calculations, especially DICex, to this reduction in variability in salinity and hence alkalinity?](#)

The salinity range has negligible effect on DICex because the DIC dependence on pCO₂ is effectively unchanged over our observed salinity range. In fact, we get nearly identical results if we just use a reasonable constant salinity. Below, the DIC dependence on pCO₂ for a fixed salinity is shown for S = 31 (blue) and S = 32 (green). There is an offset between the lines – this DIC dependence on salinity is exactly what is subtracted when we create the DICex variable – but the curvature is nearly identical. The orange line below is the S = 32 line shifted downward by a constant. The slight difference between blue and orange lines is the size of the error that remains if we use an estimated salinity value that is ~1 PSU different than the true value we were unable to measure. The CTD failure would have been much more problematic if we worked in an estuary with a large enough salinity range so substantially change the DIC-pCO₂ relationship. Alkalinity *does* depends strongly on salinity (unlike DICex), so we do not estimate alkalinity fluxes in Fig 7 for the period without salinity measurements.



- P3, I23 - 25: Alkalinity samples were taken only during the daytime. I presume they spanned the entire tidal range?

Yes, by sampling for 12 hours each day, the bottle samples covered a full tidal cycle on each of two sampling days, including high and low water times, and max ebb and flood.

- P4, I28 - 29: While the full equation is not necessary, it would be helpful to enumerate what measurements were used to calculate DIC and pH.

We have updated the text to specify measurements used for the calculation:

“DIC concentration and pH (Fig. 2d,e) for the carbonate system at equilibrium were calculated from measurements of pCO₂, salinity, alkalinity, and temperature, with constants following Dickson and Millero (1987) and Weiss (1974). We used van Heuven’s (2011) MATLAB code for Lewis and Wallace’s (1998) ‘CO₂SYs’ implementation of the equations for carbonate equilibria.”

- P5, I6 - 7 and Fig 2a, b: Generally, I would expect any gas to decrease in the summer and increase in the winter due to solubility. Is there something special about CO₂ that I am missing here?

pCO₂ increases with increasing temperature because Henry’s Law constant changes with temperature. Partial pressure is the atmospheric (headspace) CO₂ gas pressure with which the dissolved CO₂(aq) would be in equilibrium. Gas pressure increases with increasing temperature, so for a given dissolved CO₂ molar concentration, a higher equilibrium gas pressure (ie partial pressure) is required at a higher temperature. Takahashi et al., 2002 ([https://doi.org/10.1016/S0967-0645\(02\)00003-6](https://doi.org/10.1016/S0967-0645(02)00003-6)) is a good example of pCO₂ T-dependence. On the other hand, at a given pCO₂, the resulting equilibrium concentration of DIC will be higher at cold temperatures than at warm ones.

There is nothing special about CO₂ except perhaps that partial pressure is the common way to report it, while other gases like oxygen are more often reported as a concentration.

- P6, l6: Air-sea exchange is very difficult to calculate, especially in a dynamic system such as this one. How is it treated in CO₂SYS? Is it the Wanninkhoff parameterization shown in the discussion? Should the reader refer to the appendix at this point?

Air-sea flux is not a part of the CO₂SYS carbonate system equations. CO₂SYS calculates the thermodynamic equilibrium speciation of the seawater carbonate system. CO₂SYS does not compute transport processes.

Yes, the Wanninkhof parameterization is cited and reproduced as our equations 4 & 5 in section 3.5 (formerly numbered section 4.1). In section 3.2, we have added a reference to Section 3.5, where the calculation of Δ DIC resulting from air-sea flux is shown.

“DICex is presumed to be predominantly biogeochemically driven, but also includes any changes in DIC due to air-sea exchange, which we could not calculate on short time scales, but are shown to be small on daily time scales in section 3.5.”

We calculate the fluxes hourly to capture the quadratic relationship between wind speed and gas flux, but must average the hourly fluxes on weekly (or longer) time scales for them to be accurate because that is the time-resolution of the NOAA atmospheric pCO₂ data product. The Wanninkhof flux formula depends linearly on Δ pCO₂, so the weekly average of our estimate should be correct. Because of this data limitation, we do not attempt to assess air-sea flux at daily or tidal time scales. We have updated section 3.5 (formerly 4.1) to include the typical weekly Δ DIC change owing to air-sea flux to emphasize its small effect on DIC on short time scales, and clarify our justification of attributing high frequency changes in DIC to biological processes.

“The weekly averaged flux is typically between 0 and $-1\text{e-}7$ mol/m²/s which is equivalent to up to -2 umol/kg change in DICex change over a week. The maximum weekly value occurred in late September 2015, and was $-2\text{e-}7$ mol/m²/s yielding a -4 umol/kg change in DICex in one week.”

- P6 l14 - 21: There seems to be abrupt changes in the nature of the DICex data around days 265 and 290. Any explanations?

We don't know for sure, but there are several factors that may have contributed. The low value at day 265 doesn't appear to be related to any weather event and appears to follow the fortnightly beating pattern. The steady decrease in DICex from days 273-290, and subsequent rise may be related to a regional fall bloom. Our site is never stratified, but a bloom could have been triggered on the nearby shelf by a moderate wind event on day 273. This is also the time of year when water temperature transitions from rising to declining and reduced temperature variability (Fig 2b). Unfortunately the region was often cloudy so satellite-based chlorophyll estimates do not show these rapid transitions.

- P6 l26 - 28 and Fig 5: In addition to the 24-hr and M2, there are two peaks. From the x-scale, it is difficult to tell whether they are important or merely harmonics of the predominant frequencies.

Yes, these additional 2 peaks are harmonics of the 24h and M2 frequencies. They are an order of magnitude smaller than the primary peaks so do not substantially contribute to the total signal variance. We have noted this in the text:

“These February and August examples show a large daily peak and a slightly smaller M2 tidal peak for both months, and show that DICex is more variable in August than February at all frequencies. The third and fourth peaks visible in Fig. 5a are harmonics of the 24h and M2 frequencies and do not substantially contribute to the total signal variance. The variance of DICex at the 24 h and M2 frequencies are calculated from the area under the spectra...”

- P7 I19: By “lower growth,” do you mean lower primary production or photosynthesis? Growth can also be heterotrophic.

DIC only reflects net community productivity and so we cannot distinguish lower photosynthesis versus higher respiration. We have updated the sentence to use “lower net community production.”

- P7 I24 - P8 I10: Provide units of the variables given to aid dimensional analysis.

We have added units each time a variable is introduced in section 3.4: q (m^2s^{-1}), u (m s^{-1}), h (m), S (mol m^{-3} or g m^{-3}), Q ($\text{mol m}^{-1}\text{s}^{-1}$ or $\text{g m}^{-1}\text{s}^{-1}$), M (m^3 , mol , or g)

- P9 I27 - 29: Did you finish your thought here? Do you have an estimate of advection? There’s no period.

Thank you, the period was missing after DICex at the end of line 29. We cannot quantitatively estimate advection’s contribution to the local DIC budget because we do not have data on the along-channel gradient of DIC. We only feel comfortable inferring the sign of the gradient from the single-point time series data and the purpose is to constrain our discussion of the DIC budget. This very short section (4.2) has been merged with section 4.3 (DIC budget discussion) and the merged section is now numbered 3.6. The paragraphs are rearranged, but the text is unchanged.

- P12 I7: Given the spatial variability in pCO_2 , S , and T , can you assume spatially-uniform air-sea flux?

Over some small area, yes. We assume yes for the purpose of simplifying the equation, and then can decide how broadly we can apply our simplified system. We think this is a reasonable assumption within Grand Passage, where the water is well mixed vertically and laterally. We would love to be able to assess these parameter across the entire Bay of Fundy, but more spatial data is needed and, for this reason, we only include back-of-the-envelope type budget approximations in the discussion section of the paper.

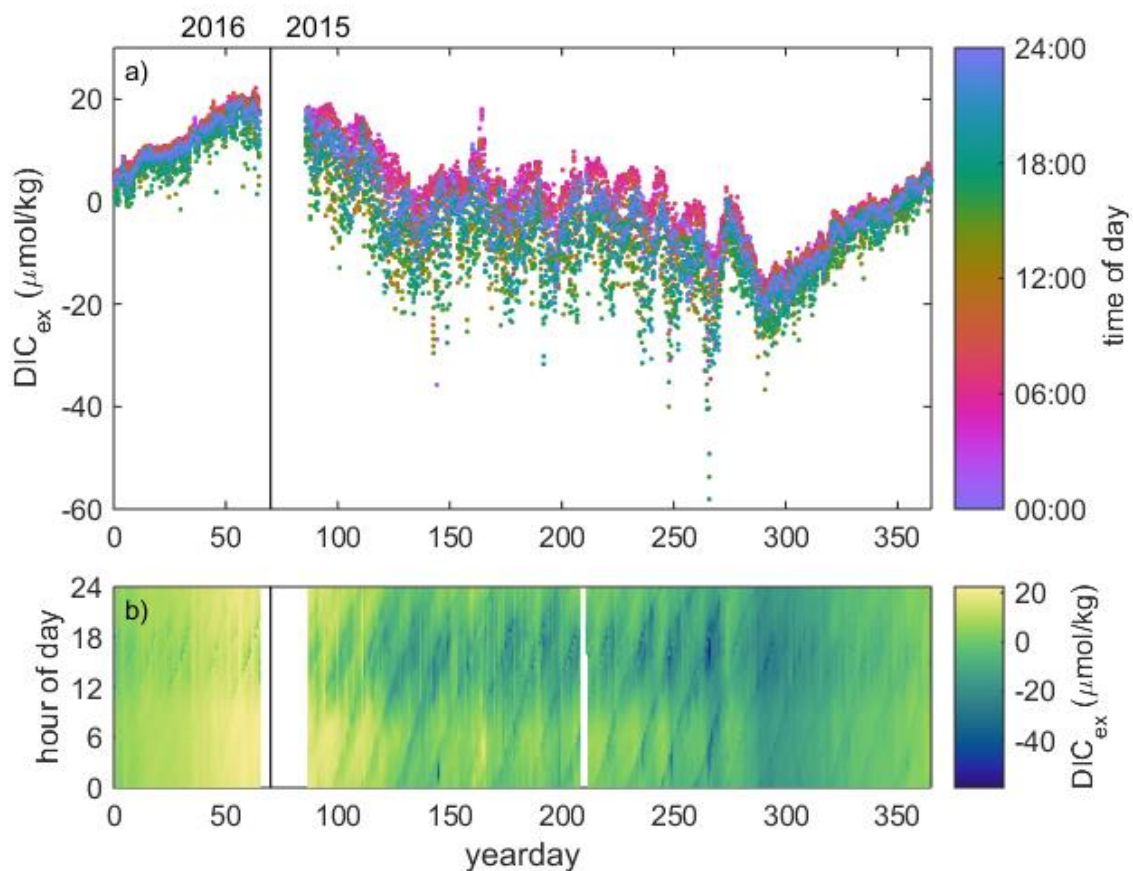
- Fig 3: There is a tail of low DIC in the tidally-predicted salinity points. Are these anomalous?

This is the event on Day 265 that you asked about earlier. As far as we know it’s real, and is a result of a real, low pCO_2 measurement on that day. It’s the only time mid-year that the measured pCO_2 value dips below the atmospheric value (blue spike below yellow line in late September, Fig 2a).

- Fig 4: I appreciate how differently a) and b) portray the exact same data. I would recommend not using a rainbow colormap for 4a. It is good that it wraps around, but the data are not represented linearly (green spans 6 hours) and it is not accessible for readers who are colorblind. Take a look at other cyclic color maps. I understand why you might want to put the winter 2016 data at the front of the figure, but

there is nothing significant about January 1st with respect to solar or lunar cycles. It's better to arrange the data chronologically and smoothly.

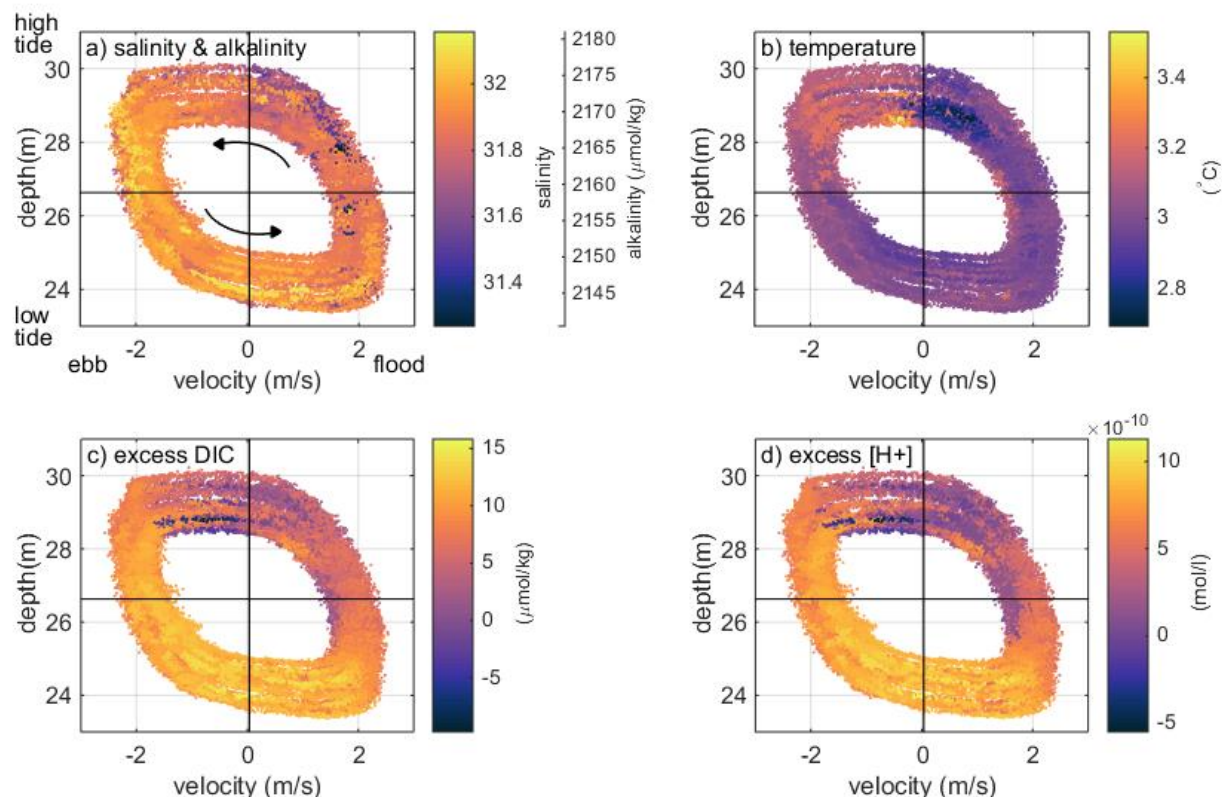
Fig 4a has been changed to a perceptually uniform, cyclic colormap based on the “phase” colormap (*cmocean* package, Thyng et al, Oceanography, 2016). Fig 4b has also been changed to the perceptually uniform “haline” *cmocean* colormap. Both colormaps are accessible to those with moderate red-green colorblindness and haline works in greyscale. We understand that a Jan 1 start to the year is not specifically related to tidal, daily, or annual biogeochemical cycles, but we choose that start because it is the conventional way of viewing a year and also highlights what fraction of a full annual cycle we missed with our deployment/recovery dates, and the close match of the start and end DIC_{ex} values even though the pCO₂ was quite different on account of warmer water that spring (shown & explained w/ Fig 2).



- Fig 6: These plots are extremely informative, but again, rainbow colormaps are ineffective at communicating data. For a) and b), use the parula colormap used in Fig 4b. For c) and d), try a diverging map (blue - white - red, for example).

The colormap has been switched to the perceptually uniform “thermal” *cmocean* colormap. We do not use a diverging colormap for (c) or (d) because the zero value is not meaningful. We use the same

colormap for all four subfigures to aid the reader in viewing the differences in how the four water properties vary around the tidal cycle.



3. Technical Corrections:

- P2, l1: Transpose “of” and “understanding.” Fixed.

- P2, l20: Remove the redundant “of.” Fixed.

- P3, l5 - 11: Descriptions of sampling frequency alternate between s and Hz. Choose one for consistency.

We switched sampling “at 1 Hz” to “every 1 s”, and also at the end of section 2.1, switched “frequency of 0.003 Hz” to “period of 5 min”

- P4, l3 - 4: Double check this link. I got a 404 error.

This link works for me without an error. However, it did point to the main page for weather station, which required an extra click to get to the hourly data. The link has been updated to point directly to the hourly data type we used, and I will check with the editor to make sure a functional link is published.
http://climate.weather.gc.ca/climate_data/hourly_data_e.html?StationID=10859

- P4, l18 - 19: Generally the past tense is preferred here. Feel free to use the first person. Fixed.

- P5, l17: Eliminate the space in “relation ship.” Fixed.

- P5, 19 - 20: These two sentences make it sound as if air-sea flux was a biological process.

We have rewritten these sentences as

"The in situ pCO₂ value is important because it determines the air-sea flux of CO₂, but is not an ideal variable to assess biogeochemical carbonate dynamics because of its dependence on temperature and alkalinity, which obfuscate the biological processes."

- P5, 130: What software is used to run CO2SYS?

We used the MATLAB version. This info has been added next to the citation for the code in the Calculating DIC methods section 2.5:

"DIC concentration and pH (Fig. 2d,e) for the carbonate system at equilibrium were calculated from measurements of pCO₂, salinity, alkalinity, and temperature, with constants following Dickson and Millero (1987) and Weiss (1974). We used van Heuven's (2011) MATLAB code for Lewis and Wallace's (1998) 'CO2SYS' implementation of the equations for carbonate equilibria."

- P7, 19 - 12: Use past tense. While the measurements occurred in the past, we presume the findings hold presently.

- Fig 6a: Should axis should read "Salinity" rather than "salt?" Fixed. Also 'alk' is now written fully as alkalinity

Referee #2

Overall structure:

I suggest to include a short paragraph that characterizes the hydrography of the Bay of Fundy. Readers outside of North America may not be familiar with the hydrographic biogeochemical conditions in that region.

We have added a new paragraph to the introduction:

“The Bay of Fundy (Fig. 1, inset) is an approximately 200 km long, 50 km wide, 75 m deep bay that extends northeastward into Canada from the Gulf of Maine in the Northwest Atlantic Ocean. The regional circulation flows southward along the Scotian Shelf as the Nova Scotia Current, follows the coastline around southern Nova Scotia to enter the southern side of the Bay of Fundy, and exits the bay along the northern coast to join the Eastern Maine Coastal Current in the Gulf of Maine (Bigelow, 1927; Greenberg, 1983; Hannah et al., 2001; Pettigrew et al., 2005; Dever et al., 2016). The mean circulation and water properties of the Gulf of Maine and the Nova Scotia Current are well described (e.g. Smith, 1989; Smith et al., 2001; Hannah et al., 2001; Houghton and Fairbanks, 2001; Aretxabaleta et al., 2008; Gledhill et al., 2015; Dever et al., 2016). Within the bay the mean flow recirculates cyclonically around the outer Bay of Fundy (Aretxabaleta et al., 2008). The geometry of the basin makes it resonant with the M2 tidal frequency and generates the highest tidal range in the world, over 16 m at the head of the bay (Garrett, 1972; Greenberg, 1983). Turbulence from the fast tidal flows keeps much of the basin well-mixed, while the deeper regions of the outer bay develop seasonal stratification. The largest freshwater source to the bay is the St. John River, on the northern coast, so owing to river plume dynamics and the general circulation of the region, this river water primarily propagates along the northern coast, into the Gulf of Maine.”

The “Discussion” contains two rather short sections (4.2 and 4.3). My suggestion is to merge these with “Results” which is then named “Results and Discussion”.

We have followed your suggestion. The former section 4.1 (air-sea flux) is now sections 3.5. We have combined the two very short sections (4.2, 4.3) into a single one (3.6), now titled *“Consideration of the local DIC budget”* to emphasize that this section is a qualitative discussion rather than quantitative result.

The CO₂ flux estimate (4.1) is of no relevance for the science in your manuscript. To satisfy those who are always hunting for such numbers, move it to the Appendix.

We understand your point that the air-sea flux is not directly needed for our result about tidal cycles. However, air-sea flux is needed to justify that most DIC_{ex} variation is due to biology, and leads towards a better understanding of the local carbon budget, even though we cannot entirely close the budget with the existing data set. Therefore, we have chosen to keep it in the body of the manuscript.

We have added two sentences to the beginning of section 3.5 (formerly 4.1) to explain the purpose of the section:

“High-frequency variability in DIC_{ex} is assumed to be driven by biological and biogeochemical processes, but air-sea flux plays a significant role on long time scales. We assess the importance of air-sea flux to the carbon budget by calculating weekly and annual fluxes, and the equivalent changes in DIC.”

Comments:

2.1 Time series measurements: The pCO₂ measurements are the basis of your study. Therefore it is necessary to give some more information about the measuring principle, precision/accuracy, response time, calibration procedure, etc. .What is meant with “flushing”?

We have updated section 2.1 to include more information about the instrument and the zeroing and re-equilibration period. We removed the term “flushing”

“The primary instrument for this experiment was a CONTROS HydroC CO₂ sensor, which uses non-dispersive infrared spectrometry (NDIR) to measure gas concentrations that have equilibrated across a hydrophobic membrane. The HydroC was calibrated by the manufacturer before and after deployment and has a resolution of <1 μatm, an accuracy of ±1%, and a response time of 65 s at 15 °C and 70 s at 5 °C. All field measurements fell within the calibrated measurement range of 200 - 1000 μatm. The HydroC was mounted 1 m above the sea floor and cabled to shore for continuous power and data transfer. It recorded pCO₂ every 1 s from March 2015 to April 2016. The instrument was zeroed every 64 minutes until 16 June 2015, and every 735 minutes for the remainder of the experiment. During zeroing the gas stream is isolated from the membrane and CO₂ is removed. Zero-channel values indicate no sensor drift over the deployment period. Following zeroing, partial pressure re-equilibrated over roughly one hour and data from these periods were omitted from analyses.”

2.4 Estimating alkalinity from salinity, p.4/line 23 “Grand passage measurements are not expected . . .”, unclear sentence, one can only guess what the meaning is. Has the intercept any biogeochemical meaning?

This sentence has been updated for clarity

“The Grand Passage salinity-alkalinity relationship was not a priori expected to be identical to the data collected 10 to 200 km offshore in the Scotian Shelf and Gulf of Maine regions, but Fig. 2f shows there is no significant change in the water mass end members between those regions, which are up- and downstream of Grand Passage in the regional circulation pattern.”

The y-intercept of the linear fit, 710 μmol/kg, represents the alkalinity of the (average) freshwater endmember.

2.5 Calculating DIC, p.4/last line: The “system of equations” is not created by Lewis and Wallace (1998), but represents the well-known thermodynamics of acid-base equilibria. Ko from Weiss (1974)?

The text has been update following your suggestion. Yes, Weiss (1974) is used by van Heuven’s (2011). *“DIC concentration and pH (Fig. 2d,e) for the carbonate system at equilibrium were calculated from measurements of pCO₂, salinity, alkalinity, and temperature, with constants following Dickson and Millero (1987) and Weiss (1974). We used van Heuven’s (2011) MATLAB code for Lewis and Wallace’s (1998) ‘CO₂SYs’ implementation of the equations for carbonate equilibria.”*

3.1 Seasonal evolution of measured and equilibrium solution variables “equilibrium solution variables”, bad term in the headline.

Section title changed to “Seasonal evolution of carbonate system variables”

p. 5/line 17: Tidal alkalinity variation of 718 μmol/kg???

Thank you very much for catching this typo. The correct value of 8.24 $\mu\text{mol/kg}$ has been added to the revised manuscript.

p.5/last paragraph: How are the first two sentences logically related to each other? DIC is a conservative variable and does not depend on temperature. The observed DIC decrease refers to different water masses, it is therefore not allowed to make any conclusions about effect of “photosynthesis and respiration”. Such changes occur on a background DIC level which is directly related to the alkalinity. In order to identify any biogeochemical DIC changes, it is thus necessary to remove the effect of the differing back-ground DIC as you have done it by calculating DIC_{ex}.

We have reworded the first 2 sentences to make a better transition from discussion pCO₂ to DIC. We got a little ahead of ourselves, knowing what the DIC_{ex} results showed later and have deleted the text.

“The in situ pCO₂ value is important because it determines the air-sea flux of CO₂, but is not an ideal variable to assess biogeochemical carbonate dynamics because of its dependence on temperature and alkalinity, which obfuscate the biological processes. DIC (Fig. 2d) does not have a strong temperature dependence so it better depicts the biological DIC variation. DIC declines steeply during the spring bloom, and then increases through the winter. ~~The cumulative seasonal effect of photosynthesis and respiration are evident.~~ During the spring bloom and throughout the summer there is a large daily range in DIC. In October, daily variability shrinks, and DIC increases steadily throughout the winter. pH varies as an approximate inverse of pCO₂. pH has an average value of 8.01 (= -log₁₀ < [H⁺] >) and daily and M2 variation are equivalent to changes in pH of 8 to 8.03 and 8 to 8.01, respectively.”

3.2 Unravelling daily and tidal cycles of biogeochemical driven changes in DIC
Subscript “mix” is somewhat misleading, I prefer to call it “background DIC”.

We understand the point – that we call “mix” includes both a constant background value that is not attributed to any particular process, as well as the component correlated to salinity. We think it would be confusing to call it “background” when it varies in time owing to a known process, so we prefer “mix”. We considered further dividing the “mix” term into a constant background value plus a zero-mean salinity-dependent variable, but decided adding an extra term would unnecessarily complicate this simple equation.

We have updated the text to further clarify that our DIC_{ex} includes a background value in addition to the linear salinity dependence:

“The DIC dependence on salinity and alkalinity, DIC_{mix}, is estimated numerically with CO₂SYS using fixed values of pCO₂ and temperature. DIC_{mix} includes both a salinity-dependent component and a background constant that depends on pCO₂ and temperature. The mean pCO₂, 446 μatm , and temperature, 8°C, for the deployment period are chosen for the calculation. DIC_{ex} is calculated by subtracting DIC_{mix} from the full (observed) DIC, DIC_{obs} (Fig. 3).”

Please make clear that the zero level in Fig. 4 has no biogeochemical meaning since it depends on the choice of the reference pCO₂. You could have taken also the atmospheric pCO₂ and spring SST as reference because in many ocean regions the spring bloom starts when the surface water is approximately at equilibrium with the atmosphere. In that case the zero DIC_{ex} means “zero” biology.

We have rearranged the paragraph following Eq 2 to lead with this fact (former first sentence was moved above Eq 2) and emphasize that the mean DIC_{ex} value is not meaningful, rather than just as a justification for our results not being sensitive to our choice of pCO₂, T.

“Only the time-variation of the resulting DIC_{ex} is meaningful, not the absolute value. This time-variation is not sensitive to the choice of fixed pCO₂ and temperature from within the ranges typical of this field site. The relationship between pCO₂ and DIC that is captured in DIC_{ex} is unchanged over the small natural range of alkalinity in this region...”

p.6/2nd paragraph: Your interpretation of the seasonal DIC_{ex} pattern is confined to biological effects and ignores the effect of gas exchange. Can you roughly estimate the relative importance of the two processes?

We have estimated the air-sea flux and the equivalent change in DIC in section 3.5 (formerly section 4.1). In the original submission, we only included the annual value. We have now added the weekly change in DIC owing to air-sea flux as well. We cannot estimate the flux and resulting Δ DIC accurately on shorter time scales because the atmospheric pCO₂ data available from NOAA is only weekly.

In section 3.2 we have added

“DIC_{ex} is presumed to be predominantly biogeochemically driven, but also includes any changes in DIC due to air-sea exchange, which we could not calculate on daily time scales, but are shown to be small on weekly time scales in section 3.5.”

And in section 3.5 we have added

“The weekly averaged flux is typically between 0 and $-1\text{e-}7 \text{ mol/m}^2/\text{s}$ which is equivalent to up to -2 umol/kg change in DIC_{ex} change over a week. The maximum weekly value occurred in late September 2015, and was $-2\text{e-}7 \text{ mol/m}^2/\text{s}$ yielding a -4 umol/kg change in DIC_{ex} in one week.”

Your question specifically mentioned the seasonal cycle, though this section (3.2) is focused on the daily and tidal time scales. The air-sea flux is small on the short time scales, but makes a cumulative change in DIC_{ex} of -47 umol/kg over the entire year (given in section 3.5). Because the observed DIC_{ex} returns to near its initial value after a full year, we infer that the biology makes the opposite contribution, putting 47 umol/kg of DIC into the water over the year. However, from this data set, we cannot determine if the long term trend in DIC_{bio} is due to advection or local biology, as discussed in section 3.6 (formerly 4.3)

3.3 Tidal phasing The calculation of H⁺_{ex} makes no sense because H⁺ is a nonconservative variable and does follow conservation of mass. This is also reflected in a strong dependency of Δ H⁺/ Δ T_A and thus of H⁺_{ex} on the choice of the reference pCO₂.

We use [H⁺]_{ex} where we would have shown pH variation around a tidal period in Fig 6d because it does not make sense to do frequency-base filtering on the time series of a logarithmic variable, nor does it make sense to convert the tidal variation in [H⁺]_{ex} back into a pH range because the range would depend on the mean.

While protons (mass) are conserved, can be transported, and could be balanced at a constant temperature, we understand that forecasting changes in proton concentration from a proton transport would depend on changes/differences in buffering capacity.

Associate Editor

During your revisions, I will have to see more information about maintenance and validation of the pCO₂ sensor during the deployment of the present study since these are the foundation of your paper.

We have followed the internationally recommended procedure of having manufacturer calibration performed before and after deployment (Pereira et al., 2017, full citation below). Calibration by the user is not possible for this instrument. As recommended by the manufacturer, the zero-channel values were used to check for sensor drift and we found no significant drift over the deployment period (drift substantially less than the 1% measurement accuracy for seawater pCO₂ values).

Text in bold below has been added since the Author's Response to Reviewers to further clarify the instrument performance expectations. We have revised the text in section 2.1:

*"The primary instrument for this experiment was a CONTROS HydroC CO₂ sensor, which uses non-dispersive infrared spectrometry (NDIR) to measure gas concentrations that have equilibrated across a hydrophobic membrane. The HydroC was calibrated by the manufacturer **before and after** deployment and has a resolution of <1 µatm, an accuracy of ±1%, and a response time of 65 s at 15 °C and 70 s at 5 °C. **All field measurements fell within the calibrated measurement range of 200 - 1000 µatm.** The HydroC was mounted 1 m above the sea floor and cabled to shore for continuous power and data transfer. It recorded pCO₂ every 1 s from March 2015 to April 2016. The instrument was **zeroed** every 64 minutes until 16 June 2015, and every 735 minutes for the remainder of the experiment. **During zeroing the gas stream is isolated from the membrane and CO₂ is removed. Zero-channel values indicate no sensor drift over the deployment period.** Following zeroing, partial pressure re-equilibrated over roughly one hour and data from these periods were omitted from analyses."*

Full citation: Pereira, E., U. Schuster, V. Rérolle, P. Brown, T. Gkritzalis, B. Downing, K. Simpson, C. Lønborg, G. Carlin, S. Aßmann, and R. Spaulding, 2017: Biogeochemical Parameters: pCO₂. In: A user's guide for selected autonomous biogeochemical sensors. An outcome from the 1st IOCCP International Sensors Summer Course [Lorenzoni, L., M. Telszewski, H. Benway, A. P. Palacz (eds.)]. IOCCP Report No. 2/2017, pp. 31-42.

High-frequency variability of CO₂ in Grand Passage, Bay of Fundy, Nova Scotia

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Abstract. Assessing changes in the marine carbon cycle arising from anthropogenic CO₂ emissions requires a detailed understanding of the carbonate system's natural variability. Coastal ecosystems vary over short spatial and temporal scales, so their dynamics are not well-described by long-term and broad regional averages. A year-long time series of *p*CO₂, temperature, salinity, and currents is used to quantify the high-frequency variability of the carbonate system at the mouth of the Bay of Fundy, Nova Scotia. The seasonal cycle of *p*CO₂ is modulated by a diel cycle that is larger in summer than in winter, and a tidal contribution that is primarily M2, with amplitude roughly half that of the diel cycle throughout the year. The interaction between tidal currents and carbonate system variables leads to lateral transport by tidal pumping, which moves alkalinity and DIC out of the bay, opposite to the mean flow in the region, and constitutes a new feature of how this strongly tidal region connects to the larger Gulf of Maine and Northwest Atlantic carbon system. These results suggest that tidal pumping could substantially modulate the coastal ocean's response to global ocean acidification in any region with large tides and spatial variation in biological activity, requiring that high-frequency variability be accounted for in assessments of carbon budgets of coastal regions.

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1 Introduction

Oceanic uptake of anthropogenic carbon dioxide (CO₂) moderates the rise of atmospheric CO₂ concentrations and leads to changes in the ocean carbon cycle. CO₂ uptake acidifies the oceans, potentially altering ecosystems and leading to adverse effects for the societies and industries that depend on them. Assessing the vulnerability of these resources to long-term change in ocean acidification requires a detailed understanding of the carbonate system's natural variability that any anthropogenic trend may add to or alter. Coastal ecosystems vary on shorter temporal and spatial scales than the shelf or open ocean so predicting

how they may change under future climate scenarios is more difficult, and requires an ~~of understanding~~ understanding of the system's high-frequency components.

The Bay of Fundy (Fig. 1, inset) is an approximately 200 km long, 50 km wide, 75 m deep bay that extends northeastward into Canada from the Gulf of Maine in the Northwest Atlantic Ocean. The regional circulation flows southward along the Scotian Shelf as the Nova Scotia Current, follows the coastline around southern Nova Scotia to enter the southern side of the Bay of Fundy, and exits the bay along the northern coast to join the Eastern Maine Coastal Current in the Gulf of Maine (Bigelow, 1927; Greenberg, 1983; Hannah et al., 2001; Pettigrew et al., 2005; Dever et al., 2016). The mean circulation and water properties of the Gulf of Maine and the Nova Scotia Current are well described (e.g. Smith, 1989; Smith et al., 2001; Hannah et al., 2001). Within the bay the mean flow recirculates cyclonically around the outer Bay of Fundy (Aretxabaleta et al., 2008). The geometry of the basin makes it resonant with the M2 tidal frequency and generates the highest tidal range in the world, over 16 m at the head of the bay (Garrett, 1972; Greenberg, 1983). Turbulence from the fast tidal flows keeps much of the basin well-mixed, while the deeper regions of the outer bay develop seasonal stratification. The largest freshwater source to the bay is the St. John River, on the northern coast, so owing to river plume dynamics and the general circulation of the region, this river water primarily propagates along the northern coast, into the Gulf of Maine.

Seasonal and inter-annual variability in air-sea CO₂ flux, along with the key carbon cycling processes, have been documented both upstream from the Bay of Fundy on the Scotian Shelf (e.g. Shadwick et al., 2010, 2011; Thomas et al., 2012; Craig et al., 2015), and downstream in the Gulf of Maine (Salisbury et al., 2009; Vandemark et al., 2011), and the mean circulation and water properties of the Gulf of Maine and the Nova Scotia current – the ocean source waters for the Bay of Fundy – are well described (e.g. Smith, 1989; Smith et al., 2001; Hannah et al., 2001; Houghton and Fairbanks, 2001; Aretxabaleta et al., 2008; Gledhill et al., 2015). Within the bay, salt marshes have been shown to be weak emitters of CO₂ to the atmosphere (Magenheimer et al., 1996), but these results might not be representative of fully submerged regions. Basin-wide estimates of CO₂ fluxes have come as part of larger-scale coastal studies where the Bay of Fundy is included as part of the Gulf of Maine region. Using historical *p*CO₂ data and satellite algorithms, Signorini et al. (2013) identified the Gulf of Maine as a weak source of CO₂ to the atmosphere. In contrast, results from a coupled biogeochemical-circulation model indicate the Gulf of Maine to be a relatively strong sink of CO₂ compared to surrounding areas (Cahill et al., 2016).

The coastal carbon budget and thus the rate at which alkalinity will be able to buffer future ocean acidification depend on the exchange processes between coastal and open oceans. In shallow marshy estuaries, tidal budgets have been estimated for oxygen from dissolved oxygen measurements (Nidzieko et al., 2014) and for carbon from a linear model based on pH and oxidation-reduction potential (Wang et al., 2016). However, to the best of our knowledge, the tidal transport of carbon in this macrotidal system, or far from large freshwater or nutrient sources, has never been addressed.

To investigate this issue, a year-long, high-frequency time series of ~~of~~ *p*CO₂, temperature, salinity, and currents was measured via a cabled-to-shore platform in Grand Passage, a tidal channel at the mouth of the Bay of Fundy, Nova Scotia (Fig. 1). This location is ideal for tracing the main input of water into the Bay from the Scotian Shelf. We quantify carbonate system variability on hourly to seasonal timescales, unravel the interaction between the daily and tidal cycles, determine the phase

relationship between tidal currents and carbonate system variables, and estimate lateral transports by tidal pumping, which moves alkalinity and dissolved inorganic carbon (DIC) out of the bay, opposite to the mean flow in the region.

2 Measurements and data processing

Grand Passage is narrow passage (1 km wide, 4 km long) separating Brier Island from Long Island at the end of the Digby Neck peninsula, which juts out into the mouth of the Bay of Fundy from the southwest corner of Nova Scotia (Fig. 1, inset). The tidal range is 5 to 6 m and peak tidal velocities range from 2 to 3 m s⁻¹.

2.1 Time series measurements

A year-long record of high-frequency measurements of *p*CO₂ (Fig. 2a), temperature (Fig. 2b), and pressure, four months of salinity (Fig. 2c), and one month of velocity data were collected via a cabled-to-shore observatory on a bottom frame that was deployed in approximately 10.5 m mean water depth (location indicated on Fig. 1).

The primary instrument for this experiment was a CONTROS HydroC CO₂ sensor, which uses non-dispersive infrared spectrometry (NDIR) to measure gas concentrations that have equilibrated across a hydrophobic membrane. The HydroC was calibrated by the manufacturer before and after deployment and has a resolution of < 1 μatm, an accuracy of ±1%, and a response time of 65 s at 15° C and 70 s at 5° C. All field measurements fell within the calibrated measurement range of 200 - 1000 μatm. The HydroC was mounted 1 m above the sea floor ~~-.The HydroC was-and~~ cabled to shore for continuous power and data transfer~~,-and it-. It~~ recorded *p*CO₂ at every 1 s from March 2015 to April 2016. The instrument was ~~flushed for calibration-zeroed~~ every 64 minutes until 16 June 2015, and every 735 minutes for the remainder of the experiment. ~~Following flushing~~During zeroing the gas stream is isolated from the membrane and CO₂ is removed. Zero-channel values indicate no sensor drift over the deployment period. Following zeroing, partial pressure re-equilibrated ~~across the semi-permeable membrane~~ over roughly one hour and data from these periods were omitted from analyses.

A CTD was collocated with the HydroC and recorded salinity, temperature, and pressure data every 30 s from March through July 2015. The CTD was recovered and redeployed to record data every 60 s until April 2016. The conductivity sensor bio-fouled soon after redeployment so only temperature and pressure are available for the second half of the experiment.

Salinity measurements were despiked and a linear drift of 0.41 over the first deployment period was removed. The drift was determined by matching the final measured tidal cycle to the initial tidal cycle values from the redeployment of the CTD on the following day (prefouling). Salinity was estimated for the remainder of the year using tidal harmonic analysis (Pawlowicz et al., 2002; Codiga, 2011) of the available four months of data. Salinity variation at frequencies lower or higher than the tidal harmonics is absent from the latter part of the data set, but do not change the final results of this work because the direct effect of salinity and alkalinity (Sect. 2.4) variation is subtracted from the DIC_{ex} variable (Sect. 3.2) used for quantitative analyses.

An RDI Workhorse 600 kHz ADCP was deployed nearby, in approximately 27 m water depth, for part of the experimental period. The upward-looking ADCP recorded velocity in 0.5 m bins at 2 Hz from April 8 - 26, 2015.

All time series variables were low-pass filtered with a cutoff ~~frequency of 0.003~~ period of 5 min and then subsampled at a ~~300-5~~ min interval.

2.2 Bottle samples

Bottle samples were collected from the ferry wharf on the west side of Grand Passage over two days in February 2016. On 16 Feb 2016, 12 bottles were filled hourly from 07:30 to 18:30 local time, using a Niskin off the wharf, from 0.5 - 1m below the surface. On 17 Feb 2016, 22 samples were collected half-hourly from 07:00 to 18:00. The Niskin was used for seven samples, until it broke. Later samples were collected from the adjacent shore, approximately 5 m from shore in 1.5 m water depth, from 0.5 m below the surface. On 18 March 2017, 15 bottle samples were collected between 09:00 and 13:00 ADT (UTC-3) via Niskin casts off the *Nova Endeavor*, alternating between the center, east, and west sides of Grand Passage across a transect adjacent to the cabled instruments.

Bottles samples for total alkalinity analysis were poisoned with a supersaturated mercuric chloride solution to halt biological activity, and stored for later analysis. Total alkalinity was analyzed by potentiometric titration on a Versatile Instrument for the Determination of Titration Alkalinity (VINDTA 3C). Analytical methods were based on Dickson et al. (2007), including the use of certified reference materials for regular instrument calibration.

2.3 Other data sources

Hourly wind speeds and daily precipitation for the entire experiment period were obtained from the Environment and Climate Change Canada (ECCC) weather station on Brier Island, on the western side of Grand Passage (http://climate.weather.gc.ca/climate_data/hourly_data_e.html?StationID=10859).

Atmospheric CO₂ concentrations were obtained from the NOAA Greenhouse Gas Marine Boundary Layer Reference data product (Dlugokency et al., 2015). At the time of data processing, ~weekly (1/48 of a year) values were available through 2015 for both zonal average values for 44 - 45° N and global average. Monthly global average values were additionally available through September 2016 (ftp://aftp.cmdl.noaa.gov/products/trends/co2/co2_mm_gl.txt) so estimates for 44 - 45° N were constructed for Jan - Apr 2016 by adding the difference between the zonal and global values for 2013 - 2015, averaged by calendar-week, to the global values for 2016.

Alkalinity and salinity data from the Gulf of Maine shown in Fig. 2f and used in Eq. 1 were obtained from the NOAA Ocean Acidification Program (Salisbury, 2017).

Alkalinity and salinity data from the Scotian Shelf shown in Fig. 2f and used in Eq. 1 were collected at all stations as part of the Atlantic Zone Monitoring Program (AZMP) (Fisheries and Oceans Canada, 2013-2014) in Fall 2013 and Spring 2014. Samples were collected and processed following the methods described in Shadwick and Thomas (2014) for the 2007 AZMP data set.

2.4 Estimating alkalinity from salinity

A linear relationship between salinity, S , and alkalinity, TA , (Fig. 2f) ~~is~~ was calculated with data from the bottle samples collected at the field site in February 2016 ($n = 34$) and March 2017 ($n = 15$), from the AZMP Fall 2013 ($n = 357$) and Spring 2014 ($n = 467$) cruises, and from the Gulf of Maine in 2015 ($n = 286$).

$$5 \quad TA = (45.75 \pm 0.39)S + (709.72 \pm 12.76) \quad (1)$$

The Grand Passage data covers a small ($<1 \Delta$ PSU) salinity range so a regression from only the Grand Passage field site was not robust. ~~Grand Passage measurements are not~~ The Grand Passage salinity-alkalinity relationship was not a priori expected to be identical to the data collected 10 to 200 km offshore in the Scotian Shelf and Gulf of Maine regions, but Fig. 2f shows there is no significant change in the water mass end members between ~~the Scotian Shelf and Gulf of Maine~~ those regions, which are
10 up- and downstream ~~-, respectively, of Grand Passage~~ in the regional circulation pattern. A time series of alkalinity (Fig. 2c) is calculated from salinity using Eq. 1.

2.5 Calculating DIC

DIC concentration and pH (Fig. 2d,e) for the carbonate system at equilibrium were calculated ~~using~~ from measurements of pCO_2 , salinity, alkalinity, and temperature, with constants following Dickson and Millero (1987) and Weiss (1974). We
15 ~~used~~ van Heuven's (2011) MATLAB code for Lewis and Wallace's (1998) system of equations, with constants following Dickson and Millero (1987)'CO2SYS' implementation of the equations for carbonate equilibria.

3 Results and Discussion

3.1 Seasonal evolution of ~~measured and equilibrium solution~~ carbonate system variables

Grand Passage connects two adjacent embayments, St. Mary's Bay and the Bay of Fundy, and because the water properties in
20 these embayments can differ, the strong semi-diurnal (M2) tide causes tidal period variability in the carbonate system. pCO_2 varies on annual, daily, and tidal time scales, and the size of the daily and tidal signals also changes with the season. The seasonal evolution of pCO_2 (Fig. 2a) is dominated by the effect of temperature (Fig. 2b), rising in summer and declining in winter, while biological processes only modulate this cycle. pCO_2 ranges from a minimum of $307 \mu\text{atm}$ in spring 2015 up to a maximum of $557 \mu\text{atm}$ in early fall, with daily and M2 period variation of $32 \mu\text{atm}$ and $10 \mu\text{atm}$, respectively. In November,
25 the daily range drops to $11 \mu\text{atm}$ and pCO_2 decreases throughout the winter. Final measured values in March 2016 were $30 \mu\text{atm}$ higher than the those measured the previous spring, owing to the difference in water temperature.

Temperature (Fig. 2b) has a strong seasonal cycle, increasing from 2°C in April 2015 up to 14°C in September. Temperature decreases from October 2015 through March 2016, when it reaches an annual minimum of 3.5°C , 1.5 degrees higher than the previous springtime minimum. The ranges of daily and M2 tidal variation are 0.35°C and 0.7°C , respectively, in the summer,
30 and 0.1°C and 0.15°C during fall through spring.

The salinity (Fig. 2c, right axis) average for our March - July period of data ~~return-availability~~ was 31.9 with a 0.18 tidal variation and no daily signal. Salinity was not correlated with local wind or precipitation. Alkalinity mean and tidal variation were 2177 and ~~718-8.24~~ $\mu\text{mol kg}^{-1}$, respectively, based on the linear ~~relation-ship~~ relationship between salinity and alkalinity measured with bottle samples (Fig. 2f and Sect. 2.4).

- 5 The in situ $p\text{CO}_2$ value is important because it determines the air-sea flux of CO_2 . ~~However, the, but is not an ideal variable to assess biogeochemical carbonate dynamics because of its dependence on~~ temperature and alkalinity ~~dependence of $p\text{CO}_2$ obfuscates, which obfuscate~~ the biological processes. DIC (Fig. 2d) does not have a strong temperature dependence so it better depicts the biological DIC variation. DIC declines steeply during the spring bloom, and then increases though the winter. ~~The cumulative seasonal effect of photosynthesis and respiration are evident.~~ During the spring bloom and throughout the summer
- 10 there is a large daily range in DIC. In October, daily variability shrinks, and DIC increases steadily throughout the winter. pH varies as an approximate inverse of $p\text{CO}_2$. pH has an average value of 8.01 ($= -\log_{10} < [H^+] >$) and daily and M2 variation are equivalent to changes in pH of 8 to 8.03 and 8 to 8.01, respectively.

3.2 Unraveling daily and tidal cycles of biogeochemically-driven changes in DIC

- In order to isolate the biogeochemically mediated changes in DIC from the variability due to purely physical processes, we
- 15 define the variable ‘excess DIC’ as the DIC remaining after the concentration expected from the physical mixing of water masses of different salinities and alkalinities has been subtracted. The DIC dependence on salinity and alkalinity, DIC_{mix} , is estimated numerically with CO2SYS using fixed values of $p\text{CO}_2$ and temperature. DIC_{mix} includes both a salinity-dependent component and a background constant that depends on $p\text{CO}_2$ and temperature. The mean $p\text{CO}_2$, 446 μatm , and temperature, 8 $^{\circ}\text{C}$, for the deployment period are chosen for the calculation. DIC_{ex} is calculated by subtracting DIC_{mix} from the full (observed)
- 20 DIC, DIC_{obs} (Fig. 3).

$$\text{DIC}_{\text{ex}} = \text{DIC}_{\text{obs}} - \text{DIC}_{\text{mix}} \quad \text{where} \quad \text{DIC}_{\text{mix}} = \text{DIC}(p\text{CO}_2 = 446, T = 8, S, \text{TA}) \quad (2)$$

- ~~The mean $p\text{CO}_2$, 446 μatm , and temperature, 8 $^{\circ}\text{C}$, for the deployment period are chosen for the calculation.~~ Only the time-variation of the resulting DIC_{ex} is meaningful, not the absolute value, ~~so the results are.~~ This time-variation is not sensitive to the choice of fixed $p\text{CO}_2$ and temperature from within the ranges typical of this field site. The relationship between
- 25 $p\text{CO}_2$ and DIC that is captured in DIC_{ex} is unchanged over the small natural range of alkalinity in this region, so DIC_{ex} is not sensitive to the choice of a measured, tidal harmonic, or even constant salinity estimate. DIC_{ex} is presumed to be predominantly biogeochemically-driven, but also includes any changes in DIC due to air-sea exchange, which we could not calculate on daily time scales, but are shown to be small on weekly time scales in section 3.5.

- DIC_{ex} (Fig. 4a) decreases rapidly April and May due to the spring bloom, and more gradually over the summer, as explained
- 30 by Craig et al. (2015). Following a decline in October (yearday 270-290) suggestive of a fall bloom, DIC_{ex} increases steadily through fall and winter. The daily cycle of DIC_{ex} is evident throughout year when highlighted by use of color to indicating local time of day in Fig. 4a. Daily maxima occur in early morning ($\sim 06:00$, ~~green-pink~~ dots) following nighttime respiration, and minima in late afternoon ($\sim 17:00$, ~~blue-green~~ dots) following the peak hours of sunlight and photosynthesis. This

cycle is shifted several hours earlier than the one reported on the Scotian Shelf by Thomas et al. (2012). The daily range of DIC_{ex} is approximately three times as large in summer as in winter, consistent with higher summer sunlight supporting higher phytoplankton growth.

The solar and tidal cycles combine to create a fortnightly cycle (visible in Fig. 4a, but more clear in Fig. 4b). This beating pattern in the time series is due to the difference between the 12.42 h M2 tidal and 24 h diel frequencies. Mathematically, this effect is identical to a spring-neap tidal variation, but here the daily cycle is due to solar insolation, rather than the solar gravitational force. The diagonal banding pattern in Fig. 4b shows the M2 tide progressing 50 minutes later each day. The daily morning peak and afternoon low appear as broad horizontal stripes, and are most visible for yeardays 100-275. A similar daily pattern has been observed on the Scotian Shelf (Thomas et al., 2012), but no tidal signal was detected there. The pulsing of the strength of the morning high and afternoon low is due to the coincidence of an M2 maximum or minimum with the time of the daily minimum or maximum.

The overlapping daily and tidal cycles apparent in Fig. 4 can be separated and quantified by spectral analysis. Power spectral densities of DIC_{ex} , $P_{DIC_{ex}}(f)$ for frequency f , were calculated by Welch's method on detrended time series for each month with eight approximately week-long Hamming windowed segments with 50% overlap. The position of peaks in spectra of month-long DIC_{ex} time series (Fig. 5a) identify the frequencies with the greatest variability, and the area under each peak equals the contribution of that frequency to the total signal variance. These February and August examples show a large daily peak and a slightly smaller M2 tidal peak for both months, and show that DIC_{ex} is more variable in August than February at all frequencies. The third and fourth peaks visible in Fig. 5a are harmonics of the 24h and M2 frequencies and do not substantially contribute to the total signal variance. The variance of DIC_{ex} at the 24 h and M2 frequencies are calculated from the area under the spectra using a 5-point peak width, $\sigma_{DIC_{ex}}^2 = \sum P_{DIC_{ex}}(f) \Delta f$. The total DIC_{ex} variance is ten times higher in August than in February but in both seasons, the daily and M2 frequencies represent the majority of the variability: 56% (56%) and 19% (7%), respectively, of the total DIC_{ex} signal variance in August (February).

The strengths of M2 and daily cycles in DIC_{ex} evolve with the season (Fig. 5b). The range of DIC_{ex} variation at a particular frequency is defined as $2A$ for amplitude A , i.e. the “peak to trough” difference of a sine wave. The RMS values of a sinusoid equals $A/\sqrt{2}$, so the range of the daily or tidal DIC cycle equals $2\sqrt{2}\sqrt{\sigma_{DIC_{ex}}^2}$. Months from April through September have a similar size daily signal near $15 \mu\text{mol kg}^{-1}$, with lower values throughout the winter. The tidal variation is always smaller than the daily variation, but is also generally larger in summer and smaller in winter. However, unlike the daily signal, June and July have smaller tidal variation than the shoulder months of April, May, August and September. Changes in the strength of tidal signal reflects changes in spatial gradients of DIC_{ex} , presumably owing to season fluctuations in the spatial variation of biological activity.

3.3 Tidal phasing

The relationship between the tidal flow and DIC_{ex} , temperature, salinity/alkalinity, and H_{ex}^+ are depicted in Fig. 6 for April 2015, when velocity measurements were available. This tidal phase information complements the daily cycle of DIC_{ex} emphasized in Fig. 4a.

Salinity and corresponding alkalinity (Fig. 6a) are lowest during late flood, and highest between max ebb and early flood (see ebb/flood directions on Fig. 1). Salinity values are lower during flood compared to those on ebb, which indicates that the water from St. Mary's Bay/Scotian Shelf that enters the Bay of Fundy through Grand Passage each flood tide is fresher than what exits during ebb. This tidal asymmetry in salinity holds for all months of the year.

- 5 Temperature (Fig. 6b) is lowest in late flood and peaks a short time later during early ebb, and overall the water is colder during flood than during ebb. Unlike the salinity asymmetry, the temperature asymmetry changes sign with the seasons. The shallower St. Mary's Bay is more sensitive to surface heat fluxes than the deeper Bay of Fundy, so it is warmer in spring and summer and colder in fall and winter. As a result, the oscillating tides move heat into the Bay of Fundy half of the year, and out half the year.
- 10 DIC_{ex} (Fig. 6c) peaks at low slack and the lowest values occur ~~at~~ during late flood and early ebb. H_{ex}⁺ (Fig. 6d) also peaks at low slack and has the lowest values during early ebb. This pattern suggests lower ~~growth-net community production~~ in the bay than on the shelf, likely a result of a stronger spring bloom on the shelf than in the bay, which is advected by the mean currents around southern Nova Scotia. Smaller scale spatial variation in nutrient or light availability owing to different water depths or mixing rates could also contribute to different growth rates on the two sides of Grand Passage.

15 3.4 Lateral transport by tidal pumping

- Transport of carbon through Grand Passage is driven both by net volume transport and by *tidal pumping* - oscillatory tides moving water masses with different properties back and forth on each tidal cycle. Water volume flux per meter of channel width, ~~$q = \bar{u}h$~~ (m^2s^{-1}) ~~$= \bar{u}h$~~ , for water depth h (m) and depth-averaged velocity \bar{u} (m s^{-1}) can be decomposed into a time-mean ($\langle \rangle$) and fluctuating ($'$) part, $q = \langle q \rangle + q'$. By definition, there is no net water volume transport by the time-varying
- 20 volume flux used to calculate tidal pumping. The fluctuations in volume transport (Fig. 7a) that drive tidal pumping vary in magnitude over the spring-neap cycle, but return to zero each tidal cycle.

- Any correlation between the tidal water volume flux, q' , and fluctuations in conserved carbonate system concentration variables, $S' = S - \langle S \rangle$ (g m^{-3} ~~or~~ mol m^{-3}), leads to a scalar flux by tidal pumping, $Q_{pump}^S = \langle q' S' \rangle$ ($\text{mol m}^{-1}\text{s}^{-1}$ ~~or~~ $\text{g m}^{-1}\text{s}^{-1}$), when averaged over times scales longer than a tidal cycle. Salinity is nearly vertically uniform at this field site (Razaz
- 25 et al., 2018), and we assume DIC is also vertically uniform because the vertical mixing time scale is much shorter than the time scale of gas exchange owing to the high turbulence in the Bay of Fundy (appendix A1), i.e. $\int_0^h S(z)u(z)dz = S\bar{u}$. Fluctuations of the conserved variable that are not correlated with fluctuations in water volume flux, such as the daily or seasonal cycles shown in Fig. 4a, are in S' but do not contribute to Q_{pump}^S because they are not correlated with q' .

- Cumulative along-channel transports, M (m^3 ~~mol~~ ~~or~~ g), of water volume, alkalinity, and DIC_{ex} (Fig. 7) are calculated by
- 30 multiplying q' , $q'TA'$, and $q'DIC'_{ex}$ by the width ($w = 800$ m) of Grand Passage, and integrating in time, t . We assume spatial uniformity of water properties across the section.

$$M_S(t) = \int_0^t q' S' w dt \quad (3)$$

The fluctuating water volume flux, q' , used to compute these transports is a tidal harmonic solution based on a fit to the month of ADCP data from April 2015. The harmonic fit represents 93% of the observed variability (i.e. $R = 0.97$) in water volume flux. By contrast, the tidal harmonic fit to the four months of salinity measurements (Sect. 2.1) is not well-correlated with the observations ($R = 0.35$) owing to the non-sinusoidal shape of the salinity signal as well as longer period variability.

5 Due to this poor fit, alkalinity fluxes are not computed for the period without direct salinity measurements. DIC_{ex} is not affected by the salinity, as described in Sect. 3.2, so DIC_{ex} transport is calculated for the full year.

For the first half of 2015, salt and alkalinity (Fig. 7b) are pumped southward, out of the Bay of Fundy by the tides. DIC_{ex} (Fig. 7c) also has net negative (southward) transport over this period, but has shorter periods of near zero or positive transport in March, mid-April, and early June.

10 Tidal pumping for DIC_{ex} is also calculated for the second half of the deployment year (Fig. 7d) and continues the negative trend until January 2016, when the flux becomes slightly positive for the last two months of the measurement period. Salinity from a seasonal climatology (e.g. Richaud et al., 2016; Signorini et al., 2013) suggests that the sign of the lateral salinity gradient is the same all year, indicating that the sign of the alkalinity flux will stay the same throughout the year.

Notably, these transports move alkalinity and DIC_{ex} in the opposite direction of the mean flow of the region, which follows the coast clockwise around southwestern Nova Scotia, moving northward into the Bay of Fundy near Grand Passage (e.g. Aretxabaleta et al., 2008). Within Grand Passage, salinity/alkalinity transport by tidal pumping is roughly 20% of that by the mean volume flux through the channel (appendix A2). The exact fraction may vary outside the channel, but the important point is that tidal pumping likely plays a first order role in carbon transport budgets anywhere with large tides and spatial gradients in the biogeochemical water properties, including the entire width of the mouth of the Bay of Fundy.

20 While the mean volume transport through Grand Passage cannot be extrapolated to the full width of the Bay of Fundy, the tidal pumping term could plausibly apply over the eastern side of the mouth, where salinity gradients are positive into the bay. If the transport by tidal pumping is applied out to just 10 km from shore ($\sim 15\%$ of the width of the mouth of the bay), which is a ~ 50 m deep region, the DIC_{ex} transported out of the Bay of Fundy through lateral advection by tidal pumping would be 5×10^8 kg in a year. This value is three times what is estimated to leave the Bay of Fundy by outgassing to the atmosphere if the Grand Passage air-sea fluxes (Sect. 4.13.5) applied over the whole bay.

4 Discussion

3.5 Air-sea CO_2 flux

30 High-frequency variability in DIC_{ex} is assumed to be driven by biological and biogeochemical processes, but air-sea flux plays a significant role on long time scales. We assess the importance of air-sea flux to the carbon budget by calculating weekly and annual fluxes, and the equivalent changes in DIC. Oceanic $p\text{CO}_2$ was lower than atmospheric $p\text{CO}_2$ (Fig. 2a) for the first two months of observations, April and May, and then rose and remained higher than atmospheric $p\text{CO}_2$ for the following ten months, June through March, giving an annual net negative CO_2 flux (i.e. outgassing) at this site.

Atmospheric and oceanic CO₂ concentrations (Fig. 2a) and wind speed (Sect. 2.3), are used to calculate the flux of CO₂ between the atmosphere and ocean at the field site. Atmospheric and oceanic pCO₂ data were interpolated onto the hourly wind time base. Air-sea flux, F (mol m⁻² s⁻¹), is calculated following Wanninkhof et al. (2009) Eq. 3, here using the convention that F is positive for a flux of gas from the atmosphere into the ocean.

$$F = -kK_0(p\text{CO}_{2w} - p\text{CO}_{2a}) \quad (4)$$

where K_0 is the solubility of CO₂ (mol m⁻³ Pa⁻¹) and k (m s⁻¹) is gas transfer velocity. k (cm h⁻¹) can be represented well for wind speeds, U (m s⁻¹), below 15 m s⁻¹ at Schmidt number $Sc = 660$ with the empirical formula (Wanninkhof et al., 2009, Eq. 37)

$$k_{660} = 0.24\langle U_{10}^2 \rangle \quad (5)$$

U_{10} is the 10 m wind speed measured at the ECCC station on Brier Island. ~~Oceanic pCO₂ was subsampled hourly and atmospheric pCO₂ was interpolated onto the hourly time base.~~ U_{10} was also computed as the difference between the air and water speeds (up to ± 2 m s⁻¹), which increased the air-sea flux estimates by approximately 5%. Air-sea flux is initially computed on an hourly time scale to fully capture the quadratic wind-speed dependence, but only weekly (or longer) averages of F are robust owing to the weekly time scale of the available atmospheric pCO₂ data.

The average air-sea CO₂ flux at this site is -4.6×10^{-8} mol m⁻² s⁻¹, which is similar in magnitude to previous Gulf of Maine flux estimates, but with outgassing most of the year rather than the more even split between positive and negative fluxes reported at a deeper site (Vandemark et al., 2011) or for regional averages (Signorini et al., 2013; Cahill et al., 2016). If this gas exchange was spatially uniform over the Bay of Fundy (approx. 10^4 km²), this air-sea flux would release 1.75×10^8 kg carbon ($= 1.45 \times 10^{10}$ mol) into the atmosphere per year.

~~This~~ The annual local flux is equivalent to a -47 $\mu\text{mol kg}^{-1}$ change in DIC_{ex} when applied to 30 m water depth in Grand Passage over the year-long deployment.

$$\Delta\text{DIC}_{\text{air-sea}} = \frac{F_{\text{air-sea}}}{h} \Delta t \quad (6)$$

~~If this gas exchange was spatially uniform over the Bay of Fundy (approx. 10^4 km²), this air-sea flux would release 1.75×10^8 kg carbon into the atmosphere per year. The weekly averaged flux is typically between 0 and -1×10^{-7} mol m⁻² s⁻¹, which is~~ equivalent to up to -2 $\mu\text{mol kg}^{-1}$ change in DIC_{ex} over a week. The maximum weekly value occurred in late September 2015, and was -2×10^{-7} mol m⁻² s⁻¹, yielding a -4 $\mu\text{mol kg}^{-1}$ change in DIC_{ex} in one week.

4.2 DIC_{ex} advection

~~We did not directly measure spatial gradients of DIC_{ex}, but can infer that the local along-channel gradient is positive (increasing northwards) from the observation that the highest and lowest values tend to occur near low and high slack water, respectively~~ (Fig. 6). A positive along-channel gradient carried by a northward regional circulation decreases local DIC_{ex}

4.3 Closing a local DIC budget

3.6 Consideration of the local DIC budget

Observed DIC_{ex} variation is due to the difference between local (water column and sediment) net community production (NCP), local air-sea flux, and advective changes due to spatial gradients of biological production or air-sea flux (Appendix A3). Daily variation in DIC_{ex} can reasonably be attributed to the local time rate of change, and the tidal variation is likely advective. Longer cycles of variation could have both a local seasonal cycle and advective contributions from seasonal variation occurring weeks or months upstream.

We did not directly measure spatial gradients of DIC_{ex} , but can infer that the local along-channel gradient is positive (increasing northwards) from the observation that the highest and lowest values tend to occur near low and high slack-water, respectively (Fig. 6). A positive along-channel DIC_{ex} gradient carried by a northward regional circulation decreases local DIC_{ex} .

DIC_{ex} returns near to its initial value over the full annual cycle (Fig. 4a) so the annual mean $\partial\text{DIC}_{\text{ex}}/\partial t$ is zero. The outgassing air-sea flux and along-channel advection both decrease DIC_{ex} , so to close the DIC budget (Eq. A6) the biologically-driven change in DIC must be positive (community $\text{NCP} < 0$) on average over the year, even though it is negative in the spring.

4 Conclusions

Open ocean carbon cycles can be described by annual and daily variations, and taken to be uniform over large spatial scales, but near the coast, ecosystems change markedly over short distances, so the dynamics of the carbonate system cannot be well-described without resolving the spatial variation or capturing the effects of lateral advection.

We unravel tidal advection from the diel production and respiration cycles due to solar radiation, and show that the tides pump both alkalinity and DIC out of the Bay of Fundy into the open ocean, opposite to the transport via the residual flow. This tidal pumping process, in contrast to any residual flow, does not result in a net transport of water, but can greatly enhance the exchange of passive scalars like DIC. In regions with strong tidal currents and spatial variation in biological activities, tidal pumping could substantially modulate the coastal ocean's response to global ocean acidification.

High-frequency measurements reveal previously unaccounted for tidal variations in the carbonate system, in addition to more precise quantification of the familiar daily cycles and annual blooms. These results are crucial prerequisites to a deeper understanding of coastal systems' resilience or vulnerability to anthropogenic change.

Data availability. The data that support the findings of this study are available from the corresponding author upon reasonable request.

Appendix A

A1 Vertical mixing

In this highly turbulent, unstratified water column, the vertical mixing time scale (Eq. A1) is much shorter than the time scale of gas exchange (Eq. A2).

$$5 \quad T_{\text{mix}} = \frac{h^2}{A_\nu} \sim \frac{h^2}{(\kappa u_* h / 12)} = \frac{h}{\kappa u_* / 8} \approx \frac{25 \text{ m}}{0.4 \times 0.1 \text{ m/s} \times 0.125} = 5000 \text{ s} = 1.4 \text{ h} \quad (\text{A1})$$

$$T_{\text{air-sea}} = \frac{h}{k_{660}} \approx \frac{25 \text{ m}}{4 \times 10^{-5} \text{ m/s}} = 6.25 \times 10^5 \text{ s} = 7 \text{ days} \quad (\text{A2})$$

where h is total water depth at the ADCP site, k_{660} value is average from the dataset, A_ν is eddy viscosity estimated as the mid water depth value of a cubic eddy viscosity profile for a logarithmic near-bed velocity profile and zero surface wind stress (e.g. Lentz, 1995), κ is the von Karman constant, u_* is shear velocity with value chosen from McMillan et al.'s (2013) Grand

10 Passage site “GP2” very close to the one used in the present study.

A2 Mean volume transport

The mean volume flux, $\langle q \rangle$, is derived from both the mean depth-averaged along-channel velocity and the mean volume transport due to asymmetries in the tidal cycle $\langle q \rangle = \langle \bar{u} h \rangle = \langle \bar{u} \rangle \langle h \rangle + \langle \bar{u}' h' \rangle$. At the ADCP location, $\langle \bar{u} \rangle = 0.036 \text{ m s}^{-1}$ and $\langle h \rangle = 26.6 \text{ m}$, which are indicated by the solid black lines in Fig. 6, yielding $0.95 \text{ m}^2 \text{ s}^{-1}$ volume flux.

15 The position of the data points in Fig. 6 compared to the mean axes made by $\langle \bar{u} \rangle$ and $\langle h \rangle$ values, shows that the water tends to be deeper during ebb than during flood. If the tide was a perfect standing wave (slack at high and low water, and max ebb and flood speeds occurring at the mean water depth), the shape of the depth-velocity points would form a circle. The mean volume flux due to this tidal asymmetry, $\langle \bar{u}' h' \rangle = -1.61 \text{ m}^2 \text{ s}^{-1}$, which is larger than, and in the opposite direction of, the volume flux by the mean depth-averaged velocity.

20 Assuming spatial uniformity over the channel width the volume flux by the mean depth-averaged velocity applied to the mean salinity of 31.9 yields a salt flux of $2.3 \times 10^4 \text{ kg s}^{-1}$ and the volume flux by tidal asymmetry generates a salt flux of $-4.0 \times 10^4 \text{ kg s}^{-1}$.

The salt flux driven by total $\langle q \rangle$ from both components is $-1.6 \times 10^4 \text{ kg s}^{-1}$, which is five times the salt flux by tidal pumping shown in Fig. 7. However, the mean velocity and especially the phase lag between the tide depth and velocity is

25 generated by friction and therefor sensitive to the specific channel geometry (e.g. Geyer and MacCready, 2014) and may vary across the mouth of the Bay of Fundy.

A3 Budget for biological DIC production

The change in observed DIC_{ex} , is given by

$$\frac{\partial \text{DIC}_{\text{ex}}}{\partial t} = \frac{\partial \text{DIC}_{\text{bio}}}{\partial t} + \frac{\partial \text{DIC}_{\text{air-sea}}}{\partial t} \quad (\text{A3})$$

Biology and air-sea exchange both drive local changes in time, and both could potentially have changes in time due to advection of spatial gradients, which is what we (almost definitely) observe over the tidal cycle. e.g.

$$\frac{\partial \text{DIC}_{\text{bio}}}{\partial t} = \frac{\partial \text{DIC}_{\text{bio,local}}}{\partial t} - u \frac{\partial \text{DIC}_{\text{bio}}}{\partial x} \quad (\text{A4})$$

where x is along-channel distance, and $\partial \text{DIC}_{\text{bio,local}}/\partial t$ corresponds to local carbon consumption (i.e. equal to $-\text{NCP}$). So in

5 total

$$\frac{\partial \text{DIC}_{\text{ex}}}{\partial t} = \frac{\partial \text{DIC}_{\text{bio,local}}}{\partial t} + \frac{\partial \text{DIC}_{\text{air-sea,local}}}{\partial t} - u \frac{\partial \text{DIC}_{\text{bio}}}{\partial x} - u \frac{\partial \text{DIC}_{\text{air-sea}}}{\partial x} \quad (\text{A5})$$

If we assume the air-sea flux is spatially uniform, $u \frac{\partial \text{DIC}_{\text{air-sea}}}{\partial x} = 0$, then the change in observed DIC that is attributable to biological activity, DIC_{bio} , is given by

$$\frac{\partial \text{DIC}_{\text{bio,local}}}{\partial t} - u \frac{\partial \text{DIC}_{\text{bio}}}{\partial x} = \frac{\partial \text{DIC}_{\text{ex}}}{\partial t} - \frac{\partial \text{DIC}_{\text{air-sea}}}{\partial t} \quad (\text{A6})$$

- 10 *Author contributions.* R.M.H. performed the research and wrote the manuscript with the guidance of H.T., who, with A.E.H., initially conceived of the project. R.M.H. and H.T. developed analysis trajectory. A.E.H. provided velocity, temperature, salinity, and pressure data. R.C. and W.B. programmed, deployed, and maintained the instruments. J.S. provided Gulf of Maine salinity and alkalinity data. All authors consulted on the manuscript.

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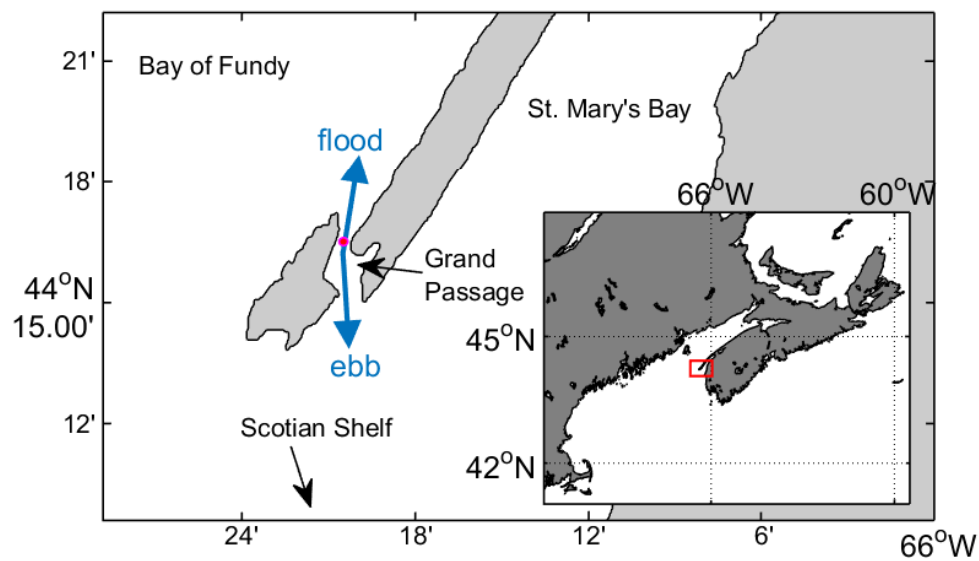


Figure 1. Map of Grand Passage, which cuts through a peninsula in southwest Nova Scotia. Instrument location indicated by pink dot. Flood and ebb tide flow directions shown blue arrows. Inset: Map of the region with red box indicating field site at the mouth of the Bay of Fundy.

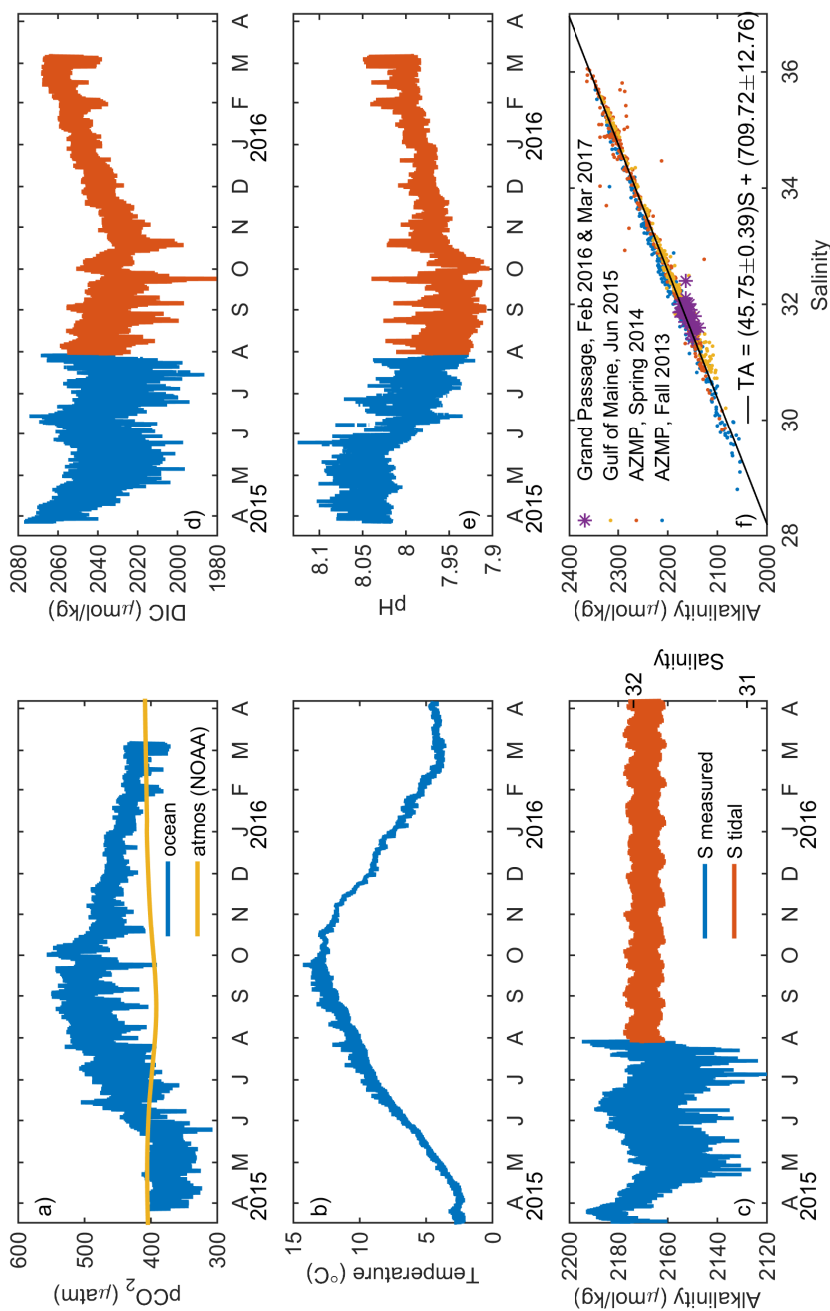


Figure 2. (a-c) Measured variables and (d,e) timeseries generated from the carbonate system equilibrium solution for data shown in (a-c). (a) $p\text{CO}_2$ in Grand Passage (blue) and NOAA's weekly atmospheric zonal average for 44–45° N (yellow). (b) Temperature (c) Salinity (right y-axis) and alkalinity (left y-axis) from periods with salinity data (blue) and generated from a tidal prediction when measurements were not available owing to instrument failure (orange) (d) DIC (e) pH. (f) Alkalinity vs. salinity from bottle samples at the Grand Passage field site in 2016 and 2017 (purple) as well as from the Scotian Shelf via the Atlantic Zone Monitoring Program in 2013 (blue) and 2014 (orange), and the Gulf of Maine in 2015 (yellow). Linear regression (black) used to generate alkalinity shown in (c)

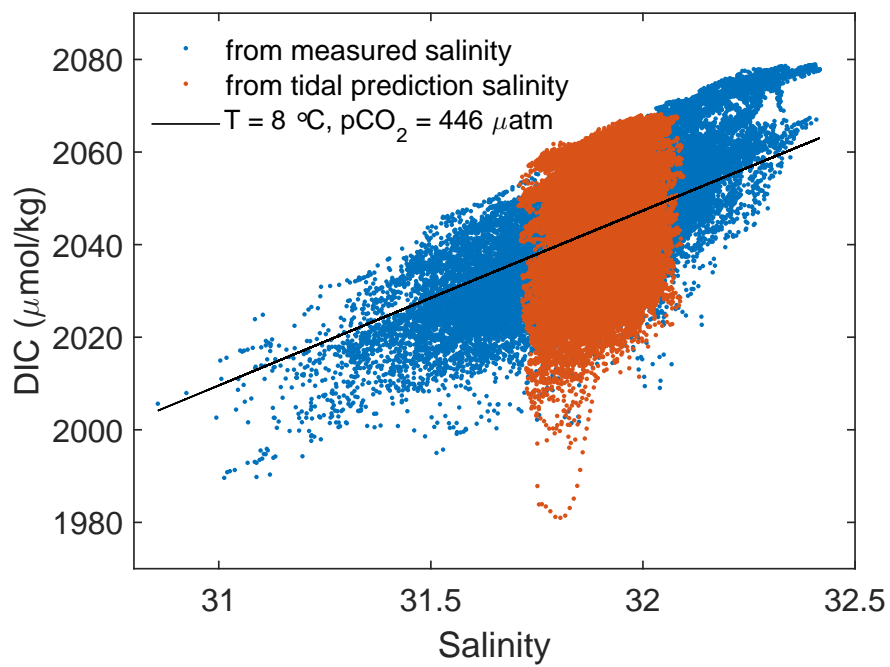


Figure 3. DIC vs. salinity for measured (blue) and tidal reconstruction (orange) carbonate system solutions. DIC at fixed $p\text{CO}_2$ ($446 \mu\text{atm}$) and temperature (8°C) (black) is subtracted from observed DIC to create DIC_{ex} .

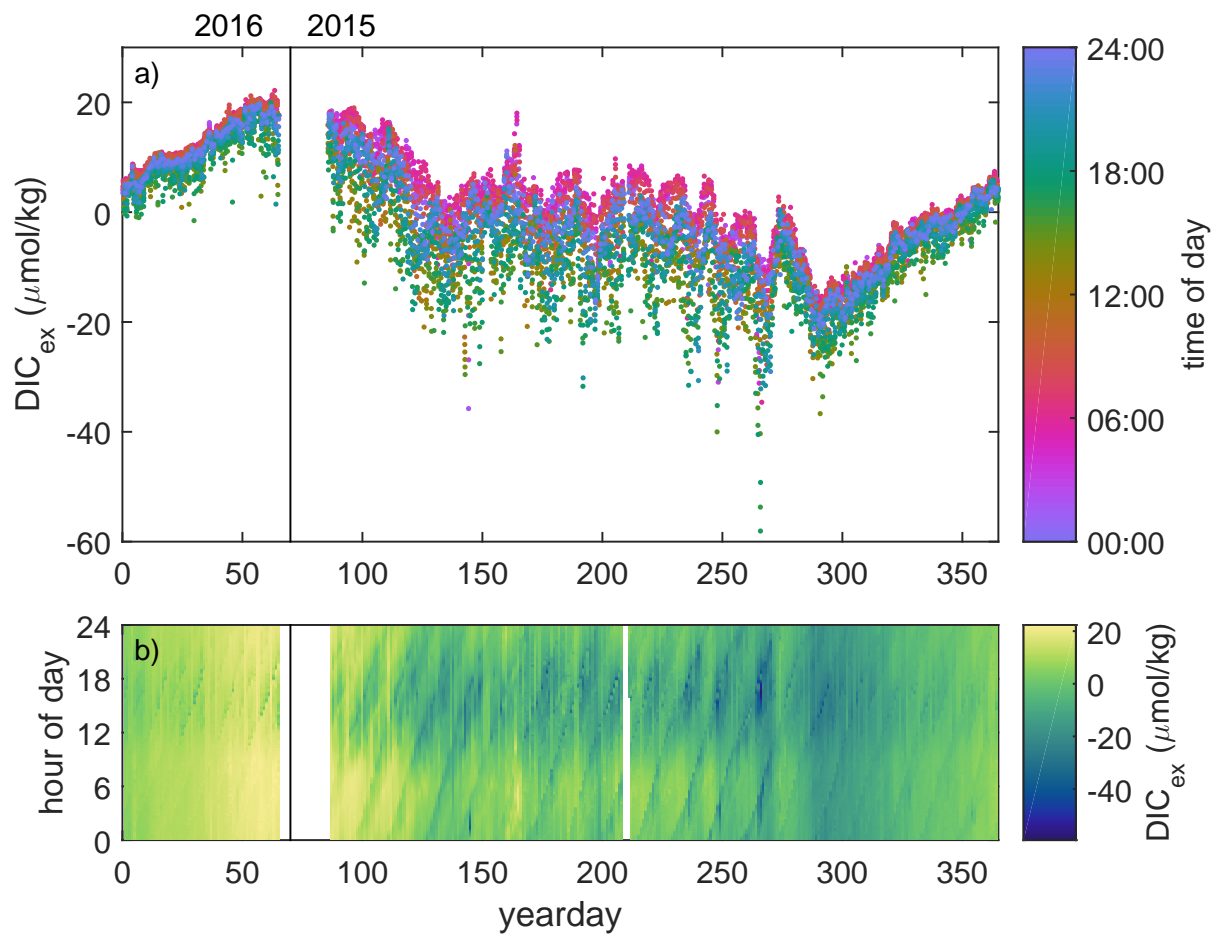


Figure 4. (a) DIC_{ex} for a calendar year with local time of day indicated by color. The time-variation of the resulting DIC_{ex} is meaningful, while the total value depends on the specific choice of fixed $p\text{CO}_2$ used for the computation. (b) DIC_{ex} (color) for each hour of the day over a calendar year.

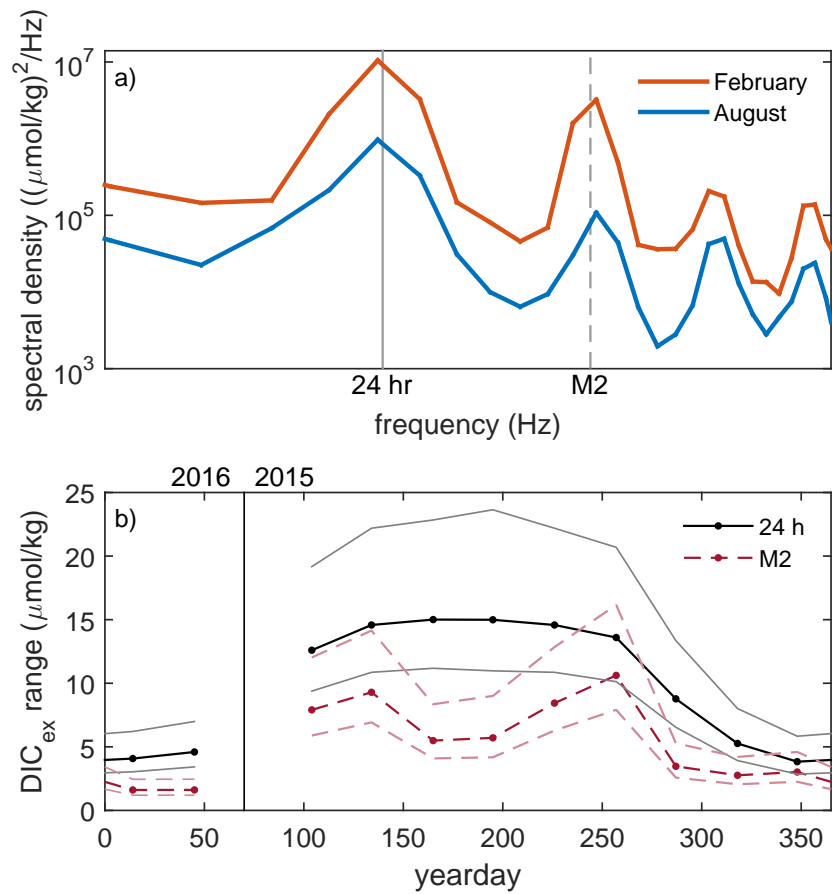


Figure 5. (a) Spectra of DIC_{ex} in February (blue) and August (orange). (b) DIC_{ex} range over daily (black, solid) and M2 (red, dashed) cycles for each month of the year. Amplitude determined from area beneath peaks in spectra, such as examples shown in (a). 95% confidence intervals in lighter colors.

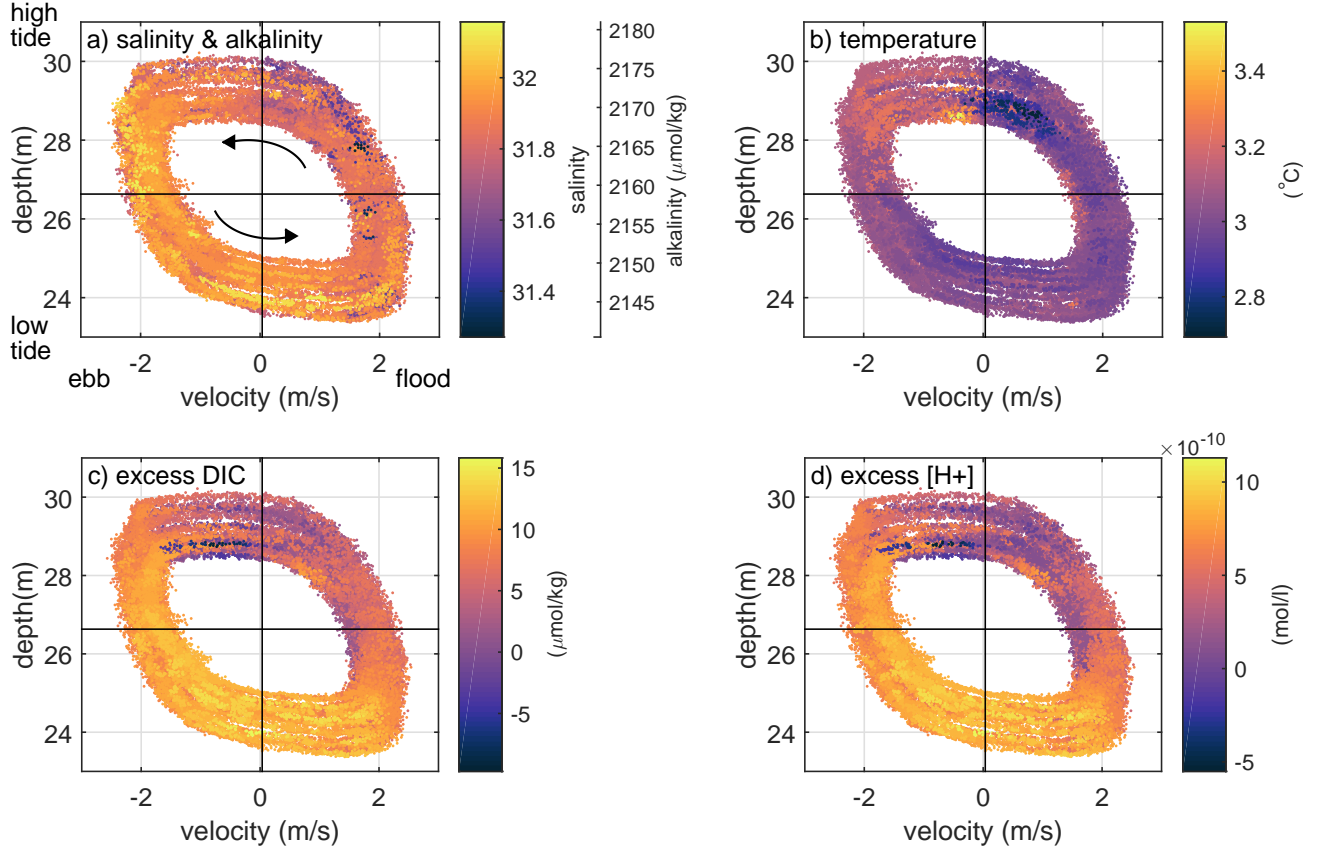


Figure 6. The relationship between the tidal flow and (a) salinity/alkalinity, (b) temperature, (c) DIC_{ex} , and (d) H_{ex}^{+} are depicted for April 2015, when velocity measurements were recorded. The phase of the tide is indicated by ADCP water depth on the y-axis and depth-average along-channel velocity on the x-axis (positive in flood direction, i.e. northward, into the Bay of Fundy), with mean values indicated by black lines. Phase progression is counter-clockwise, shown by arrows in (a). Scalar concentration is indicated by color, e.g. more red-yellow data points visible on the left side of (a) indicates higher salinity during ebb tide, when water is leaving the Bay of Fundy. The variation in position of the tidal ellipse between each pass of the tidal cycle reflects the changes in tidal range and maximum speed associated with the spring-neap cycle. For all variables shown by colors, 18-hr high pass filtered values plus mean are plotted to visually highlight the M2 variability by eliminating the daily signal; the filtering is not used for data analyses. H_{ex}^{+} is computed by the same method as DIC_{ex} , for $\text{H}^{+} = 10^{-\text{pH}}$.

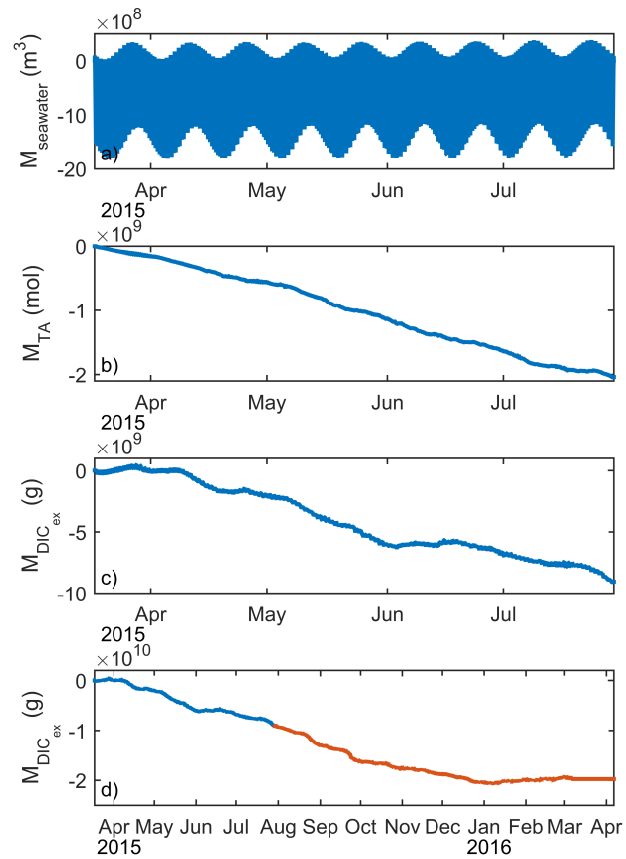


Figure 7. Cumulative along-channel transport since the start of the deployment period by tidal pumping of (a) water volume, (b) alkalinity, and (c) DIC_{ex} for March-July 2015 and (d) DIC_{ex} for the full year; orange color indicates period not shown in (a-c). Salt or alkalinity fluxes are not computed for the full year because fluxes from the constructed tidal salinities will only reflect the mean trend already seen in Fig. 7b and not contain changes in phase or magnitude that might occur in the fall or winter.