List of Modifications made to: Glider-Based Observations of CO_2 in the Labrador Sea

Nicolai von Oppeln-Bronikowski et al., 2020

November 12, 2020

Abstract:

I would recommend the addition of some key figures from the text…

- Addition of key numbers (sensor accuracy, response time, scales) from results section to engage reader

I also think that the questions posed in the introduction could be summarised more clearly in the abstract

- Summarizing of the main paper goals in more clear way

The justification of the IR sensors only being used on the SeaCycler is not needed
The few lines discussing the Pro CV also adds to the confusion in the last few sentences when referring to "this" and "the" sensor.

- Clarity of text improved by reworking sentences and editorial suggestions as per Reviewer 1 and 2.

Introduction

I would also suggest the author look at the weather vs climate objectives for sensor performance as defined by GOAON (2nd edition).

- Added additional references from GOAON report (Newton et al., 2015).

Line 63 – perhaps the author could make reference to the term "foil"
Line 76 – the term "extended" perhaps the author could use re-deployed

- Editorial suggestions as per Reviewer 1 and 2.

Data and Methods

Figure 1 – the caption could clarify the importance of red vs. blue boxes around the profile data.

- Improved the Figure 1 layout, labels for clarity and the captions

What is the PCO2 sensorCO2 Prototype 4797? Is this the optode? Or is it the SN57?

- Improved clarity here and elsewhere to distinguish CO_2 Pro CV and CO_2 Optode.

Winkler titrations to not to my knowledge allow you to determine DIC/TA only oxygen Please can you clarify the instruments used to measure DIC/TA as this may influence the precision/accuracy of these data. In addition, any information on the collection of DIC/TA (e.g. poisoning, storage medium etc). - Line 156– please quote the constants you used for CO2SYS and the errors associated with the calculated pCO_2. These will compound any instrument specific offsets.

- Added Appendix section to explain in detail the reference samples taken in the tank test at DFO and uncertainty for the measurements.

L158. You present T, S, O_2 offsets – what about the other variables?

- Added table to summarize the tank-test results. Added more sensor accuracy information including Pro CV

L141. Profile of temperature to capture this?

- Figure 2 was improved to include T-S data from Trinity Bay

Glider Data Processing

Was the calibration curve used to calculate pCO_2 from the foils from the pre-trinity bay mission testing or from Dariia's paper? - Was the same correction used for both VITALS and trinity bay?

- Improved the clarity on different calibration models applied to the CO_2 optode (VITALS vs. Trinity Bay).

Fig3. labels

- Figure 3 labels were improved

Glider CO2 Optode Performance

I find the figure 4 (the authors way to display this) confusing. perhaps the p-values could also be shared to demonstrate Perhaps the author could expand the sentence that refers to the VITALS glider profiles vs. Trinity Bay step profiles

- Improved Figure 4 distinguishing clearly between VITALS and Trinity Tests
- Figure 4b was modified as a box plot for the 2 deployments. The plot complement Table 2.
- Fit was modified to simple linear-least squares with more information on the figure. The fit ignores the VITALS data with large scatter about the origin.

L239. Could tabulate some of the response time findings

A table was added to summarize more clearly the figure and response time from each deployment

I am also not clear on the fitted t95 – is this from the equation listed in the text in line 233? I would suggest the author rephrase to focus on the sensor response (as a whole) rather than the time taken to respond (as I think this may be their intention). I am not sure what value figure 4a brings as it is not discussed in the text in any detail.

- We reworded the discussion for clarity and brevity.
- All discussion focussed around improved Figure 4 and Table 2.

I am also concerned by the sentence in 246 which states there was a significant temperature dependence on response time. The previous paragraph does not demonstrate this, nor in my opinion figure 4.

- We fixed the wording with regards to the temperature bias that is shown in Figure 4.

I am not sure if figure 5 a and b are useful plots, as the glider profiling would presumably match less precisely to the CTD-style sea cycler profiles where they remain at the same depth for 20 minutes. The scatter in the data (creating the low r2 on the linear fits) I suspect is also due to the binning implemented to try and maintain a match in data records

- We took out original Figure 5 – agreeing that the figure does not add value in the context of this discussion.

I note the difference in the dphase range between the VITALS and Trinity bay data, yet a not dissimilar CO2 range. The temperature range is significantly wider in trinity bay yet there is no overlap in the dphase values. I was wondering if the author could additionally comment on this (is it a result of the conditioning to local conditions, indicator bleaching?) as it is mentioned only in passing in line 260.

- Mention of the difference added into the text, mentioning possible bleaching.

O2 and CO2 Observations

Fig6 and Fig7. You switch to DO2 without explanation or reference elsewhere in the text and use just O2 in the caption. Also colour bars/legend required Figure 7 – the K1 mooring and SeaCycler locations are denoted I think by red and blue lines respectively – these are used within the colour scheme-perhaps white or gray could be considered as alternatives? The O2 data doesn't have the glider profiles used for plotting on?

- Figure labels were modified in (original Figures 6, 7) now Figure 5,6, including color choices and adding location of oxygen glider data on Figure 6.
- Accuracy of glider data from the SeaCycler-glider comparison added
- Table to summarize residuals added

Glider Observed Spatial and Temporal Variability

Take care as figure 9/10the legend appears to obscure data points at the start of a track. Perhaps the legend would be better suited on the right-hand side, or outside the plot.

- Figure 8 – Hovmüller Diagram improved, removing legend and using text labels consistent with the rest of the text
- Added uncertainty into the qualitative variability discussion

Please rephrase line 276, as "weak in an average sense" doesn't make sense to me.

- Used numbers in the text to improve clarity of the arguments

Spatial and Temporal Variability Line 310 – please remove the word “somewhat”. I would also advise using numbers to make your point clearer. The following sentence is also a bit vague – potential CO2 cycling? Perhaps the authors could clarify what they mean by this.

- Improved legibility of paragraphs when referring to the different scales and interpretation

Conclusions

I would also suggest that the author summarise some of the extra work, mentioned throughout the rest of the paper as a forward look(e.g. more tests to evaluate the influence of flow field on sensor performance in situ and a response time model?)

- Reworked second paragraph to summarize extra work done in the study with regards to the goals of the paper

I would also suggest the author clarify the timescale of the temperature change in line 392

- Improved clarity of numbers mentioned in the text.

Following editorial changes were directly implemented in the text

- L3. Remove repeat of ‘capable’
- L43. Use carbon sink (not carbon sinks)
- L44. Plural gliders to remove
- L56. ‘Periods’
- L59. Insert ‘a’ (from a..)
- L87. Fall of 2016
- L91. VITALS is an acronym? Fig1 caption requires more detail
- L102. Clarify that 4797 is the CO2 optode
- L106. Selected stop depths
- L108. Validate rather than calibrate
- L114. Would be good to know precision too?
- L136. Use cold instead of frigid
- Line 179 – remove Also.
- L195. Remove duplicate of ‘the’
- Line 198– correct to “ the sensor began to display inconsistent behaviour...” (or similar)
- Line198 – I would also change the word last to final, as this is clearer as the end of the experiment, rather than a relative statement.
- L270. To a depth of large change in O2 and CO2?
- L318. Change ’another’ to ‘from each other’
- L327 add year to the Chatfield reference(1998)
- L337. Its OK to switch to T and O2 but be consistent (in full again on L334)
- Line 360 -I think it should read “highly variable changes” not “highly varying”.
- Line 363 – I don’t think you mean CO2 solubility - do you mean strength of uptake? Or are you referring to the changing T&S increasing or decreasing the solubility?
- Perhaps the term “staircase missions” could be used in the sections where the authors refer to step profiling to maintain consistency with the conclusion.

Author's Response to Reviewer Comments 1

Journal of Ocean Science Interactive Discussion

Paper Title: *"Glider-Based Observations of CO_2 in the Labrador Sea"*

Nicolai von Oppeln-Bronikowski et al.

* Red ink is author response if some other change/ comment was necessary.

Referee #1 Comments

General Comments:

Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure

1) **I am not convinced that the CO2-CV sensor is ideal for validating data against (and is not necessarily the model referred to in the reference to Jiang et al., 2014).**

- We will correct the reference and state that it is not the PRO-CV rather the technology that is referenced.

2) **Ideally the tank comparisons would also involve validation with state-of-the-art equilibrator systems. Attention should also be paid to errors in CO2 estimates arising from indirectCO2 estimates (using CO2sys).**

- We will try to consider this in future experiment designs involving this sensor. DIC and TA were estimated in the lab and pCO2 was calculated from CO2Calc (Robbins et al., 2010). TA and DIC are estimated from coulometry (Johnson et al., 1993) and potentiometric titration (Mintrop et al., 2000). In the calculation they used the CO2 equilibrium constants from (Mehrbach et al. 1973 refit. by Dickson and Millero 1987), total boron constant (Lee et al., 2010), and KHSO4 constants (Dickson 1990). I regret the error in the original text which was oversight. The samples were analyzed in the lab. of Fisheries & Oceans Canada and at the moment they are not setup to measure the uncertainty of the pCO2 estimate in CO2calc from DIC and TA. Reported uncertainty in the procedure for DIC and TA were 3 and 4 umol/kg respectively. Unfortuantely CO2calc is not available to me. From repeating the calculations with the same settings mentioned above and using CO2sys, using the uncertainty in TA and DIC, we arrive at an uncertainty of 4.48 uatm for the lab lab-based pCO2 estimates mentioned in the text.

3) **The paper could also be improved with increased use of tables and attention to detail on the figures (eg: colour legend when required).**

- Where appropriate and as pointed out by you in below specific comments, these changes have been implemented. Thank you so much. We modified or slightly adjusted Figures 1-10 with respect to specific comments. We will add a summary table of data mentioned in the text or in the figures near Figure 3 and Figure 4.

Editorial and Other Specific Comments

L53. May not be necessary to spell out CTD but it is an acronym?

Noted. In this case given the journal and audience it probably is safe to leave as an acronym.

L124. Is CO2 accuracy really 2-75uatm? It seems a large range (and may depend on the concentration?)

Accuracy range is the results so far available in the literature as described in Atamanchuk et al 2014, 2015. The large range, points (in our opinion) to a large range in foil performance under ambient conditions also the range in manufactured foils. Some work better than others…

Temperature and concentration gradients definitely have an impact. Large gradients (see our results) seem to produce more reliably strong signals in the sensor than small gradients. Absolute accuracy is pretty low and foil chemistry was not designed for that. It is not sensitive to absolute concentrations but the change of pH which then induces a fluorescent response of the foil chemistry.

L130. Would benefit from putting the dominant current flow onto the map perhaps?
Will try to add arrows. If it is too busy we may omit them as they are not as important to the main story of the paper.

L141. Profile of temperature to capture this?
I will add the average T-S structure from Trinity Bay into the paper

L158. You present T, S, O2 offsets – what about the other variables?
A table would help Fig3. Put T and S on the axis (titles and units)
Summary tables for CO_2 conditioning offsets and improvement to Figure 3 will be implemented in the next revision.

L239. Could tabulate some of the response time findings Fig5. Caption could be clearer on what VITALS is so the figure can stand alone
Figure 4 and 5 will be modified given feedback from Reviewer 2 and a Table will be used to summarize results from Figure 4.

L272. Compared 'to' O2..   Fig6 and Fig7.   You switch to DO2 without explanation or reference elsewhere in the text and use just O2 in the caption. Also colour bars/legend required
Will change DO2 to just O_2 to avoid confusion. Will double check if legend placement/colorbar can be improved in the next revision.

All editorial comments/changes below will be addressed in the next revision of the paper.
L3. Remove repeat of 'capable'
L43. Use carbon sink (not carbon sinks)
L44. Plural gliders to remove
L56. 'Periods'
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Author's Response to Reviewer Comments 2

Journal of Ocean Science Interactive Discussion

Paper Title: *"Glider-Based Observations of CO_2 in the Labrador Sea"*

Nicolai von Oppeln-Bronikowski et al.

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Referee #2 Comments

Abstract:

- I would recommend the addition of some key figures from the text such as optode performance (precision/accuracy), response time, or length of deployment time. These are well utilised in the conclusions so could be used to entice readers within the abstract.
  Thank you – results from text have been added to the abstract.

- The justification of the IR sensors only being used on the SeaCycler is not needed in the abstract, as it is not the focus of the paper and it is not relevant to the abstract to refer to Jiang et al. paper.
  Some details will be omitted to add clarity. Also some suggestions from Reviewer 1 will be adapted here.

- The few lines discussing the Pro CV also adds to the confusion in the last few sentences when referring to "this" and "the" sensor. I also think that the questions posed in the introduction could be summarised more clearly in the abstract
  Thank you, abstract has been clarified with regards to the questions from the introduction and to avoid the confusion between mentioned sensors.

Introduction:

- I would also suggest the author look at the weather vs climate objectives for sensor performance as defined by GOAON (2nd edition).
  Thank you for the additional source. Additional mention and short sentence to be added into the text.

- Line 63 – perhaps the author could make reference to the term "foil"
  Reference added.

- Line 76 – the term "extended" with respect to the trinity bay work implies that it was continuous from the VITALS mission- however further on I understood there was some additional testing between the missions – Am I mistaken? If not perhaps the author could use re-deployed
  Corrected in text.

Data and Methods:

- Figure 1 – the caption could clarify the importance of red vs. blue boxes around the profile data.
  Figure clarified

- I would also request the profiles on the right hand side have consistent axis (x axis on the top or on the bottom).
  Done.

- Are the profiles from the SeaCycler as assuming the blue axis links them to the VITALS work, are there any shipboard CTD's to provide background for the trinity bay?
  Clarified in caption. Profiles are from glider. As per Reviewer 1, Trinity T-S structure added to the text to Figure 2.

- What is the PCO2 sensorCO2 Prototype 4797? Is this the optode? Or is it the SN57? IS this 4797 on the Sea-Cycler – is any data from this presented? Clarify why not
  4797 is the CO2 Optode Prototype sensor which had the manufacturers serial number 57. Clarified text as per Reviewer 1 suggestion

- With the Pro CV can we have some details on how it performs detailed? (e.g. the stability and accuracy calculated from the measurements?).
  The Pro CV had a zero-referencing routine that corrected the drift of the zero point of the sensor (Atamanchuk et al., 2019, supplement section.) Accuracy was given by prior calibration from the manufacturer. Additional references to explain this will be added to the text.

- Given that the Jiang study was based aboard a vessel using an underway water supply, are there more references that apply the sensor in situ?
  We are not aware of many uses of this sensor in-situ. I would gladly include them.

- If the CO2 optode underwent testing in Dalhousie University before deployment, what was the accuracy and precision also determined prior to deployment? And based on this, the optode should have been partially conditioned under the correct conditions to limit the initial drift of the optode on the glider.
  The CO2 optode deployment in VITALS was a first test and we expected stabilization issues. The factory sensor foil calibrations indicated that the sensor met accuracy specifications. In this paper we are reporting on the actual in situ behaviour of the sensor.

- Is the SN57 the Aanderaa optode?
  Yes. Clarified in text.

- The Pre-mission testing that was undertaken for the trinity bay work – was this similar undertaken for the VITALS mission? If not this might explain the conditioning timescale difference observed between VITALS and trinity bay.
  No, there was no prior comparisons done in VITALS that could be used to estimate instrument offsets. This was a motivation for the subsequent tests in Trinity Bay and the lab experiments done with the glider at Fisheries and Oceans. Clarification was added to the text.

- I was also wondering with the inconsistent drift behaviour if there was any other odd responses from other optode (oxygen) or anything noted on the optode on the post deployment calibration? Perhaps the authors could posit some theories on the behaviour for future investigations.
  There was no biofouling or other obstruction found on the sensors during recovery of the gliders. We believe that cold environment, small signal changes (low CO2 gradients) in

the VITALS mission made the sensor response slow and stability low. Also the sensor foils have a large range in performance based on the foil batch. It could be that one foil performs better than another foil calibrated at the same time and same conditions. The oxygen optode meanwhile performed really well and no discernable drift behaviour greater than the accuracy (5 umol/L) was found, although no measurements were collected upon recovery.

- Line 155 – Winkler titrations to not to my knowledge allow you to determine DIC/TA only oxygen
  Fixed in text. TA and DIC are estimated from coulometry (Johnson et al., 1993) and potentiometric titration (Mintrop et al., 2000).

- Please can you clarify the instruments used to measure DIC/TA as this may influence the precision/accuracy of these data. In addition, any information on the collection of DIC/TA (e.g. poisoning, storage medium etc).
  Instruments used include: VINDTA 3D (Versatile INstrument for the Determination of Total Alkalinity; manufactured by Marianda, Kiel, Germany) DIC analyzer connected to a coulometer (UIC, USA, model 5015O), VINDTA 3S (TA) analyzer using open cell differential potentiometry equipped with a reference (Metrohm, Canada, model 6.0729.100) and pH glass (Thermo-Orion, Canada, model 8101BNWP Ross half-cell) electrode, which were both referenced against a grounded platinum electrode. Samples were collected in the lab in 500 mL BOD bottles and were poisoned 100 uL of saturated Mercuric-Chloride ($HgCl_2$) and allowed to warm in a temperature controlled bath (25C +/- 0.1 C) before analysis.

- Line 156– please quote the constants you used for CO2SYS and the errors associated with the calculated pCO_2. These will compound any instrument specific offsets.
  We regret an error in the text. CO2calc (Robbins et al., 1999) and not CO2sys (Lewis and Wallace, 1998) was used in the determining pCO_2. In the calculation they used the CO_2 equilibrium constants from (Mehrbach et al. 1973 refit. by Dickson and Millero 1987), total boron constant (Lee et al., 2010), and $KHSO_4$ constants (Dickson 1990). The samples were analyzed in the lab. of Fisheries & Oceans Canada and at the moment they are not setup to measure the uncertainty of the pCO_2 estimate in CO2calc from DIC and TA. Reported uncertainty in the procedure for DIC and TA were 3 and 4 umol/kg respectively. I do not have access to CO2calc. Using CO2sys with above constants and to repeat the calculations with the uncertainty in TA and DIC, I arrive at an uncertainty of 4.48 uatm for lab experiment pCO_2 estimates we reference in the text.

Glider Data Processing:

- I like the idea of using the ascent/descent as the ZM from Fiedler. I believe Fiedler also used ZM's to reduced drift of the response – were the authors able to do similar?
  This is an interesting idea and could be tested in a future tank experiment. Using in-situ data it is hard to reach a conclusion on sensor drift and ways to mitigate the effect.

- Was the calibration curve used to calculate pCO2 from the foils from the pre-trinity bay mission testing or from Dariia's paper?
  Separate foil coefficients were used for both missions which were both determined in the CERC laboratory at Dalhousie. Clarified in the text.

- Was the same correction used for both VITALS and trinity bay?
  The conditioning offset from VITALS was estimated by comparison with SeaCycler. The Trinity Bay offsets were not applied as the drift was non linear and a single offset to deal with the conditioning affect was not possible to apply. The same CO2 Optode SN57 was used in both tests. Clarified in text.

Glider CO2 Optode Performance:

- I understand the authors are(quite sensibly) looking for relationships between the response time and temperature changes in situ – which is a challenge using only in situ data. The authors undertake a comparative analysis with two parameters, the temperature gradient, and the initial sensor temperature. However, I find the figure 4 (the authors way to display this) confusing. More specifically on Figure 4 – the legend for the colour bar should be next to the bar (ideally rotated) rather than at the top of the figure which implies it is the figure title.
  Figure 4 will be improved in a variety of ways:
  - We will display a variety of fits (linear least-squares, robust bi-square method as the distribution of the data is not normal but heavily tailed, median and mean responses
  - Colorbars labels will be fixed as per your suggestion

- I am also not clear on the fitted t95 – is this from the equation listed in the text in line 233?
  Yes. Will be clarified.

- The authors normalise by dividing the temperature change by 900s. I assume delta T is the minimum and maximum temperatures observed during the 900sintervals?
  Yes, will be clarified.

- I am not sure what value figure 4a brings as it is not discussed in the text in any detail.
  We understand our initial version was a bit confusing. Figure 4a shows high scatter of response time (or lack of response) at low gradients. Figure 4b shows a slight bias in initial sensor temperature. However, the color coding is perhaps not required.

- The authors then discuss the difference observed between VITALS and trinity bay data – are these both represented in figures 4?
  Yes both are in the figure. Again this will be stated more clearly in the new draft.

- If so perhaps a different shape could be used to identify the two cruises while maintaining the figures.

We will color code the different data sets with colors rather than using colorbars for the RMSE and temperature gradient as no additional information is conveyed.

- Were the response time data for VITALS collected after the sensor had become suitably conditioned to the environment? If not, this could explain the scatter over the smaller temperature gradient.
  Yes, this will be added to the text.

- Perhaps the author could expand the sentence that refers to the VITALS glider profiles vs. Trinity Bay step profiles with reference to the response time (or move the sentence closer to the paragraphs below which discuss this in the context of figure 5.)
  Sentence will be moved and expanded.

- I am also interested in the data points where the response time is above 500s and the variation in RMSE values for these. Perhaps the author could comment on what this means or speculate on why these response times were longer.
  The RMSE is larger for these on average because this data is from VITALS during weak gradients. The good fits come from occasional staircase profiles in that mission that allowed the response to equilibrate. Response times were more scattered as the sensor is not as responsive to weak gradients in temperature (CO_2) leading to large tau values for weak gradients.

- Is line 244 referring to the relationship shown in figure 4a? Perhaps referring to it in the text and also modifying the spot colour to be the initial sensor T would be helpful here.
  Figure 4b. Will be referenced.

- I am also concerned by the sentence in 246 which states there was a significant temperature dependence on response time. The previous paragraph does not demonstrate this, nor in my opinion figure 4.
  Sentence will be rephrased to talk about gradients. Also added fits will help discuss the significance of these results in the context of a variety of fits. A table will be also added to summarize the results.

- It would also be good to evaluate this in comparison to Atamanchuk's lab-based experiments they utilised t63 as opposed to t95, but it would be interesting to see the difference between a lab based experiment and an in situ determination – particularly when it appears in figure 4b you have some data collected at 0.5C.
  It is a great idea to have a lab experiment and see my earlier comment on understanding the sensor response in the Glider Processing Section. If we have another opportunity to work with the sensor your point would definitely be included in future comparisons.

- Perhaps the authors could clarify the inference from line 252 – whileCO_2 solubility may have a linear relationship with temperature, I am not convinced that is relevant to the optode response time? Perhaps the author is using this to explain the ProCV response

time? I would suggest the author rephrase to focus on the sensor response (as a whole) rather than the time taken to respond (as I think this may be their intention).
Thank you. Good point! Text will be clarified to focus on sensor response to avoid confusion. We mention the linear CO2-T relationship for completeness as another argument to validate the sensor response when true CO2 concentrations are not known.

- I am not sure if figure 5 a and b are useful plots, as the glider profiling would presumably match less precisely to the CTD-style sea cycler profiles where they remain at the same depth for 20 minutes. The scatter in the data (creating the low r2 on the linear fits) I suspect is also due to the binning implemented to try and maintain a match in data records
  Good point and I see the argument against having panels a and b. We will play around with the binning. It maybe ok to not include these.

- I also noted the low R2 values – perhaps the p-values could also be shared to demonstrate that these relationships are indeed significant and provide weight to the "linear trend" statement in line 259.
  Good point. Will be added and perhaps panels a, b removed from the Figure.

- I note the difference in the dphase range between the VITALS and Trinity bay data, yet a not dissimilar CO2 range. The temperature range is significantly wider in trinity bay yet there is no overlap in the dphase values. I was wondering if the author could additionally comment on this (is it a result of the conditioning to local conditions, indicator bleaching?) as it is mentioned only in passing in line 260.
  This is an excellent point and question. We are speculating at this point and not sure for certain what changes the range in the foil angles. This is something we can mention more clearly in the text.

O2-CO2 Observations:

- Please rephrase line 276, as "weak in an average sense" doesn't make sense to me.
  Numbers added to clarify sentence

- Figure 7 – the K1 mooring and SeaCycler locations are denoted I think by red and blue lines respectively – these are used within the colour scheme-perhaps white or gray could be considered as alternatives? The O2 data doesn't have the glider profiles used for plotting on? The oxygen data demonstrates the suitability of the multi-platform approach to in situ calibration
  Figure will be modified for legibility and clarity.

- Spatial and Temporal Variability Line 310 – please remove the word "somewhat". I would also advise using numbers to make your point clearer.
  Done and numbers added

- Take care as figure 9/10the legend appears to obscure data points at the start of a track. Perhaps the legend would be better suited on the right-hand side, or outside the plot.
  The legend was placed to avoid masking observations by the glider, but we are happy to move the legend outside the figure for clarity

- The following sentence is also a bit vague – potential CO2 cycling? Perhaps the authors could clarify what they mean by this.
  Will be clarified. In the text we discuss fine-scale temperature variability, which can contribute to fine-scale variability of CO2 sinks. The complex dynamics that drive ML and below MLD CO2 variability are unfortunately out of scope for this paper.

Conclusions:

- I would also suggest the author clarify the timescale of the temperature change in line 392 (is it0.5 degrees over the 123.59 seconds?)
  Yes 123.59 seconds is the average time constant we determined from the in-situ data which corresponds to gradients of 0.5 deg C. We will pay attention to the text to clear up any confusing bits.

- I would also suggest that the author summarise some of the extra work, mentioned throughout the rest of the paper as a forward look(e.g. more tests to evaluate the influence of flow field on sensor performance in situ and a response time model?)
  Excellent suggestion and the comments provided to the Methods and Sensor Response sections will serve as a good starting point.

Following editorial changes were directly implemented

- Line 179 – remove Also.
- Line 198– correct to " the sensor began to display inconsistent behaviour..." (or similar)
- Line198 – I would also change the word last to final, as this is clearer as the end of the experiment, rather than a relative statement.
- Line 360 -I think it should read "highly variable changes" not "highly varying".
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- Perhaps the term "staircase missions" could be used in the sections where the authors refer to step profiling to maintain consistency with the conclusion.

Glider-Based Observations of CO_2 in the Labrador Sea

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Abstract. Ocean gliders can provide high spatial and temporal resolution data and target specific ocean regions at a low cost compared to ship-based measurements. An important gap, however, given the need for carbon measurements, is the lack of capable sensors for glider-based CO_2 measurements. We need to develop robust methods to evaluate novel CO_2 sensors for gliders. Here we present results from testing the performance of a novel CO_2 optode sensor (Atamanchuk et al., 2014), deployed on a Slocum glider, in the Labrador Sea and on the Newfoundland Shelf. ~~We demonstrate our concept of validating data from this novel sensor during a long glider deployment using a secondary autonomous observing platform – the SeaCycler. Comparing databetween different sensors and observing platforms can improve data quality and identify problems such as sensor drift. SeaCycler carried an extensively tested gas analyzer: the Pro-Oceanus's CO_2-Pro CV, as part of its instrument float. The CO_2-Pro CV has shown stable performance during lengthy observations e.g.(Jiang et al., 2014), but has a slow response time for continuous profiling, and its power consumption is not affordable for glider operations. This CO_2~~ This paper (1) investigates the performance of the CO_2 optode on two glider deployments; (2) demonstrates the utility of using the autonomous SeaCycler profiler mooring (Send et al., 2013; Atamanchuk et al., 2020) to improve in-situ sensor data; and (3) presents data from moored and mobile platforms to resolve fine scales of temporal and spatial variability of O_2 and pCO_2 in the Labrador Sea. The Aanderaa CO_2 optode is an early prototype sensor that has not undergone rigorous testing on a glider ~~,~~ but is compact and uses little power. ~~This paper summarizes the test results for this sensor on a Slocum glider. We capture the performance of the sensor, and for the Labrador Sea mission, comparing the glider data against the SeaCycler 's measurements to compute an in-situ correction for the optode. We use the referenced data set to investigate trends in spatial and temporal variability captured by~~ Our analysis shows that the sensor suffers from instability and slow response times(τ_{95}>100 s), affected by different behaviour in weak (<0.1 °C) vs. strong (>10 °C) temperature gradients. We compare the glider data with the SeaCycler O_2 and CO_2 data and estimate the glider data ~~, pointing~~ uncertainty as $\pm$ 6.14 μM and $\pm$ 44.01 μatm respectively. From the Labrador Sea data, we point to short time ~~and distances scales as~~ (<7 days) and distances (<15 km) scales as important drivers of change in this region.

1 Introduction

The ocean plays a crucial role in absorbing the effects of changes to the Earth's atmospheric composition due to anthropogenic activities. Roughly one-third of all human-made CO_2 (C_{ant}) released into the atmosphere since the beginning of the industrial revolution has been taken up by the ocean, a total of 155 ± 31 GtC as of 2010 (Khatiwala et al., 2013). For the decade 2009–2018 alone, the global ocean carbon sink absorbed 2.5 ± 0.6 GtC·yr^{-1}, against fossil fuel emissions of 9.5 ± 0.5 GtC·yr^{-1} (Friedlingstein et al., 2019). Ocean carbon sinks are not equally distributed across the globe. Very intense carbon sinks and regions of anthropogenic carbon storage are located in subpolar ocean regions (Volk and Hoffert, 1985; Sabine et al., 2004), such as the Labrador Sea in the North Atlantic (DeGrandpre et al., 2006) and the Southern Ocean's Weddell Sea (van Heuven et al., 2014). Deep mixing in these regions is adding anthropogenic carbon to the deep ocean water mass transports, linking these high-latitude carbon pumps to the global ocean (Broecker, 1991; Fontela et al., 2016). Increased carbon storage in the ocean ~~, has~~has, over the past decades, caused pH levels to drop in many places (Doney et al., 2009), at a rate of change that is faster than found in the geological record (Zeebe et al., 2016). Resulting ocean acidification (OA) has already severely impacted marine habitats ~~around the world~~worldwide, including such important ecosystems as the Great Barrier Reef (Cohen and Holcomb, 2009; Guinotte and Fabry, 2009).

Predicting shifts in future carbon uptake scenarios requires ~~an in-depth~~ a detailed understanding of the processes driving uptake and distribution of absorbed carbon ~~,~~ across all oceanic scales. We need to advance the global ocean carbon measurement system because existing observations are limited in coverage and quality (Borges et al., 2010; Okazaki et al., 2017). There have been recent advances in autonomous sampling strategies to expand, improve and build-on existing global biogeochemical observing networks (Johnson et al., 2009). The existing Argo float program is ~~being expanded to include~~ expanding, including biogeochemical (BGC-Argo) sensors measuring oxygen, nitrate, chlorophyll, turbidity, irradiance and pH. BGC-Argo ~~is aimed at observing~~ aims to observe seasonal to decadal-scale variability, although currently only about 8% of Argo floats are equipped with biogeochemical sensors (Johnson et al., 2017; Li et al., 2019). Improvements in resolution and frequency of surface CO_2 measurements have also ~~been made with the development of~~ come from developing stable ship-based in-situ measurement systems installed on container ships and tankers with regular routes across ocean basins. These results made possible the creation of a 1° global resolution (up to 1/4° coastal zones) Surface Ocean CO_2 Atlas (Bakker et al., 2016). However, these data do not provide ~~researchers with the information at depth~~ at-depth information needed to understand the localized processes that drive and shape the strength of carbon sink regions such as the Labrador Sea. Advances in glider technology and sensors (Rudnick, 2016; Testor et al., 2019) can help address those gaps.

Advancing glider-based measurements of CO_2 requires addressing key issues such as stability, responsiveness, compactness and ~~power-consumption~~power consumption. (Clarke et al., 2017a, b; Fritzsche et al., 2018). Another important factor is to ascertain the uncertainty of sensor-based observations (Newton et al., 2015). So far, most carbon glider observations are limited to testing, and there remain concerns about data quality. The most mature and commonly used type of in-situ CO_2 probe is based on infrared (IR) detection, such as the CONTROS Hydro C™ or Pro Oceanus CO_2-Pro CV™ sensors. Unfortunately, commercial IR based detection systems are not yet small enough to easily fit ~~on~~ existing gliders or float designs. Long equilibration times make profiling ~~application~~ applications of sensors extremely challenging, requiring detailed knowledge of response times and data processing (Fiedler et al., 2013; Atamanchuk et al., 2020). These sensors are also very power hungry compared to other sensors like optodes or CTD's, making battery-powered deployments challenging even for moored applications. Another approach to determining in-situ CO_2 is through pH measurements using established Total Alkalinity (TA) and Salinity (S) relationships (Takeshita et al., 2014). Saba et al. (2018) applied a novel ISFET pH sensor (Johnson et al., 2016) developed by MBARI with help from Sea-Bird Scientific on a glider. These tests showed remarkable response time characteristics and stability over periods of several weeks or longer.

Another candidate for glider carbon observations is the Aanderaa CO_2 optode sensor (Atamanchuk et al., 2014). It is nearly identical in size and power consumption to the commonly used oxygen optode by the same company but lacks prior glider testing. The optode detects the luminescent-quenching response from a CO_2 sensitive membrane. In general, there are multiple challenges to using photo-chemical sensors on profiling applications Bittig et al. (2014): (1) placement of the sensor on the glider dictates boundary layer thickness and response time; (2) response time is non-linearly temperature-dependent and steep temperature gradients induce additive error; and (3) the sensor is highly dependent on prior foil calibration and can suffer from drift. In particular, the foil design has multiple temperature-dependent rate-limiting processes inside the foil to sense the ambient change in pH, which ~~is correlated~~ relates to changes in pCO_2 (~~S. M. Borisov,~~ Sergey Borisov, sergey.borisov@tugraz.at, *personal communications*). On the upside, the CO_2 optode is an attractive candidate for gliders ~~,~~ due to its small size, ease of integration, and low power consumption, all similar to the Aanderaa oxygen optode. Because of the need for increased spatial and temporal resolution of CO_2 observations and the advantages gliders offer compared to other methods, assessing the CO_2 optode on a glider is an important step in furthering community knowledge on the current state of mobile CO_2 system technology.

In 2016, as part of the Ventilations, Interactions and Transports Across the Labrador Sea (VITALS) project, we devised an observing strategy to carry out novel in-situ observations to ~~:~~ (1) ~~Reach~~ reach the deep convection region with a glider to carry out sampling with the novel foil-based pCO_2 sensor from Aanderaa with minimal ship resources for launch and recovery~~.~~ ; and (2) ~~Use~~ use measurements provided by an autonomous moored profiler - the SeaCycler (Send et al., 2013), carrying the larger payload CO_2-Pro CV instrument for glider in-situ calibration points. This mission attempted to use a moored sensing platform as an in-situ reference point for experimental sensors deployed on a glider to advance data quality and coherence of novel biogeochemical measurements. ~~This is an important step~~ As technology plays a catch-up game, such mission concepts will be important in the next steps towards targeted oceanic carbon measurements~~as technology is playing a catch-up game~~. We re-deployed the glider in September 2018 on the Newfoundland Shelf, in Trinity Bay, to further test the concepts from VITALS, flying the glider near a small fishing boat from which reference casts were taken using a similar ~~Pro~~ CO_2-Pro CV instrument. We utilize these two real ocean deployments to improve sensor characterization and the quality of the collected data. In this paper, we present the data and our analysis and discussion around three central questions:

- How suitable is the CO_2 optode for glider-based applications?

- How can multiple autonomous platforms be used to improve sensor data?

– How can combined data from moored and mobile platforms resolve scales of temporal and spatial variability?

Addressing these questions should improve and shape our ~~current~~ plans for carbon observing systems utilizing glider and other platforms, especially as new sensors, are being developed.

2 Data and Methods

2.1 Labrador Sea Deployment

In ~~the Fall~~ fall 2016, a moored vertical profiler, the SeaCycler (Send et al., 2013; Atamanchuk et al., 2020) and a G2 Slocum glider were deployed into the central Labrador Sea near the longtime German deep convection mooring K1 (Figure 1). The K1 mooring, located about 25 km west of former OWS BRAVO (Avsic et al., 2006), has been deployed biennially since 1994 to monitor activity in the central deep convection patch in the Labrador Sea (Lavender et al., 2002; Koelling et al., 2017). The objective of VITALS was to characterize the spatial and temporal structure of oxygen and CO_2 in the deep convection zone. Other activity in conjunction with VITALS, included a hydrographic section AR7W maintained by the Bedford Institute of Oceanography (BIO) and Argo floats released with several profiles captured near the SeaCycler site and the glider deployment area. Many observing efforts came together, utilizing multiple complementary efforts across different scientific programs, relying on ~~both~~ traditional and novel observational approaches.

The SeaCycler was deployed near 52.22°W and 56.82°N, 30 km away from the German deep convection mooring K1 (52.66°W and 56.56°N) to improve the vertical and temporal characterization of O_2 and CO_2 cycling in this region. The SeaCycler operation and deployment techniques are described in Send et al. (2013). It has an underwater winch assembly, parked at 160 m depth with an instrument float that can profile the top 150 m. A tethered communication allows for two-way telemetry over Iridium Satellite. Below the winch assembly, a single-point mooring line with instruments continues to the ocean depth of approximately 3500 m. For this deployment, the instrument float carried a CTD, velocity and various gas sensors, including oxygen sensors (Sea-Bird 43, Sea-Bird 63, Aanderaa 4330) and CO_2 optode prototype sensor 4797 as well as membrane equilibrator-based infrared (IR) CO_2 gas analyzer CO_2-Pro CV, based on non-dispersive infrared refraction (NDIR) technology made by Pro Oceanus Ltd, Canada (www.pro-oceanus.com). Previous tests with ~~this sensor~~ a similar sensor design showed excellent stability in multi-month vessel-underway missions (Jiang et al., 2014). The instrument float collected data over the top 150 m of ocean depth with an average resolution of 0.3 m from June 2016 to May 2017, while the Pro CV was sampling for 20 minutes at selected stop depths (10, 30, 60, 120 m) to allow equilibration with ambient seawater pCO_2. These stops resembled bottle stops done from ships with the water rosette to validate new sensors. The K1 mooring was also equipped with oxygen sensors to allow for later cross mooring comparisons. The SeaCycler data were corrected for sensor drift using pre- and post-deployment calibration of the sensors (Atamanchuk et al., 2020). The oxygen data were also corrected for a response time delay using the response time values from Bittig et al. (2014) and the algorithm described in Miloshevich et al. (2004). Overall the accuracy of the oxygen data was 2.89±4.17 ~~μM~~ µM based on residuals between the upcast and discrete downcast data. The Pro CV had a zero-referencing routine that corrected the drift of the zero-point of the sensor Atamanchuk et al. (2020)

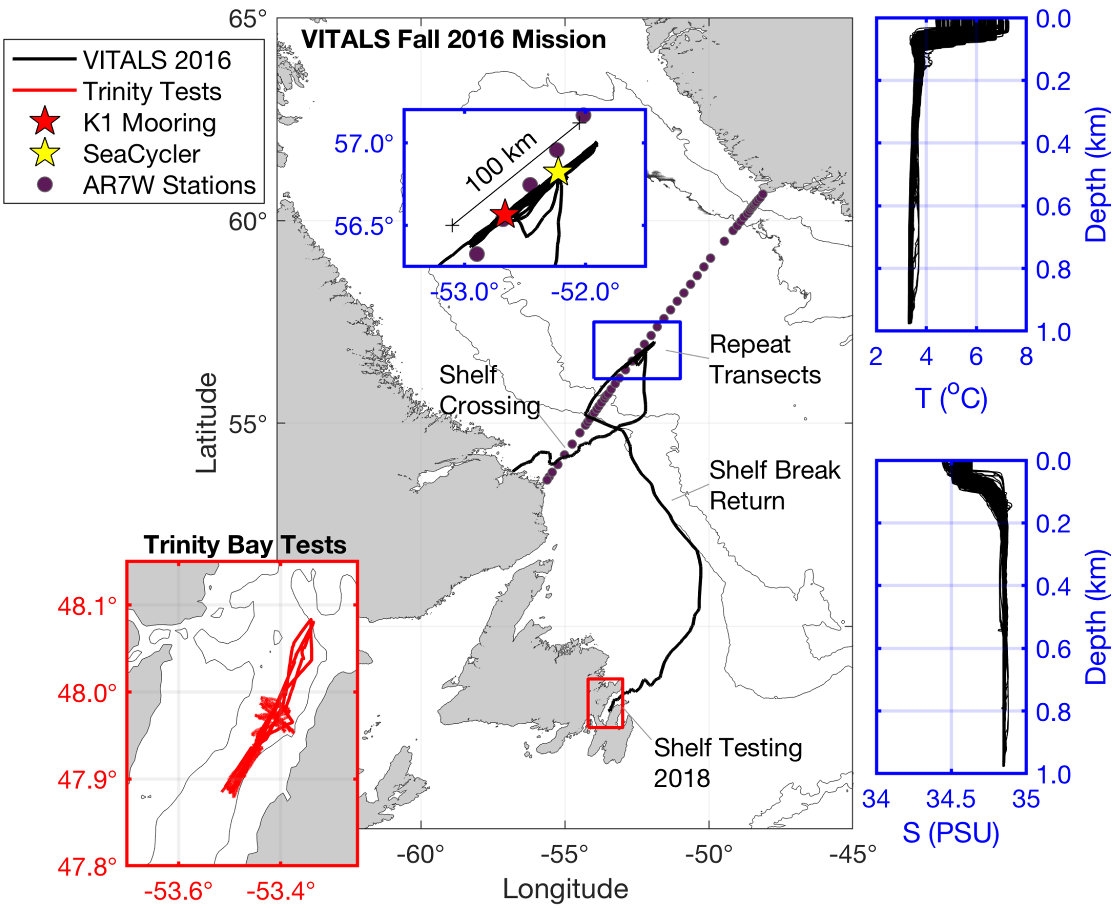

Figure 1. Map of data collection sites: main map (center) shows Ventilation, Interaction and Transport Across the Labrador Sea (VITALS) glider track with blue inset focusing on the repeat transects along the AR7W line. Contours are the 1500 m and 3000 m isobaths. Highlighted in blue are also the corresponding T–S profiles collected by the glider in that time period. The red inset map in the lower left shows the glider track from the 2018 glider CO_2 optode tests conducted in Trinity Bay, NL.

. Fully-equilibrated pCO_2 data were obtained by averaging the last ~~30 seconds~~ 30s of the measurements at each stop depth. Accuracy of pCO_2 data was determined from the accuracy of the instrument, i.e., 0.5 % ~~of the total range and a precision of 0.01 ppm~~over the full range (0–1000 μatm) with an initial manufacturer quoted accuracy of ± 2 μatm.

The glider (Unit 473) was deployed from the Labrador shelf to reach the K1 – SeaCycler site and complete 30 to 100 km long transects between the two moorings, collecting high-resolution spatial data. The glider was launched near Cartwright, Labrador, from a small fishing boat and reached the deep convection zone near K1 and SeaCycler early in October, sampling there until November 22. In total, the glider completed 18 full transects collecting valuable hydrographic and gas data. The modified glider with an extended battery bay carried Sea-Bird glider payload CTD and the Aanderaa Data Instruments (AADI)

CO_2 optode prototype sensor (model 4797) described in Atamanchuk et al. (2014), and the well established Aanderaa oxygen Optode (Tengberg et al., 2006) model 4831, SN 333. ~~Initial accuracy of the Glider CTD from the manufacturer calibration sheet~~ Glider CTD manufacturer calibration showed an initial accuracy better than ±0.0005 S/M, ±0.005 °C and 0.1% of the total pressure range. ~~Initial~~ The initial accuracy of the calibrated O_2 optode from the manufacturer was better than $\pm$ 4 μM. Accuracy of the CO_2 optode pre-deployment was unknown, but the accuracy range in Atamanchuk et al. (2014) is between ± 2–75 ~~μatm~~μatm. The CO_2 optode (SN57) was equipped with a standard foil to enhance deployment stability. These optode sensors were mounted in the aft cone of the vehicle. Also, a thruster was installed to speed up the ~~crossing of the shelfand to~~ shelf's crossing and enable staircase profile sampling. The glider sampled in the central Labrador Sea ~~deployment location~~ for two months, limiting CO_2 optode profiles to the top 200 m to save energy. In December, the glider began its journey back to Newfoundland following the 1500 m isobath inside the Labrador Current and reaching Trinity Bay (see map) on December 31, 2016. The glider was flown along the shelf break to take advantage of the southward flowing Labrador Current. Before deployment on the glider, the CO_2 optode underwent testing at the CERC.OCEAN laboratory at Dalhousie University to determine the calibration model fit for the optode sensor foil.

2.2 Trinity Bay Tests

After ~~completion of~~ completing the VITALS mission, to further test all the characteristics of the new CO_2 optode under glider profiling tests, we conducted another study in Trinity Bay, Newfoundland. Trinity Bay is a deep inlet (up to 600 m) and can be reached easily from various coastal communities from a fishing boat. It is fed primarily by the cold Labrador Current waters and river runoff from the western side, making its surface waters fresh and deeper portions cold and highly oxygenated and nutrient-rich. The pooling of water in the deeper portion and surface freshwater support a stable density stratification (Schillinger et al., 2000; Tittensor et al., 2002). Especially interesting for our optode tests are the large temperature gradients in the vertical of over ~~14°~~14 °C between the surface and 75 m depth. Trinity Bay has a cold water lens ~~−1°~~-1 °C between 70 m to 200 m depth (Figure 2d), and temperatures below ~~1°~~1 °C from 200 m to the bottom. In Trinity Bay, profiling through this lens leads to absolute temperature gradients of ~~10°~~10 °C or more in 200 ~~seconds~~ s or less.

In Trinity Bay, we repeated the VITALS data comparison experiment on a smaller scale ~~, without the use of~~ without using a SeaCycler. To collect in-situ reference samples, we used a winch operated Sea-Bird 19+ V2 CTD mounted on a frame, together with a O_2 Optode (Model 4831, SN 333) and a CO_2-Pro CV. We repeated staircase missions as in VITALS and did extensive calibration of the sensor ~~prior to~~ before and after the deployment. The glider was deployed from September 4–16, 2018. The setups for the external winch-operated CTD and glider are summarized in Figures 2a and 2b.

Pre-mission laboratory testing of the sensor and the glider allowed for instrument data quality control in this mission. ~~We calibrated the~~ The glider CO_2 and O_2 optode sensors were calibrated at the CERC.OCEAN laboratory at Dalhousie University using a double-walled test tank, with simultaneous O_2 and CO_2 supply for rapid step changes in these variables. ~~We recorded the optode~~ The optode sensor response in the range of ~~−1.8°~~-1.8 °C to 20 °C and O_2 concentrations ranging from 0 to 120% saturation and CO_2 concentrations from 100 to 3000 μatm were used to compute the CO_2 optode foil coefficients. Tests were initially done in freshwater and repeated for 35 ppt ~~NaCl solution. From this tank calibration exercise, new fits for the O_2 and~~

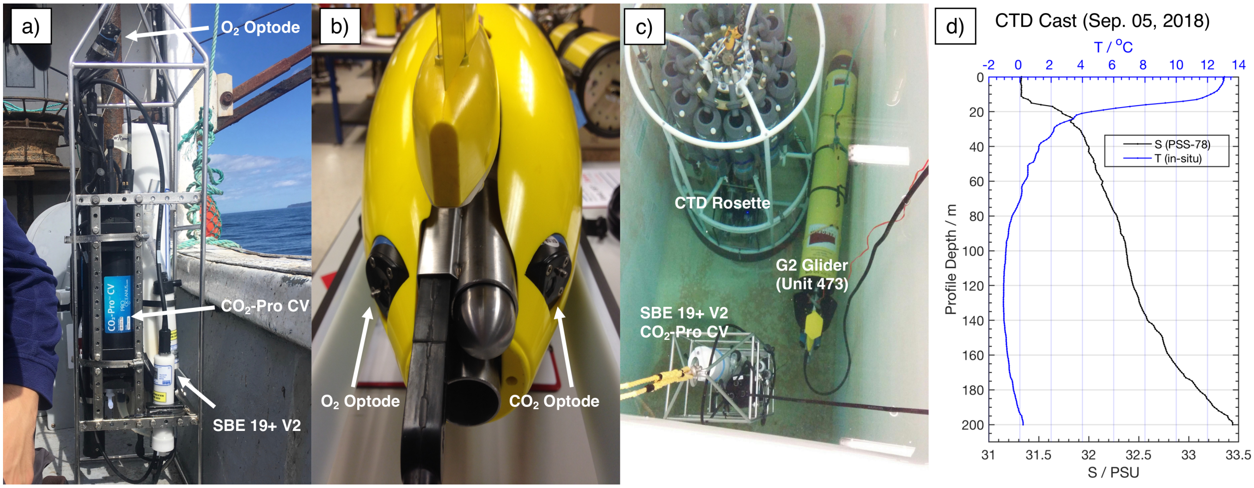

Figure 2. (a) Trinity Bay test reference CTD, (b) glider setup~~and~~ , (c) equipment tank testing in progress ~~.~~and (d) Average T–S structure observed from shipboard casts on September 5, 2018.

Table 1. Sensor offsets from DFO Tank Tests August 27, 2018

(parameter)	($\bar{x} \pm 1$ STD)	(units)	(sensor make)
Slocum glider (Unit 473)			
T	0.0024 ± 0.0555	°C	SBE41cp
C	0.0019 ± 0.0033	S/m	"
O_2	14.05 ± 0.66	μM	Aanderaa 4831
CO_2	-461.14 ± 10.28	μatm	Aanderaa 4979
CTD–Pro CV system			
T	0.0255 ± 0.0555	°C	SBE19+ V2
C	0.0033 ± 0.0033	S/m	"
O_2	25.95 ± 0.66	μM	Aanderaa 4831
CO_2^*	-51.45 ± 10.28	μatm	Pro CV

*Note: CO_2-Pro CV was located close to the tank's inlet which could be the cause of the large offset.

~~CO_2 foils were recorded inside the sensor. Furthermore, tests of all sensors together were done at the special~~ NaCl solution. Further, tests of glider sensors together with the CTD-Pro CV setup were done inside a saltwater tank at the Department of Fisheries and Oceans (DFO) in St. John's, Canada. The tank ~~facility is large enough to allow~~ allows simultaneously submerging the glider, CTD-Pro CV setup and a ~~reference CTD rosette from DFO with an~~ CTD–rosette (SBE9~~CTD, SBE 43 O_2 Sensor and~~) with Niskin bottles to ~~collect O_2 and pCO_2 reference samples for the instruments. Winkler titrations were performed on~~

~~the Niskin samples to get reference oxygen, DIC and TAconcentrations. DICand TA were converted to pCO_2 using CO2SYS (Lewis et al., 1998). From these measurements and tank calibration exercises, we computed instrument-specific offsets . For the glider we found CTD residuals were -0.022~~ obtain reference O_2, TA, DIC, T, S data. A summary of the water sample analysis and uncertainty is given in Appendix A. Based on the tank tests, we estimate initial sensor offsets for the glider and the CTD-Pro CV. Table 1 summarizes results from the DFO tank tests. Reported uncertainties are combined uncertainty of the measured offsets ($\bar{x}$) from tank tests, including the uncertainty from the lab-based results ($\pm$ ~~0.0445 $°C$ and -0.081 $\pm$ 0.0153 S/m. For the O_2 optode (SN 333) we found offsets of 13.26 $\pm$ 0.493 μM.~~ 1 STD) and the manufacturer's sensor accuracy. STD in the text refers to the sample standard deviation. A picture of tank testing in progress is shown in Figure 2c. The location of the CO_2-Pro CV (bottom left) during the tank tests is close to an inlet, which may have caused a noticeable difference in CO_2 values. Before the deployment, we find an initial offset of -461.14 μatm for the glider CO_2 optode. However, the sensor had not yet undergone conditioning. Other sensors (CTD,O_2 optode) show good agreement between each other and with the collected water samples giving a good initial reference for the sensors.

2.3 Glider Data Processing

We processed glider science data, correcting the CTD-data for temperature-induced sensor lag, applying sequential comparison between glider profiles Garau et al. (2011). To correct ~~for~~ the phase response lag in the glider oxygen data, we applied the model published in Bittig et al. (2014) using raw sensor phase angle output. Instead of using the built-in optode thermistor, we used the lag-corrected CTD temperature readings interpolated to the optode measurements as in Gourcuff (2014). From the corrected phase readings, we computed the molar oxygen concentrations (μ~~mol L^{-1}~~M or μmol/L) using (Uchida et al., 2008), with fit constants from a prior optode tank calibration. Trinity Bay, tank test and ship-based CTD profiles provided further calibration points at the start and end of the deployment.

For the CO_2 optode, there was some literature available for temperature-dependent response time corrections (Bittig et al., 2014)~~, but~~. However, each sensor has its ~~own~~ response time characteristic that ~~has to be determined prior to~~ must be determined before any field deployments. Due to the DLR technique in the foil and available field results, the sensor response is larger than the O_2 optode, which uses more straightforward foil chemistry. To correct for the long response time behaviour, we used a sequential time-lag correction (Equation 1) approach (Miloshevich et al., 2004), recently applied for an equilibrator type NDIR gas instrument (Fiedler et al., 2013). In Fiedler et al. (2013), the NDIR instrument was mounted on a profiling float, and response times are calculated to be on the order of ~~100–300 seconds~~ 100–300s between surface and depth measurements.

$$c_{i+1}^{\text{cor}} = \frac{c_{i+1}^{\text{in situ}} - [c_i^{\text{in situ}} \exp(-\Delta t/\tau)]}{1 - exp(-\Delta t/\tau)} \quad (1)$$

Here $c^{\text{in situ}}$ is the raw and c^{cor} is the corrected sensor output at each time step i. The time constant τ can be computed by fitting an exponential model to the sensor response $x(t)$ (Equation 2) using fitting constants a, b at each time interval dt.

$$x(t) = (a - b)\exp(-dt/\tau) + b \quad (2)$$

Atamanchuk et al. (2014) provided a few values for the response time. Temperatures were much warmer than found in the Labrador Sea or Trinity Bay and did not provide response characterization for varying temperature gradients. Fiedler et al. (2013) used an exponential model (Equation 2) to compare his NDIR sensors response to zero-measurements (ZM). During ZM's, the sensor strips the gas stream of CO_2, and the resulting reading should be zero. The time response of the sensor and resulting reading after ZM were used to gauge the ~~response of the sensor~~sensor's response to smaller gas gradients and drift of the gas detector itself. Because the optode sensor does not have the internal capability for independent referencing of the foil chemistry, we fitted the equation to the sensor response ~~,~~ while the glider ~~was ascending or descending~~ ascended or descended through the thermocline. Repeating this procedure for both glider deployments, we computed a temperature and response time-dependent set of values.

The staircase glider profiles in Trinity Bay were ~~especially useful for extracting~~ performed to help characterize sensor response to a broader set of positive and negative temperature gradients. Staircase profiles Figure 3, shows the least-squares fit for a single temperature gradient and optode response excursion. To compute the partial pressure of CO_2 (pCO_2) in micro-atmospheres (μatm) from the sensors corrected phase readings, we applied a calibration fit model from previous tank ~~tests~~ calibration done at CERC.OCEAN laboratory at Dalhousie University as was done in previous deployments of this sensor (Atamanchuk et al., 2015; Peeters et al., 2016). A testing regime of temperature and molar xCO_2 concentrations step changes, and sensors phase response readings were used to compute an 8-degree phase and 3-degree temperature model fit, which we applied to the sensor. The sensor data and calibration coefficients are available online (von Oppeln-Bronikowski, 2019).

The CO_2 optode sensor exhibits noticeable conditioning behaviour (Atamanchuk et al., 2015). ~~For the~~ After the sensor stabilized, we subtracted an offset (1275 μatm) for the VITALS deployment, based on the surface SeaCycler and atmospheric data, ~~we subtracted an offset (1275 μatm)~~ to correct the ~~sensor after the sensor stabilized~~ optode sensor to ambient conditions. We estimated the time scale of conditioning by fitting an exponential curve to the optode data to find the time constant at which the sensor response plateaued. In the VITALS deployment, conditioning took ~~about~~ almost a month into the deployment, while in Trinity Bay tests, the sensor response stabilized after ~~roughly a week (~~four days (offset of 994 μatm). ~~Towards the end~~ During the last 1.5 days of the Trinity Bay ~~mission~~tests, the sensor ~~began to display~~ displayed inconsistent behaviour with depth. Data from the final 1.5 days ~~was~~ were excluded from further analysis. It is not clear what caused this change in the ~~sensors response.~~ sensor's response. Perhaps cold temperatures in Trinity Bay (<-1°C) caused the foil to degrade.

To help with visualization, we bin averaged the data and mapped the data along isopycnals. For some cross-sectional plots, we also averaged data in depth-space or depth-time sections. To account for the gaps in observations, we preserved gaps larger than 10 km and more prolonged than 4 days. Smaller gaps were linearly interpolated. A 3D boxcar filter was applied to smooth 5 km in the horizontal, 5 m depth, and 3-day in time, keeping with the observing gaps in the data because the glider occupied a section between K1 and SeaCycler every 2 to 3 days and gaps between profiles were 3 km on average.

To grid the sparse O_2 and pCO_2 glider observations for spatial-temporal data inter-comparison with SeaCycler, we deviated from linear interpolation. We used an objective interpolation method using a second-degree polynomial fitting distance weighting scheme following Goodin et al. (1979). We gridded the sparse data on a 1-km by 1-day grid and then ~~interpolating~~ interpolated the data using an exponential weighting function $\exp\left(R_x^{-2} + R_y^{-2}\right)$ to fill in gaps. We determined influence radii

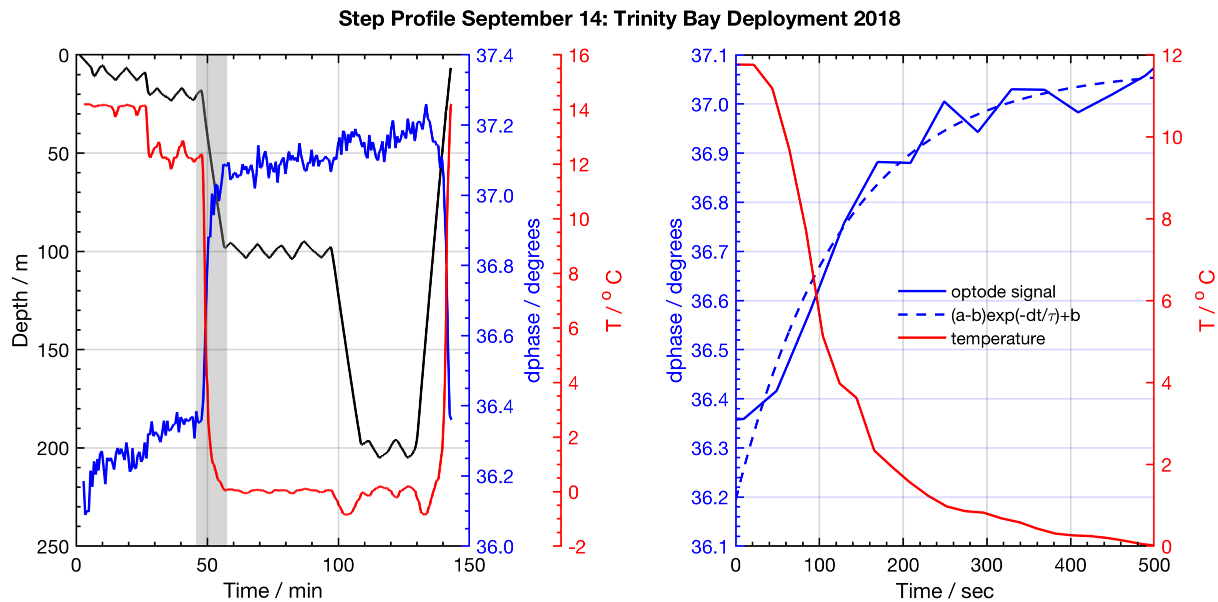

Figure 3. Example of a staircase profile used to quantify response time characteristics. Left panel shows glider staircase profile (black) overlaid with glider CTD temperature (red) and CO_2 optode signal (blue). Grey shaded area highlights an example episode of sensor response, shown in the right panel used to quantify the sensors response time and correct glider profiles. The exponential fit to the CO_2 optode response is shown (dashed blue line).

of approximately 5 km for O_2 and 20 km for pCO_2 measurements and cutoffs at 10 and 40 km respectively, based on the number of glider observations in the horizontal and along the time dimension. We set the cutoff radius at twice the spatial scale. Temporal scales are similar between the two data sets with an influence radius of 3 days and a cutoff of 6 days.

2.4 Shipboard CTD and Pro CV Casts

The Trinity Bay Tests CTD profiles together with O_2 optode and data from the Pro CV were processed by checking for outliers in the profiles. Despite the use of a pump, the Pro CV showed long signal equilibration periods (τ_{95} between 10 to 15 min). To compute the CO_2 levels for each time the CTD was parked at depth, we took the average of the CO_2-Pro CV values, once readings stabilized to within $\pm$ 6 ppm or twice the manufacturer's quoted instrument accuracy (0.5% of the total range 0 - 600 ppm). We developed a simple script that identified the first time window when the difference in sensor readings reached $\Delta CO_2 \leq 6$ ppm. Pro CV ZM~~was~~'s were subtracted from bottle stops to arrive at a high-quality in-situ referenced data set. We ~~also~~ calculated the standard deviation ~~of each~~ for each set of averaged Pro CV ~~measurement~~ measurements and flagged any data points as outliers when the standard deviation exceeded $\pm$ 6 ppm. Those data points were not included in the sensor data comparisons.

3 Results and Discussion

3.1 Glider-based CO_2 Optode Performance

~~Prior to this mission~~Before this study, the CO_2 optode ~~had not been tested~~ response had not studied on a glider, and little information was available about its response-time characteristics when profiling. We ~~assessed~~ assess the sensor response time ~~,~~ by fitting the raw "dphase" sensor signal (~~dphase) (~~ϕ_{DLR}) with ~~an exponential model , $x(t) = (a-b)\exp(-dt/\tau)+b$. Here $x(t)$ is the raw sensor signal; a and b are constants, dt is the time interval in seconds, and τ is the e-folding scale or the response time. Commonly, we define the signal response time , as the time for a signal to reach a specific strength as a percentage of total true signal, we used~~ the earlier described exponential model (Equation 2) during periods when the glider traversed through temperature gradients. From Equation 2, we use a response time definition of τ_{95}, ~~that is~~ which is the time to reach 95% of the total signal level. The larger ~~the~~ a sensors τ value, the longer it takes the sensor to ~~equilibrate to~~ respond to a change in ambient conditions. ~~Given the many hundreds of vertical profiles as well as the staircase profiles taken during the~~ We use regular yo and staircase profiles from VITALS and Trinity Bay missions ~~, we can~~ to do a comparative analysis of the sensor response time ~~bias against temperature gradient and initial sensor temperature.~~ against observed temperature gradients (ΔT). The VITALS data are regular glider profiles (yo's). Only a few staircase profiles from VITALS were available and were of low quality and are excluded from this analysis. The Trinity data are mostly regular yo's with nine staircase profiles from 3 days during the deployment (e.g. Figure 3). For both glider tests, we used data for the period after which the sensor had become conditioned to the environment as described earlier.

~~Figure 4~~

Figure 4a shows the result of response time fitting against the temperature gradient (ΔT) normalized by the total time of traversing the gradient (dt) and the sensor response (e.g. $\tau_{95,\mathrm{normalized}} = \tau_{95}/\Delta T \times 900$ ~~)~~s). We define ΔT as the total temperature change observed in the interval. ~~Panel 4a colour indicates the magnitude of root mean square error (RMSE) of least squares data fitting. In panel 4b, color represents the temperature gradient.~~ We multiply normalized values by 900 ~~seconds~~ s or 15 min to arrive at a set of equally referenced temperature gradient and response time values, all corresponding to the same time interval. We chose this interval based on the response time (~~$\tau_{95} \approx 15$~~ $\tau_{95} \approx 15$ min) of the reference sensing system used in the deployments, the Pro CV. We ~~exclude RMSE errors in fits larger than 0.1 (mean is 0.0322 with a standard deviation of 0.0205). There is a strong bias in the~~ excluded data from time segments shorter than 60 s, longer than 60 min, and τ_{95}>900 s. The VITALS data show increased τ_{95} value scatter for small temperature gradients with no noticeable trend in temperature. The Trinity Bay tests reveal a slight bias in increasing response times with negative temperature gradients. This would indicate the sensor performs better during upcasts than downcasts. We show linear least-squares fits through the Trinity Bay data points, ignoring VITALS data large scatter in the fitting result. Figure 4b summarizes the response time between ~~warm and cold temperatures, based on the large temperature gradients in Trinity Bay (< 10°C).~~ the deployments. The Trinity data is further divided into the staircase profiles and regular yo's. Contrary to our expectation, the staircase profiles did not noticeably reduce the spread of response times compared to regular yo's. A possible explanation is that the staircase profiles are close to when the sensor was still conditioning, and when the sensor began to show an strange response near the end of the mission. Only one

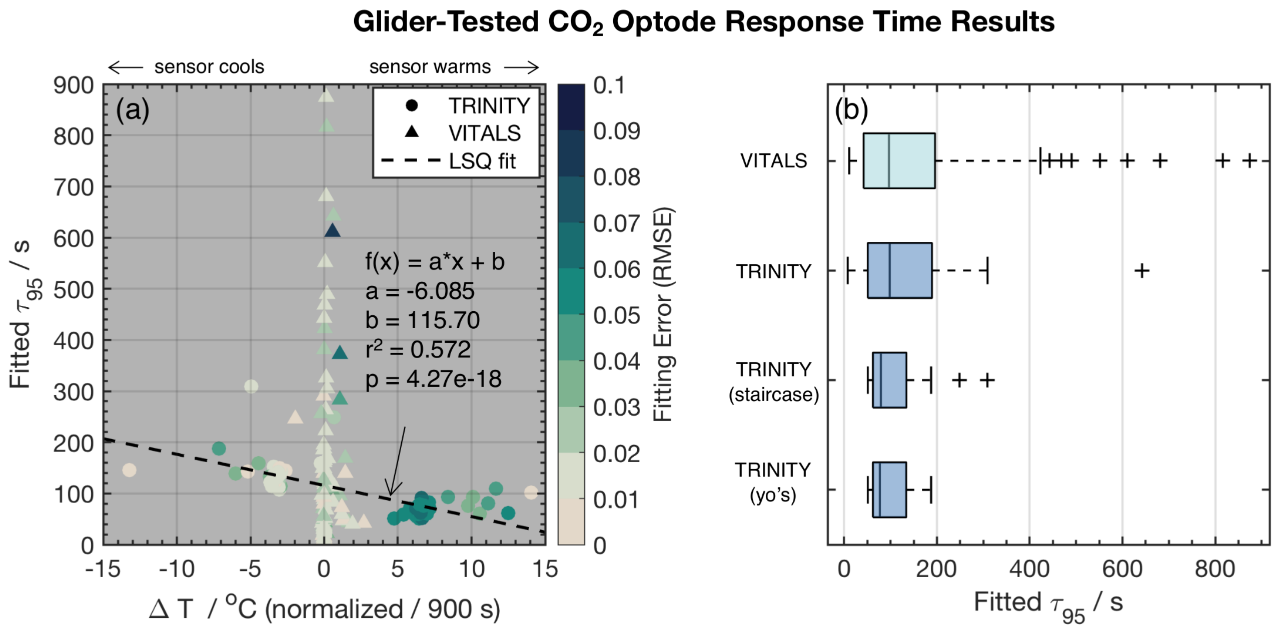

Figure 4. Panel (a) shows the CO_2 optode ~~response time and~~ τ_{95} values vs. temperature gradients ~~colored~~ ΔT normalized by dt=900 s, color-coded for RMSE of fits to the exponential model $x(t) = (a-b)\exp(-dt/\tau) + b$. Distinct markers are used to differentiate between the VITALS and the Trinity glider data. Dashed line indicated linear least squares (LSQ) fit. Panel (b) ~~response time~~ shows box plots of the fitted CO_2 optode τ_{95} values from VITALS and ~~initial sensor temperature colored for ΔT~~Trinity Bay deployments. The Trinity data is divided into staircase profiles and regular yo's.

full staircase mission was done in the middle of the deployment (September 10, 2018). A summary of the analysis of the two datasets is given in Table 2.

Based on our analysis~~we find an average~~, we find a median sensor response time (τ_{95} values) of ~~123.59 sec. with a~~ 79.18 s for the Trinity tests and 96.20 s for the VITALS data, with a mean and standard deviation of ~~181.21 sec. The median response times was 49.20 sec. Minimum values observed were 29.63 sec. and maximum of 868.02 sec. RMS values significantly increased for fits with response times above 500 seconds. We see large scatter among small gradients from~~ 99.24 ± 45.23 s and 169.80 ± 186.55 s respectively. The range of observed response times in Trinity was 50.96 – 309.08 s. In the VITALS data, ~~where stratification is less~~ the τ_{95} range is much larger (7.63 – 874.74). At the same time, ΔT gradients are smaller 0.22 ± 0.0079 ($\bar{x}$ ± STD) compared to Trinity Bay 2.70 ± 5.62. In the Labrador Sea, stratification is much reduced compared to Trinity Bay, and temperature gradients are ~~small < 3°Ccompared to Trinity Bay~~typically small <3 °C. One would expect shorter response times for smaller temperature gradients. ~~We note here that the VITALS data shown above are mostly derived from average glider profiles (yo's), while Trinity Baydata are mostly staircase profiles. Also, we see a small trend in initial sensor temperature on response time: that is, an initially colder sensor responds better to warming than a warm sensor to cooling.~~

Table 2. Response time values from glider-based CO_2 Optode tests

Trinity Tests	(units)	(mean)	(median)	(STD)	(min)	(max)
τ_{95}	s	99.24	79.18	45.23	50.96	309.08
ΔT	°C	2.70	6.23	5.62	-13.21	14.06
dt	s	1925.7	1517.0	822.0	314	3226
VITALS						
τ_{95}	s	169.80	96.20	186.55	7.63	874.74
ΔT	°C	0.22	0.0079	0.58	-1.97	2.67
dt	s	944.8	804	490.7	500	3220

~~CO_2 optode signal plotted against (a) VITALS Fall 2016 data absolute CO_2 measured by the Pro CV on SeaCycler and (b) temperature from SBE 19+. Panels (c) and (d) show Trinity Bay staircase profile data plotted against shipboard Pro CV and CTD measurements. Dashed lines are robust linear fits using the Bisquare method.~~

~~In Figure 4, we showed response time trends of the sensor profiling through weak and strongly temperature stratification and found significant temperature-dependent behaviour. While the temperature-dependence of the sensor foil is non-linear (Atamanchuk et al., 2014), the temperature behaviour of the sensor should show discernible differences when the glider is profiling versus the staircase mode operation. Superimposing measured raw CO_2 optode sensor output with high-quality temperature, salinity and absolute CO_2 measurements from the CO_2-Pro CV (Figure ??), we show different response characteristics not captured in Figure 4. For temperature and sensor response time , we expect to see a fairly linear response, as the solubility of CO_2 in seawater is reasonably linear (Weiss, 1974) over small temperature ranges (ΔT less than 10~~In Trinity Bay, the sensor encountered water temperatures colder than 0 °~~C). The unique staircase profile casts from the Trinity Bay deployment allow an investigation into sensor stability and equilibration, compared to normal glider profiling modes. To match records between observations, we use isopycnal matching, averaging recorded data over bin sizes of 0.01 kg/m^3. Figure **??** indeed, shows noticeable differences in the glider CO_2 optode data between the two deployments. In the VITALS data, for which we primarily used regular glider profiling, the scatter is much larger among temperature dependence of the response. In contrast,~~ C. From this analysis alone, it is not clear if there is a permanent effect on the sensor from these cold temperatures. However, Figure 4a does show an increase in response time values when a sensor cools. Not enough data was collected in Trinity Bay to see if this temperature gradient bias changes or persists over time. Interestingly the sensor signal (ϕ_{DLR}) range in the VITALS deployment was different than in Trinity Bay~~data (staircase profiles), scatter is reduced. Allowing the sensor to fully equilibrate with the ambient conditions, increases the linearity of the sensor response, reproducing the expected linear relationship between CO_2 solubility and temperature . For the VITALS data, we see a linear trend in the scatter plot. Still, the spread was not corrected through our methods giving a broad range of possible CO_2 values for a given temperature in the calibration model.~~ , despite the broader temperature range encountered and similar range in pCO_2. It is possible that some bleaching of the foil had occurred from sunlight despite our best efforts to keep the glider surface time to a minimum.

More work will be necessary to develop a proper response time model. We also did not consider applying a boundary layer and fluid flow model for the optode, such as considered by Bittig et al. (2014) for oxygen optodes. Improvements to the sensor response time ~~as well as~~ and more tests are required to evaluate the influence of the flow field on the sensor performance.

3.2 Comparison: Glider and SeaCycler O_2 and CO_2 Observations

A novel aspect of the VITALS deployment was the simultaneous measurement of O_2 and CO_2 from a glider and the SeaCycler profiler, allowing both space and time-varying observations. Given the challenges with validating the glider-based CO_2 optode observations, we used the SeaCycler as an in-situ reference for the glider data. For context, the glider and SeaCycler had about two months of overlapping observations. Figure 5 and Figure 6, show the time series data from SeaCycler and monthly averaged panels from the glider transects. The SeaCycler record is divided into distinct ~~time~~ periods coinciding with large changes in ~~at–depth~~ at-depth concentration of O_2 and CO_2. The glider measured both the spatial and temporal evolution of the processes captured by SeaCycler. Figure 6, shows monthly averaged panels (approximately 10 glider passes distance-averaged per month) of the glider data. The much lower spatial density of CO_2 glider profiles (at 15-20 km intervals) compared to O_2 (at least 5 km), means that the CO_2 data resolves only spatial features with scales larger than 20 km, compared to a 5 km resolution for O_2. Overall, this region is relatively uniform, with low spatial gradients. Consistent with the SeaCycler observations, we see a flip between concentrations in O_2 and CO_2 between October and November. We also note the different thickness of mixed layer regions across the spatial domain in November. ~~Smaller pockets of low or high O_2 concentrations exist in October, but these trends are weak in an average sense.~~

Table 3. SeaCycler–glider residuals

(parameter)	(mean)	(median)	(STD)	(min)	(max)	(units)
O_2	-0.66	0.64	4.66	-14.30	18.87	μM
pCO_2	17.40	5.92	43.96	-86.45	155.80	μatm
T	0.012	-0.008	0.221	-0.496	0.494	°C
S	0.0035	0.0004	0.0320	-0.0719	0.0867	PSU

~~To compare the observations between platforms and compute the~~ We intercompare platform observations and compute an in-situ reference point for the glider data from SeaCycler. For the comparison, we only ~~compared~~ consider data with similar T–S properties using isopycnal matching. We ~~used~~ use the glider and SeaCycler data from the joint observing period (3 October to 22 November), binning data across potential density ~~bins~~ (σ_0) bins of 0.01 kg/m^3 to compute the temperature and salinity residuals from both data sets. If temperature matched to within 0.5°C and salinity to within 0.1 PSU, we allowed these residuals for further comparison of O_2 and pCO_2 between platform observations. The 95% Confidence Interval (CI) is defined

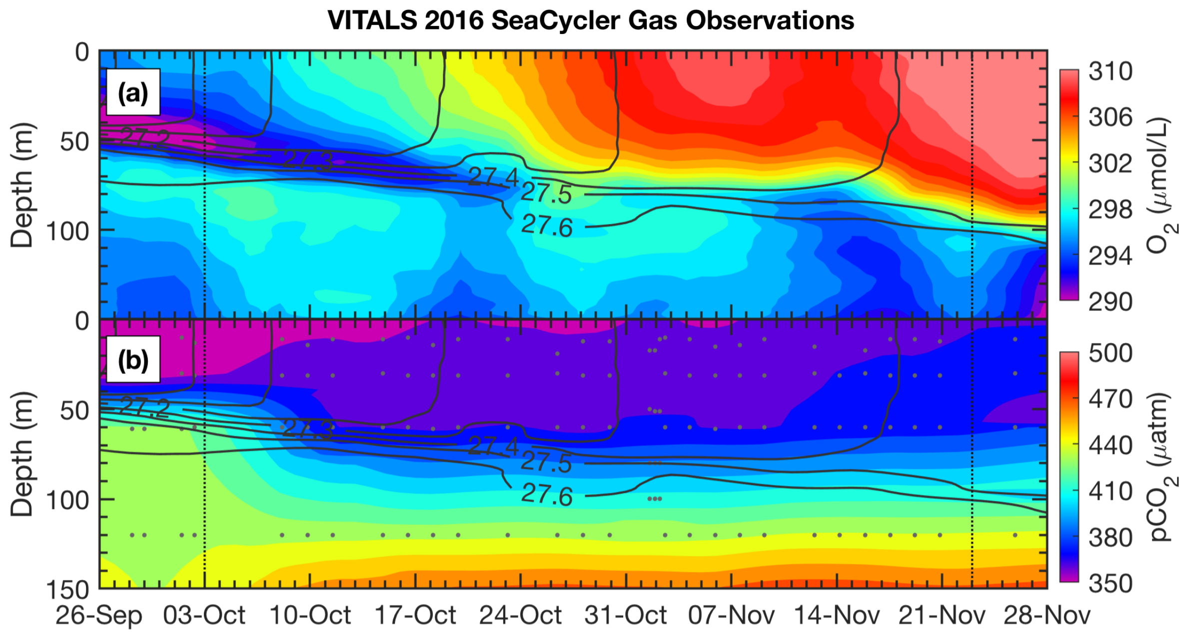

Figure 5. SeaCycler time evolution of (a) O_2 and (b) pCO_2 observations for the joint glider-SeaCycler sampling period with isopycnal anomaly contours overlaid (0.1 $kg \cdot m^{-3}$ spacing). Small grey dots are the depth and time of discrete CO_2 Pro CV measurements by the SeaCycler. Vertical dotted lines indicate the start and end of the joint sampling period.

as ~~CI = $\bar{x} \pm 1.96$~~ CI= $\bar{x} \pm$ 1.96 STD, where $\bar{x}$ is the average of the variable of interest (e.g. pCO_2) and STD is the sample ~~variance~~standard deviation. From the matching O_2 and CO_2 data, we plotted the residual cloud across ~~density~~ potential density anomaly and found strong duality in residual trends marked by the ~~27.56~~ 27.46 kg/m^3 isopycnal, coinciding with a mixed layer depth (MLD) defined as a change in $\sigma_0 \leq 0.01$ kg/m^3. We used linear, least-squares fits to compute the mean correction of the glider data required to match the SeaCycler (Figure 7), indicating trends above and below the ~~27.56~~ 1027.46 kg/m^3 isopycnal. Significant scatter ($\pm$50 μatm) is observed in CO_2 residuals below the mixed layer. Applying the residual fits from the SeaCycler–glider CO_2 offsets to the glider data as an in-situ reference (Figure 7c), we see reasonable agreement in the mixed layer. Below the mixed layer, the comparison does not fall within the 95% CI limit. However, we see good agreement and relatively little spread (within $\pm$10 μ~~mol/L~~M) of O_2 data between SeaCycler and glider sensors leading to a good in-situ reference. We observe that the mean (-0.66) and median (-0.64) offsets for O_2 are close compared to the mean (17.40) and median (5.92) offsets for pCO_2. Using the mean and standard deviation of the residuals and the SeaCycler's uncertainty ($\pm$ 4.17 μM and $\pm$2 μatm), we estimate the mean offset and uncertainty for glider O_2 and pCO_2 data as -0.66 $\pm$ 6.14 μM and 17.39 $\pm$ 44.01 μatm respectively.

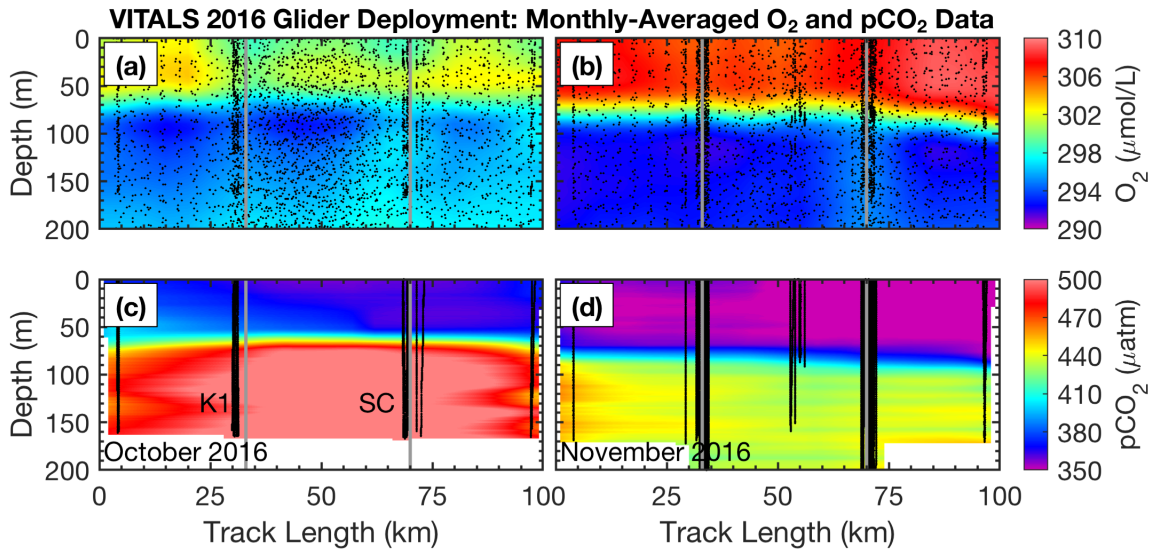

Figure 6. Glider monthly averaged spatial section of (a) O_2 in October and (b) November and for pCO_2 (c) and (d) respectively (along track positions shown in blue inset map in Figure 1). Along-track location of K1 mooring and SeaCycler are indicated with vertical lines as well as individual ~~CO_2 optode~~ glider profiles used for plotting. For glider O_2 data only every 25^{th} data point is shown for clarity.

3.3 Glider-Observed Spatial and Temporal Variability

Glider-based observations intrinsically link the spatial and time domain, making it hard to differentiate between these two dimensions. In VITALS, we took the approach of doing repeat ~~sections with the glider~~ glider sections along the same trajectory to capture both the time and spatial evolution of O_2 and CO_2 above and below the mixed layer. ~~We applied the residual fits from Figure 7 to the glider data and plotted the~~ A Hovmüller diagram ~~of O_2 and pCO_2 anomalies compared to the SeaCycler data (Figures ?? and ??) . Hovmüller diagrams are~~ (Figure 8) is useful to look at the propagation of processes across ~~the~~ a time and space varying field. ~~In this case, we look at~~

We are interested in how much variability in O_2 and pCO_2 is captured by the SeaCycler time-series data along the trajectory sampled by the glider, applying the residual fits from Figure 7 to the glider data. Because the in-situ comparison between the glider and SeaCycler CO_2 data was better at the surface, we only ~~considered the mixed-layer data captured by the glider. We average the glider data top 20 m and grid the observations on a 100 km and 50 days (3 October~~ consider data within the mixed-layer (0 – ~~22 November) long track record, subtracting SeaCycler~~ 20 ~~m surfaceaverage daily time trend~~ m). We compute surface O_2 and pCO_2 anomalies with respect to the SeaCycler by subtracting corresponding SeaCycler surface, daily averaged data from the glider ~~data. We applied~~ record. We use the objective interpolation technique described earlier, interpolating the data using an exponential weighting function to fill in gaps along a 50 day (3 October – 22 November) and 100 km grid. We could have used linear interpolation for the glider oxygen data but decided to keep mapping methods consistent between O_2

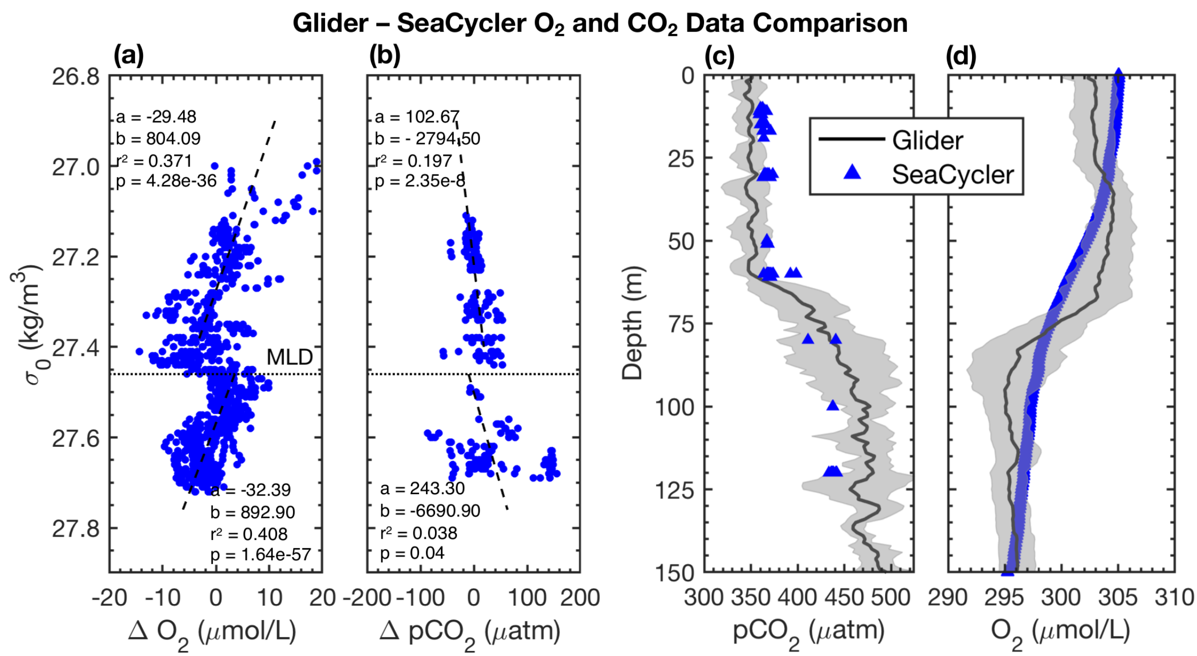

Figure 7. Glider-SeaCycler (a) O_2 and (b) pCO_2 isopycnal-matched residual comparison. Panel (c) and (d) show Glider-SeaCycler corrected depth-averaged pCO_2 and O_2 values with glider 95% CI shown as grey shading for the period from 3 October to 22 November 2016. Blue triangles are mean of SeaCycler measurements for the glider observing period. Dashed horizontal line in panels (a) and (b) is the average density of the mixed layer and dashed lines are linear ~~fit~~ least-squares fits to the residuals in density space.

and pCO_2 data. A drawback of this technique is that it can show artificial variability in the resultant interpolated surface. We applied a low pass filter removing signals shorter than 3-days (time of glider transect) and 4-km (average distance between dives). We used larger scales of 40 km for the glider pCO_2 data. Dots indicate the location of data samples. ~~The legends in the figures, only mask data where no glider datawas collected. Glider Hovmüller diagram, for CO_2 data (top 20 m) with SeaCycler data removed for period 3 October – 22 November, 2016. Dots indicate the location of data samples. Legends mask area where no glider data was collected.~~

Figure 8 shows the spatial and temporal anomalies of the glider data referenced to the SeaCycler data. We note that the scales of the anomalies are within the estimated uncertainty of the glider data. We see that ~~there are~~ only a few spatial features are visible in O_2 data~~. However,~~ , and the overall spatial structure is not as pronounced as the time variability. Towards the beginning of the record, there is a distinctly more oxygenated zone between K1 mooring and SeaCycler. This could mean that perhaps the low oxygen levels measured by SeaCycler from August to October had more considerable spatial variability. There are different patterns between moorings. Near SeaCycler, the O_2 levels are ~~higher~~ elevated by 2 μM compared to the K1 mooring, while data near the K1 mooring show lower oxygen levels over time. Towards the second half of the glider record, as storm activity increases in November, the spatial domain becomes smoother with spatial variability reduced to $\pm 1 \mu$M.

~~Glider Hovmüller diagram, for O_2 data (top 20 m) with SeaCycler data removed for period 3 October – 22 November, 2016. Dots indicate the location of data samples. Legends mask area where no glider data was collected.~~

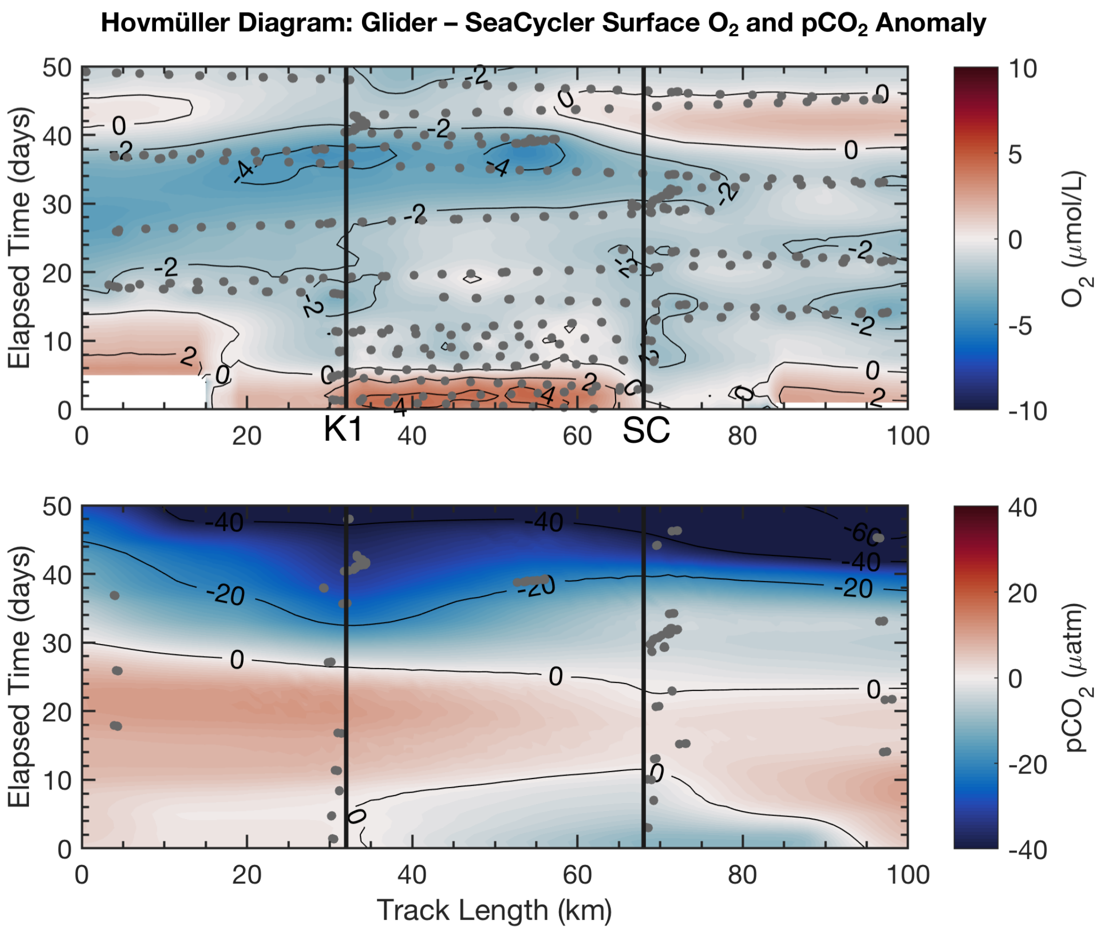

Figure 8. Glider Hovmüller diagram, for O_2 (top panel) and pCO_2 (bottom panel) surface averaged data (0–20 m) with SeaCycler data removed for period 3 October – 22 November, 2016. Dots indicate the location of data samples. Location of K1 and SeaCycler (SC) moorings shown in black.

The glider sampled O_2 daily and along the entire track length, while the CO_2 optode was only sampled at select locations and on average every 2–3 days. The CO_2 glider data sampling was too sparse and required too much smoothing to resolve signals smaller than the seasonal cycle. Therefore, the data appears very uniform along the track length. However, this type of direct comparison between platforms will become increasingly important~~in~~, especially as sensor improvements improve data accuracy. For future glider deployments, this approach may also help to achieve long term monitoring capability, ~~recalibrate sensors and quality control~~ re-calibrating sensors that suffer from drift and help with quality control of mobile platform data.

To separate temporal and spatial variability from each other~~(Figures ?? and ??)~~, we can treat each dimension independently, comparing their autocorrelation scales against each other ~~as a measure of~~ to measure the variability observed. For this analysis, we did not include the glider observations of CO_2 due to the sparse sampling across space and time. However, the scales that drive variability in ~~temperature, salinity~~ T, S and O_2 data also affect the dynamics of CO_2 solubility and the extent and strength of carbon sinks ~~Li et al. (2019); Atamanchuk et al. (2020). We used Chatfield (1998) form~~ (Li et al., 2019; Atamanchuk et al., 2020). We use the definition from Chatfield (1998) of the correlogram or autocorrelation ~~(~~$r(k)$ ~~)~~as a function of lag k.

$$r(k) = \frac{\sum_{t=1}^{N-k}(x_t - \bar{x})(x_{t+k} - \bar{x})}{\sum_{t=1}^{N}(x_t - \bar{x})^2} \tag{3}$$

Here, x_t denotes any quantity of interest (e.g. ~~temperature, salinity~~ T, S or O_2) and $\bar{x}$ is the average of x_t along dimension t, k can denote either spatial or temporal lags and N is the total number of samples along each dimension. We ~~detrend~~ detrended the gridded space-time glider data to remove non-stationary time, and spatial trends following Chatfield (1998) and compute the autocorrelation in space and time lags (km and days) for ~~salinity, temperature~~ S, T and O_2. We repeat this analysis across the ~~density contours~~ potential density anomaly contours of 27.3, 27.7 and 27.75 kg/m^3, corresponding closely to surface, intermediate and deepest water regions surveyed by the glider. We include this analysis to the 95% CI bounds defined ~~as CI = $\bar{x} \pm 1.96$~~ previously as CI= $\bar{x} \pm 1.96$ STD, where STD is computed from the range of correlation functions calculated for the whole isopycnal glider ~~space–time~~ space-time data-set.

The autocorrelation function for T, S and O_2 (Figure 9) show different spatial and time scales across all properties between surface and deeper water layers. T, S and O_2 have similar spatial first zero-crossings of approximately 7–10 km for intermediate and deep waters (27.7–27.75 kg/m^3). O_2 and T also have similar scales (6–7 km) for surface mixed layer waters (27.3 kg/m^3). S has the first zero crossings ~~of about~~ at scales around 10 km ~~scales~~ at the surface mixed layer. CI limits on T and O_2 are more similar in intermediate–depth waters and differ at the surface, where T and S seem to be more tightly related ~~, than with~~ than oxygen. Across T, S and O_2, the CI limit is constrained by 23 km on the upper end and 3 km on the lower end.

Time scales vary more between properties than ~~over~~ do spatial scales. T, O_2 and S have similar temporal correlation at the surface (11–13 days). On the other hand, O_2 has very different ~~intermediate–depth~~ intermediate-depth scales (16 days) ~~,~~ compared to T and S (7–11 days). These results suggest that there are different underlying dynamics between the surface and intermediate–deep water layers that drive T, S and O_2 time scales as observed in the temporal SeaCycler record (Figure 5. The CI time–scale limits for O_2 are also different compared to T and S in intermediate layers. The temporal scales for O_2 in the intermediate depth layer ~~,~~ fall within the mean of the CI interval (6–29 days), suggesting that the distribution of correlation values ~~is evenly centered~~ centred around this range of scales. On the other hand, T, S scales are closer to the lower limit of the 95% CI bounds (4–24 days).

Overall, spatial scales vary less dramatically between density layers ~~,~~ than temporal scales. The presence of energetic shifting of density layers (every 3 to 5 hours) in the intermediate depth waters would force spatial scales to be small. The glider takes about 3 hours to complete a full dive-climb cycle over a distance of 3–4 km. As the glider begins the next dive-climb cycle, the glider will likely see a shift in the depth of intermediate-depth density layers as it will be between 3 to 5 hours since it first

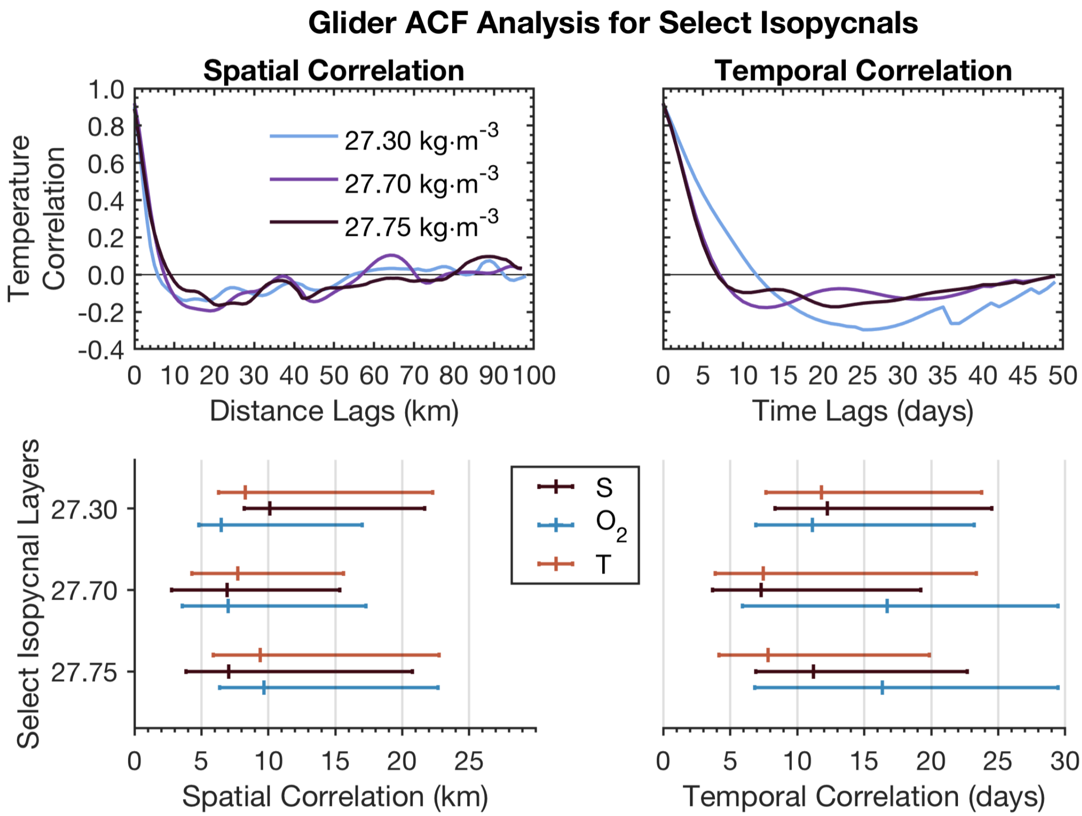

Figure 9. Upper panels show example autocorrelation functions for T as a function of distance and time lags. Lower panels summarize zero–crossings for T, S and O_2 in space and time lags for shown isopycnals together with 95% CI bounds.

measured the same density layer. A study by Sathiyamoorthy and Moore (2002) ~~explained the observed time scales, looking at buoyancy fluxes from OWS Bravo data. Their study~~ found similar time scales of T and S of around two weeks at the surface, ~~linking~~ explaining the observed time scales from buoyancy fluxes observed at OWS Bravo data. They link correlation scales in T and S to cyclonic airflow regime changes in the North Atlantic, suggesting storm activity at ~~a period of~~ roughly two weeks in the Labrador Sea in the fall. ~~This~~ Their result indicates that storms ~~,~~ occurring every few weeks are primarily responsible for changes in T, S and O_2 in the surface layer.

The significant difference in time scales between T–S (7–11 days) and O_2 (16 days) across intermediate-deep layers, however, is not intuitive. ~~A possible explanation to this question could be the presence of biological activity that affects O_2 at intermediate depth layers, but not~~ Changes in O_2 may be related to biogenic activity with a 2–week period. However, this would not explain changes in T and S. ~~A 2–week period of changes in productivity could be possible, but~~ We cannot be sure without further insights from direct observations into the fall and early winter in the Labrador Sea~~, we can not be sure~~. The small spatial scales of around 10 km, does suggest highly variable changes. Due to temperature dependence, this should also ~~include potential~~ result in localized changes in CO_2 cycling. We still do not know exactly how much carbon is taken up in the Labrador Sea, and understanding the impact of localized changes to solubility pumps is an important step. Small-scale spatial variability of pCO_2 for CO_2 uptake is important. To distinguish the changes in the strength of CO_2 uptake, we need to continue to improve spatial observations of CO_2 concentrations in these regions.

We are aware that neither time nor spatial scale results can be interpreted without being mindful of the ~~limitations of the glider platform~~glider platform's limitations due to aliasing (Rudnick, 2016) and the uncertainty of the collected data itself. However, compared to contemporary studies in other water regions, our scale results point to much higher variability across all properties, including CO_2 along time-space dimensions in the Labrador Sea. For reference, traditional annual ship sampling programs in the Labrador Sea, such as the AR7W section, cover the track of the whole glider mission in a fraction of time ~~,~~ but have spatial gaps on the order of 10s of nautical miles between stations – well above the average spatial correlation length scales observed by our glider mission. Other platforms such as ARGO floats cover larger areas ~~,~~ but lack the glider platforms' targeted sampling capability~~offered by glider platforms~~. Therefore gliders play an important role in constructing an effective observing strategy to resolve the fine-scale processes missed by other platforms.

4 Conclusions

In this study, we show data and results of testing a pCO_2 optode sensor (Aanderaa model 4979) on a glider. However, improving ~~the capability of~~ glider-based CO_2 observations is essential to capture the evolving ~~space–time~~ space-time dynamics of carbon sinks in the ocean. We addressed three questions in this paper: (1) How suitable is the novel CO_2 optode for glider-based applications? (2) How can multiple autonomous platforms be used to help improve sensor data? (3) How combined moored and mobile platforms can resolve scales of temporal and spatial variability? We view answering these questions as essential to advance current sensor technology and glider-based CO_2 observing capabilities.

Our deployments were the first glider-based tests of the novel pCO_2 optode. We deployed the glider in an initial test as part of a mission to collect data between two moorings in the central Labrador Sea. From initial evaluations of this mission and questions about the sensor performance in small temperature gradients (<3 °C) characteristic for the Labrador Sea, we re-deployed the glider in Trinity Bay, Newfoundland, where temperature gradients are large (>10 °C). For the second test, we focused on extensive initial tank comparisons between the CO_2 optode and reference sensors using a large saltwater tank that allowed us to submerge all systems at once. We also attempted various glider missions such as the staircase mission vs. regular glider profiles to differentiate between the sensor performance. Several difficulties in using the sensor on a glider were observed, such as drift and long response times. ~~We demonstrated the utility of our approach to use staircase missions to improve the quality of sensor data, quantifying more accurately the response time by letting the sensor attain equilibrium with ambient conditions.~~ In both missions, ~~initially the conditioning is followed an~~ the sensor foil conditioning effect is initially observed by a steep exponential curve, flattening after some time. In the VITALS mission, the sensor showed strong conditioning effects in the first cycle of the deployment and stabilized after about a month into the deployment. We calculated an initial conditioning offset of 1275 μatm by comparing the sensor data with atmospheric measurements and SeaCycler. For the Trinity tests, the sensor stabilized after about ~~a week~~4 days (offset of 994 μatm), but the sensor showed a non-linear depth-dependent response towards the end of the mission~~and almost 2~~ , and almost two days of data had to be excluded. ~~From the deployments we measured~~

From the VITALS Labrador Sea deployment, we calculated average response times of the sensor ~~in standard glider profiling mode of 123.59 seconds~~ (τ_{95}) 169.80 ± 186.55 s for temperature gradients of ~~0.5~~ 0.22 ± 0.58 °C~~but with a large standard deviation of 181.21 seconds. Using the staircase referenced optode data, we~~ . In Trinity Bay, with larger temperature gradients of 2.70 ± 5.62 °C, we find response times are 99.24 ± 45.23 s. We were able to correct ~~for the response time of the sensor~~the sensor's response time, applying methods similar to those in Fiedler et al. (2013). However, more tests are required to validate our results and characterize the influence of other factors, such as the boundary layer in the sensor's flow field. We identified ~~increased~~ a large scatter in sensor response times for small temperature gradients ~~(<3 °C)~~in the Labrador Sea data. We also detected a small bias in performance towards positive temperature gradients, suggesting the sensor performs better in upcasts than in downcasts. Presently the sensor does not yet have the reliability ~~on its own~~ to measure pCO_2 from a glider. The sensor's drift and conditioning ~~of the sensor~~ are not well understood, and not much prior published test results are available for comparison. ~~It is likely that the sensing foil~~ The sensing foil likely needs more work to improve stability. The optode has ~~a number of~~ some key strengths, such as its small size, easy integration and low power consumption. If the foil stability and sensitivity could be improved, the sensor could become a desirable candidate for ocean gas measurements similar to the commonly used O_2 optode.

In the Labrador Sea mission, we demonstrated how to use the SeaCycler CO_2 PRO-CV instrument as an in-situ mid-deployment reference point to validate the glider CO_2 data. Our corrections for the experimental glider CO_2 optode, using SeaCycler data, yielded a robust surface mixed layer correction of the glider data, but the subsurface data remained noisy. For the more reliable O_2 optode, this method worked well, and agreement in data to within ± 10 ~~μmol/L~~ μM was achieved. Using the residuals from the glider–SeaCycler comparison, we estimate the mean offset and uncertainty for glider O_2 and pCO_2 data as -0.66 ± 6.14 μM and 17.39 ± 44.01 μatm respectively.

The unique capability to synchronize and synthesize data from different sensor systems allowed us to investigate the high-resolution glider observations' spatial and temporal character~~of the high-resolution glider observations~~. The repeat sections of the glider yielded a dynamic picture across all measured properties (T, S, O_2, CO_2) in both time and space. On average, we observed spatial scales across measured properties of less than 10 km and temporal scales of 15 days or less. ~~We found agreement of our results~~ Our results agreed with previous studies pointing to increased storminess in the fall ~~as an explanation for~~ to explain the roughly 2-week period in time scales. We lacked enough data ~~to also~~ also to quantify time and spatial scales of pCO_2~~, but~~ . However, given the strong dependence between T and CO_2, our results point to the importance of having targeted winter-time glider observations to observe small-scale spatial variability of CO_2 cycling. Overall, our analysis points to much finer scale and localized processes than commonly described in the literature or captured by other observing systems, underlining the importance of repeat glider observations in this region.

These results clearly show that there remain challenges to achieve reliable glider-based CO_2 observations. ~~One~~ The CO_2 optode sensor does not yet meet the targets for ocean acidification observations, as discussed by Newton et al. (2015). In the meantime, one option is to measure pH rather than CO_2. The work by Saba et al. (2018), testing an ISFET pH sensor on a

Slocum glider, found accuracy to be better than 0.011 pH units and is indeed very promising. These sensors are already in regular use on BGC Argo floats. Calculation of pCO_2 from pH requires knowledge of at least one other carbonate parameter. On the other hand, pH vs pCO_2 relationships measured at fixed platforms like SeaCycler could support this calculation. One limitation of the pH sensor is that one could not use the data to measure air-sea gas exchange ~~,~~ because it is not a direct measurement of pCO_2. No matter which sensor one chooses, we believe that in-situ referencing between platforms can add value to existing and future sensors deployments on autonomous platforms such as floats~~and gliders and add value, at the same time, to the moored measurements .~~, gliders and moorings.

Data availability. VITALS 2016 glider deployment data is available at https://doi.org/10.17882/62358. Processed CO_2 optode data from both deployments is available from the authors upon request.

Appendix A: DFO Sample Analysis

Niskin bottle samples were collected in the lab in 500 mL BOD bottles. They were poisoned 100 μL of saturated Mercuric-Chloride ($HgCL_2$) and allowed to warm in a temperature-controlled bath (25°C ± 0.1 °C) before analysis. Winkler titrations were performed on water samples to calculate oxygen concentrations. Uncertainty of the Winkler titrations were ±0.01 ml/L or ±0.44 μM (± 1 STD). TA and DIC were estimated from coulometry (Johnson et al., 1993) and potentiometric titration (Mintrop et al., 2000). Equipment used to estimate TA and DIC was as follows: VINDTA 3D TA–DIC analyzer connected to a coulometer (UIC, USA, model 5015O), VINDTA 3S (TA) analyzer using open cell differential potentiometry equipped with a reference (Metrohm, Canada, model 6.0729.100) and pH glass (Thermo-Orion, Canada, model 8101BNWP Ross half-cell) electrode, which were both referenced against a grounded platinum electrode. Based on TA and DIC, pCO_2 was calculated using CO2calc (Robbins et al., 2010), with CO_2 equilibrium constants from (Mehrbach et al., 1973; Dickson and Millero, 1987), total boron constant (Lee et al., 2010), and KHSO4 constants (Dickson, 1990). Analytical instrumentation at DFO undergoes a daily operational evaluation of accuracy using CRM's, from which estimated uncertainty for DIC and TA measurements are 3 and 4 μmol/kg, respectively (Gary Maillet,gary.maillet@dfo-mpo.gc.ca, *personal communications*). Including the TA-DIC inputs' uncertainty into CO2calc, we estimate pCO_2 uncertainty as ±4.48 μatm.

Author contributions. NVOB carried out research and initiated the paper, BDY and DA contributed research ideas. All authors contributed to revisions and comments of the paper.

Competing interests. None declared.

Acknowledgements. We thank Mingxi Zhou, Mark Downey~~for field work~~, for fieldwork support, Chris L'Esperance~~with sensor calibration and~~, with sensor calibrations, Fisheries and Oceans Canada for access to their saltwater-tank facility ~~. We thank~~ and Gary Maillet for help with water sample analysis. We acknowledge funding from the National Science and Engineering Research Council (NSERC), Climate Change and Atmospheric Research (CCAR) network~~for funding this research~~.

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