Re: Biogeosciences manuscripb bg-2017-428
Author Comment in response to Review 2

Dear Editor and Reviewers:

We would like to thank Reviewer 2 for their thorough review of the manuscript. Reviewer 2 felt the paper had substantial scientific value and recommended publication in Biogeosciences. They were enthusiastic about the gas exchange aspect of the study and recommended major revisions to the productivity portion of the paper before publication.

Please find our detailed response to Reviewer 2 below. Reviewer comments are in black and our responses are in blue.

Thank you,
Cara Manning

Review of Manning et al Changes in gross oxygen production, net oxygen production, and air-water gas exchange during seasonal ice melt in the Bras d'Or Lake, a Canadian estuary"

The study of Manning et al presents 1) estimates of gas transfer velocity under almost complete ice cover and ice-free waters; and 2) measurements of Net and Gross Oxygen production rates under ice, during and immediately after the spring ice melt, in Whycocomagh Bay, a semienclosed estuary in Nova Scotia. The study described in the manuscript is novel and has important implications for studies of the polar regions. I am very enthusiastic about the first part of the paper, focused on the gas exchange, but have more reservations about several aspects of the 2nd part of the paper (estimates of NOP and GOP). Thus, I have just a few comments on the former, and outline more detailed concerned on the latter. Overall, I recommend the paper for publication after major revisions.

I. Gas exchange estimates
Estimating rates of gas exchange in ice-covered seas is of great importance for biogeochemical studies in polar and subpolar regions, yet gas piston velocities have been notoriously difficult terms to estimate, and remained poorly constrained. The authors used a clever approach, where they released a dual tracer (3He/SF6) and monitored the change in the two tracers ratio through time. All physical processes (mixing, dilution within the water column) except for gas exchange with atmosphere affected both tracers equally, while the difference in solubilities of the two gases controlled the changes in the tracer ratio thus allowing for robust determination of piston velocities. I believe this part of the study is of a substantial scientific value and is a great contribution to future studies

of polar regions.

Thank you for these positive comments.

Specific comments

1) The ice edge on April 7th was located at approx. 1 km from the sampling site (based on Fig. 1a). I wonder what was the influence of this open water patch on the estimated k600? From Figure 4, it looks like the 3He/SF6 ratio dropped substantially on Day 10. What would be k value if this last point is excluded from the fit?

The position of the ice edge was already included in the interpretation of the Injection 1 results (new/modified text is in italics):
"We mapped out the location of the ice edge closest to Little Narrows by boat on 26 March, 7 April, and 12 April (Figure 2a). Using these surveys and shoreline data, we calculate that for the surface area of the bay between the injection site and Little Narrows, f = 0.01 on 26 March, 0.05 on 7 April, and 0.08 on 12 April. The f experienced by the tracer patch during Injection 1 is likely between *0.02*--0.08 because the tracer *was injected on 30--31 Mar* and flowed through the open water near Little Narrows between 6--11 April."

We also added in the following text:
"One source of uncertainty in estimating the correct value of f is that the transit speed between the injection site and Little Narrows was non-constant. The mean current velocity at Little Narrows channel was 3.4 km d^{-1}*, but the tracer took approximately 8 days to flow 7 km from the injection site to Little Narrows."*

Regarding the selection of data points, we added in the following text (in italics):
"The tracer ratio did not display a consistent decrease over the three days we sampled it at Little Narrows, *which may be* due to the substantially lower gas transfer velocity, *as well as the very low tracer concentrations potentially increasing measurement uncertainty.*"

We performed a sensitivity analysis when calculating *k* for each injection. For Injection 1, if the day 10 measurement is excluded from the fit, k_{600} is 0.0485 (0.0024) m d^{-1}, 7% higher than the value reported above. Including (excluding) the measurement on day 10, k_{600} for injection 1 is 6% (7%) of the value for injection 2. Given the small difference in *k* when day 10 is added or removed, we think it is most appropriate to include all 4 measurements.

2) It would be useful to give the actual values of molecular diffisitivities for 3He and SF6 (e.g. somewhere in Section 3.2.1)
We added in the Schmidt numbers of the two gases in this section (the ratio of diffusivity to kinematic viscosity of water): *"The Schmidt number at a salinity of 4 PSS and temperature of 2* ^{o}C *is 305 for* ^{3}He *and 2684 for* SF_6*."*

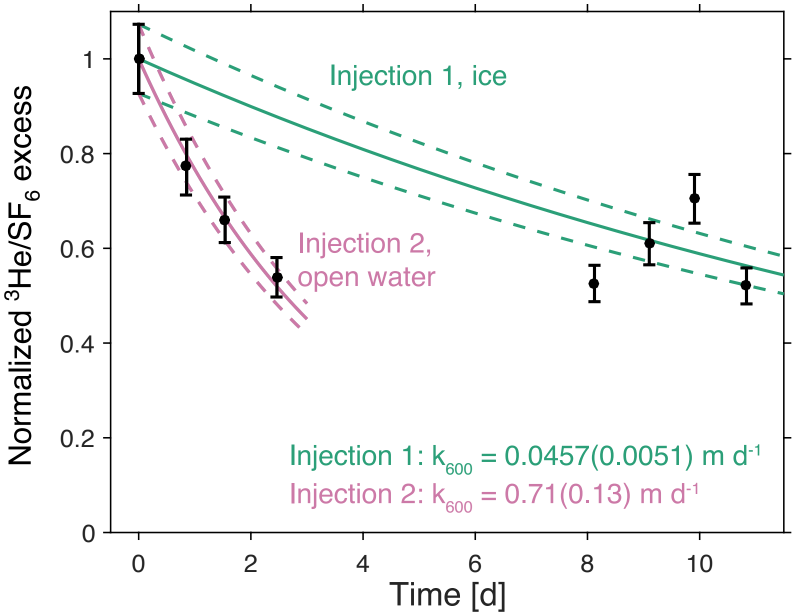
3) Is there a reason for the 3He/SF6 increase in the first 3 data points after Injection 1? Or this is likely a “noise” signal? This issue is addressed on p. 10, line 23-25, but some clarification would good. What was the tidal status when these 3 data points were taken (other than “visual observations” mentioned in the subsequent lines on the same page)?

This is likely a noise effect. We stated on page 10, line 23;
"For Injection 1, the excess SF6 and 3 He concentrations were reduced by two orders of magnitude by the time the tracer reached Little Narrows (7–11 days after injection). The tracer ratio did not display a consistent decrease over the three days we sampled it at Little Narrows, likely in part due to the substantially lower gas transfer velocity."

The concentration of both tracers was lower than expected by the time the tracer reached Little Narrows (as the transit time was longer than expected), so there is some uncertainty in the ratio in each individual measurement. However, the calculated *k* is relatively insensitive to our choice of data points.

Typos:
There is a typo in Fig. 4 (k600 of the 2nd injection should be 0.7, not 0.07)

Than you for noticing this important error. We have fixed the figure as shown below:



P. 6, line 30 should read “ The Lott and Jenkins solubility is ~2% higher”
Done.

II. Estimates of NOP and GOP rates
The 2nd part of the study was devoted to estimates of NOP and GOP at the Little Narrows

sampling location. The productivity terms have been poorly constrained in ice covered and partially ice covered high latitude seas. Thus, the value of this part of the study is in expanding our (currently very limited) knowledge of these terms in the polar regions, despite some limitations (in setup, calculations and interpretation), which I address next.

Specific comments

1. Setup of the study:

O2/Ar monitored and samples for $_{17}\Delta$ were collected at the Little Narrows, which has been ice free all through the length of the time series (based on Figure 1a). How valid it is to apply the piston velocity determined for the ice covered conditions at the ice free Little Narrow study site?

To address this issue, a more through description of the Little Narrows study site is needed: what is residence time of surface water in this channel? Current velocities? In other words, how well measured here O2/Ar and $_{17}\Delta$ signals represent the conditions within the Bay? While the authors do state that spatial variability within the Bay is likely to be small, the issue at hand here is – are the reported NOP and GOP rates really the rates under ice (for the time period between March 31 and April 18th) or are they more representative of the very local ice free waters in the Little Narrows?

Regarding current velocity, we added in the following text in the section "sampling setup at Little Narrows":

"We deployed a Nortek acoustic Doppler current profiler (ADCP) at ~4 m depth in the middle of the channel from 7--28 Apr. The mean current speed at 0.5 m depth was 3.4 km d^{-1} (3.9 cm s^{-1}) with an orientation toward 31° (approximately along the channel axis), indicating the transit time through Little Narrows is relatively short."

Regarding the influence of the open water between the ice edge and Little Narrows on the GOP/NOP calculations, we added in the following text in the section on GOP results:

"We believe that the O_2 measurements at Little Narrows from the beginning of the time-series through 16 April (the date when the fraction of open water in Whycocomagh Bay began to increase rapidly) are generally representative of the under-ice rates due to the rapid transport of water through Little Narrows channel. The mean current speed at Little Narrows channel at 0.5 m depth was 3.4 km d^{-1}. The distance between the ice edge and the sampling intake ranged from ~0.4–1 km between the beginning of the time-series and 12 Apr. Assuming a gas transfer velocity for O_2 of 0.5 m d^{-1} once the water mass encountered open water and a mixed layer depth between 0.8 to 2 m, the residence time of O_2 in the mixed layer was 1.6–4 d. Assuming a current speed of 3.4 km in open water, the water mass would have only been exposed to open water for between 0.1–0.3 d (20 % or less of the residence time of O_2). However, we recognize that the current speed near the ice edge may have been somewhat slower than the speed at the constriction at Little Narrows, therefore the transit time in open water may have been somewhat longer than 0.1–0.3 d."

2. Calculations:

Equation (5) modified from Prokopenko et al 2011 (equation S8 in that paper, would be good to give a citation) contains two terms, O2 and h (in the NSS term). In Prokopenko et al, O2 and h were assumed constant, while the $_{17}\Delta$ was time-dependent. However, in the study of Manning et al, this is clearly not the case, particularly for the O2 term. In fact, there appears to be a discrepancy between Equation (5) and (11). In the former, O2 is treated as if it in a steady state, while in Equation 11 O2 (as O2/Ar) is treated as a time-variable term.

So, one question is what were the actual values of O2 that the authors used to calculate the reported GOP terms for every time point? Similarly, what were the values of h (though the latter is probably less important, at least for the period between March 30-April 10, when mixed layer depth remained more or less constant, however the changes in h after April 10_{th} are more substantial)?

Based on the above, I am not sure that the approach chosen by the authors to calculate the NSS term is fully correct. I would suggest that the authors redo the calculations using the approach presented in Haskell et al (2017), published in Global Biogeochemical Cycles, which presents an alternative treatment of the NSS term in NOP and GOP calculations under non-steady state conditions.

Thank you for these suggestions. We think you were referring above to equation (9) of our paper, which is the equation for GOP, rather than equation (5), which is the equation for k_{eff}. We have added the citation to Prokopenko et al. (2011) as you suggested.

As indicated in equation (10), the value of $[O_2]$ used to calculate GOP was determined from the O_2/Ar ratio of the sample and assuming [Ar] is at equilibrium, i.e.

$$[O_2] = \Delta(O_2/Ar)_{samp}\,[O_2]_{eq}.$$

The value of *h* (mixed layer depth) was the instantaneous value interpolated from our CTD profiles (black dot-dashed line in Figure 3 a and b).

You state above that "in Prokopenko et al., O_2 and h were assumed constant, while $^{17}\Delta$ was time dependent." We believe that is incorrect. In Prokopenko et al. (2011), equation 5, which is time-dependent in O_2 concentration and isotopic composition, is used to derive equation S8. In other words, the time-dependency in O_2 concentration is already built into eq. 5 and S8. It is correct that the change in mixed layer depth with time is not included. However, we have concluded that including a time-variable mixed layer depth in the GOP and NOP calculations would require knowledge of the gradient in O_2 concentration and isotopic composition as a function of depth below the mixed layer. For example, when O_2 diffuses upward into the mixed layer, the rate of O_2 addition to the mixed layer will depend on the O_2 concentration below the mixed layer. This must be added as an additional term in the O_2 mass balance equation. For example, see Howard et al. (2010) equation 9, Nicholson et al. (2014) equations 12 and 13 and Munro et al. (2013) equation 5 and 7.

Additionally, we reached out to the authors of Haskell et al. (2017). It is true that equation 1a in Haskell et al. (2017) incorporates a non-steady state mixed layer, whereas the equation we used did not. However, when we carefully derived an equation with a non-steady state mixed layer depth, we did not achieve the same equation as in Haskell et al. (2017). In particular, we believe that equation 1a Haskell et al. (2017) double counts the change in O_2 by including it within the time rate of change term because equations 5 and S8 in Prokopenko et al. (2011) already account for the time rate of change in O_2 concentration without it appearing directly in the equation. Thus, we are concerned that there may be a mistake in equation 1a of Haskell et al. (2017) and do not want to use it for this paper.

The reviewer stated that including a time-dependent O_2 term is very important and that including a time-dependent mixed layer term is less important. Since we have already done the former and are concerned about the accuracy of the Haskell et al. (2017) equation, we have decided to leave the GOP calculations unchanged in the revised manuscript.

3. Interpretation:
An obvious problem of the study is the lack of information about the water column below the mixed layer. Are there any published studies on the water column winter conditions? Clearly, TOI was presented by Manning is the first of this kind in the Bay. But it would be very important to know the degree of oxygenation of the water column during winter months. If the Bay goes anoxic (or very low O2), estimates of NOP are impossible to make without knowing how much of this winter low O2 signal contributes to the mixed layer.

We now state in the section on the sampling setup:
"This CTD package was also equipped with an O_2 sensor, but unfortunately the O_2 sensor malfunctioned throughout the experiment. Therefore, we can characterize vertical structure of salinity and temperature but not O_2."
We did not mention this detail in the original manuscript in the interest of brevity but have added it to better explain our experimental design.

Regarding subsurface O_2 levels, we now added the following text in the section "site description", a new section that Reviewer 1 recommended we include:
"To our knowledge, there are no previously published measurements of water column chemistry in Whycocomagh Bay in ice-covered conditions. Measurements from July 1974 showed that the western portion of the Whycocomagh Bay became anoxic in the isolated deep waters below 25 m depth whereas measurements in the eastern portion of the basin (closer to Little Narrows) showed the water column had an O_2 saturation of 61% at the bottom depth of 30 m (Krauel, 1975; Gurbutt and Petrie, 1995). Measurements collected from 1995–1997 (from late April to late September) showed O_2 concentrations in Whycocomagh Bay from 1–5 m depth were near equilibrium (94 to 112 % saturation) throughout the bay. In the deeper waters, O_2 concentrations in eastern Whycocomagh Bay ranged from 69 % at 25 m depth on 28 April 1996 to 54 % at 13 m depth on 26 Sep 1995 and 30 % at 30 m depth on 23 Sep 1996, and the western basin was persistently anoxic (Strain et al., 2001)."

We regret not obtaining a Niskin bottle for subsurface discrete sample measurements of triple oxygen isotopes and have added this recommendation for future work to our conclusions section.

"In future studies in similar settings, we recommend authors collect measurements of O_2/Ar and triple oxygen isotopes below the mixed layer in order to better correct for the impact of vertical processes on the O_2 mass balance. For tidally-influenced regions, surveys of lateral variability in O_2/Ar and $^{17}\Delta$ could also help to constrain the influence of horizontal advection on the O_2 mass balance (Munro et al. 2013, Howard et al. 2017)."

The problem is likely less acute for GOP, as the absolute difference between the water column and the mixed layer $_{17}\Delta$ is likely to be smaller than for O_2/Ar (and one could assume $_{17}\Delta$ being as low as at atmospheric equilibrium value). However, the drop in GOP observed after the ice melt is really difficult to explain: obviously, increased ventilation should not lower GOP, thus the drop of $_{17}\Delta$ is driven, in addition to increased ventilation, by dilution of the mixed layer $_{17}\Delta$ with waters carrying lower 17O-excess. GOP does not require new nutrients (as the authors themselves point out), thus even when all the nutrients are consumed, GOP should not be affected.

The problem with NOP estimates is likely be more acute, but since the O2 concentration below the mixed layer is not known, it is more difficult to assess quantitatively.

As discussed in our response to Reviewer 1, we have now eliminated the GOP and NOP estimates during the period 16-19 April where the estimates are very uncertain due to uncertainty in the parameterization of *k*. Additionally, we have included more text emphasizing the uncertainties associated with the variable mixed layer depth and lack of depth-resolved measurements. We eliminated much of the discussion of explanations for the decreasing NOP at the end of the time-series.

New text added to the section on GOP "results and discussion":
"Before interpreting the GOP results, we emphasize that the impact of changing mixed layer depth on the O_2 mass balance is not accounted for in our calculations. The mixed layer deepened from 8--23 Apr and then appeared to shoal from 23--28 Apr. If the $^{17}\Delta$ value below the mixed layer were higher (lower) than $^{17}\Delta$ in the mixed layer, this would cause us to overestimate (underestimate) GOP as the mixed layer deepened."

New text added at the beginning of section "NOP results and comparison of NOP and GOP":
"As for GOP, we do not present NOP estimates during 16–19 Apr due to the uncertainties associated with the rapid decrease in ice cover. There are additional uncertainties in NOP from 12–23 Apr due to the increasing mixed layer depth, which may have entrained lower-O_2 waters into the mixed layer. Historical O_2 data from Whycocomagh Bay showed that there is a strong decrease in O_2 with depth below the mixed layer, however, to our knowledge, no prior measurements during ice melt have been published (Krauel, 1975; Gurbutt and Petrie, 1995; Strain et al., 2001)."

New text added at the end of section "NOP results and comparison of NOP and GOP"
"The mixed layer depth was ~0.8 m from the beginning of the time-series until 12 April, deepened from 12–23 Apr and then increased until the end of the time-series. The apparent decrease in volumetric NOP beginning around 12 April could be due to a number of factors

including: an increase in respiration and recycling of organic carbon by autotrophs and/or heterotrophs, and/or vertical processes that are not taken into account in our calculations. We note that the mixed layer NOP was actually lowest and $\Delta O_2/Ar$ was decreasing between 23–27 Apr, a period where the mixed layer actually appeared to shoal. Therefore a deepening mixed layer cannot be the only driver of the decrease in NOP following ice melt."

On the positive side, this study provides a very interesting and novel example of using the 17O-excess method in waters different from VSMOW, and this part of work is of great value.
Thank you.

Smaller comments:
P. 15, line 22 - Pls, add original reference for "published relationship between d17O-H2O and d18O-H2O , where only the reference to Manning et al (2017) is currently given).
We've added citations to Luz et al (2010) and Li et al (2016).

P. 17, line 15-17 – what was the actual values for the fractionation factor used in calculations (as based on Luz and Barkan, 2011)?
We now specify "$\alpha^{18}{}_{p} = 1.0033890$ and $\alpha^{17}{}_{p} = 1.0017781$."

P. 20, line 20 should read " the mixed layer-integrate GOP"
Done.

In summary, my recommendation for Interpretation part would be to re-write the discussion of the NOP and GOP estimates, clearly stating the above limitations first and substantially shorten the discussion of zooplankton and heterotrophy. It appears that the estimates of NOP rates are likely strongly affected by mixing of the O2-depleted signal and it would not be possible to evaluate the magnitude of this effect). As to GOP – I wonder if using the approach of Haskell would modify the estimated GOP trend through the time series (and some estimates of the degree of dilution of $_{17}\Delta$ signal could be made).

As discussed above, we have continued to use the equation of Prokopenko et al. (2011) to calculate GOP, as this equation already incorporates non-steady state O_2 concentration and isotopic compostion. We believe that correcting the GOP estimates for non-steady state mixed layer would require knowledge of the O_2 concentration below the mixed layer, data which is not available to us. We have highlighted the uncertainties as you suggested.

Thank you again for your thorough review and suggestions that have improved our manuscript.