Smith et al. Biogeochemical controls on wintertime ammonium accumulation in the surface layer of the Southern Ocean

Response to Reviewer's comments

We thank the Reviewers for their final comments and for their recommendation that our manuscript be accepted after we respond to their final notes. Below are our responses, in blue text, to each of the Reviewer comments.

Reviewer 1: Anonymous

General comments

The authors have done a good job in simplifying this study and their responses to earlier comments seem appropriate and acceptable. Though there remain several speculative assumptions within the discussion, on balance I think that these are now more carefully handled and presented in a manner that makes clear the limitations of what is known about the N cycle in the South Ocean. I note a few areas where the methodological details still need to be clarified (see below) but overall this should make a nice contribution to the literature.
Response: We appreciate the Reviewer's comments regarding our efforts to improve the manuscript.

Specific comments

Abstract:

L35-37: The presented data would seem to support this statement, however I would encourage the authors to downplay the extrapolation of their results to the entire Southern Ocean. It is evident from recent circumpolar pCO2 observations there is considerable spatial and temporal variability in the strength of the Southern Ocean as a sink or source and it may not be true to state that the entire Southern Ocean becomes a biological source of CO2 for half the year. See for example figure 2 in Sutton et al 2021.
Sutton, A. J., Williams, N. L., & Tilbrook, B. (2021). Constraining Southern Ocean CO2 flux uncertainty using uncrewed surface vehicle observations. Geophysical Research Letters, 48, e2020GL091748.

<span style="color:blue">Response: We take the Reviewer's point. However, our intention with this statement is not to highlight a new finding about the Southern Ocean's carbon sink, but rather to offer an additional (complementary) explanation for why Southern Ocean biology drives a net outgassing of CO_2 in winter, with the latter idea one that is already established and widely supported by both model results and observations (e.g., Gibson & Trull, 1999; Gray et al., 2018; Hauck et al., 2015; Mongwe et al., 2018; Shadwick et al., 2015). In other words, while we agree that there is bound to be spatial and temporal variability in the biologically-driven flux of CO_2 from ocean to atmosphere, it is already known that *in net*, the biological pump in both the Subantarctic and Antarctic Zones is weak in winter (red lines in **Figure R1** below), with heterotrophic CO_2 production occurring at a far higher rate than autotrophic CO_2 fixation. In the Antarctic Zone, this wintertime biological CO_2 production is stronger than the CO_2 drawdown facilitated by the solubility pump (blue line) such that the region becomes a net source (i.e., not just a biological source) of CO_2 to the atmosphere. By contrast, in the Subantarctic Zone, the solubility pump is comparatively far stronger in winter and the region never becomes a net CO_2 source to the atmosphere *despite being a biological source in winter*. The mechanism that is typically invoked to explain why the wintertime Southern Ocean is a biological source of CO_2 (i.e., the lack of photosynthesis) manifests as weak autotrophic nitrate removal, as least relative to the rate of the upward supply of nitrate, which is accompanied by a stoichiometric quantity of CO_2. Our point is y that in addition to this commonly invoked mechanism, the sustained net production of ammonium in excess of the autotrophic process that remove it (i.e., evincing net heterotrophy in the Southern Ocean mixed layer) contributes to biological CO_2 outgassing in winter.
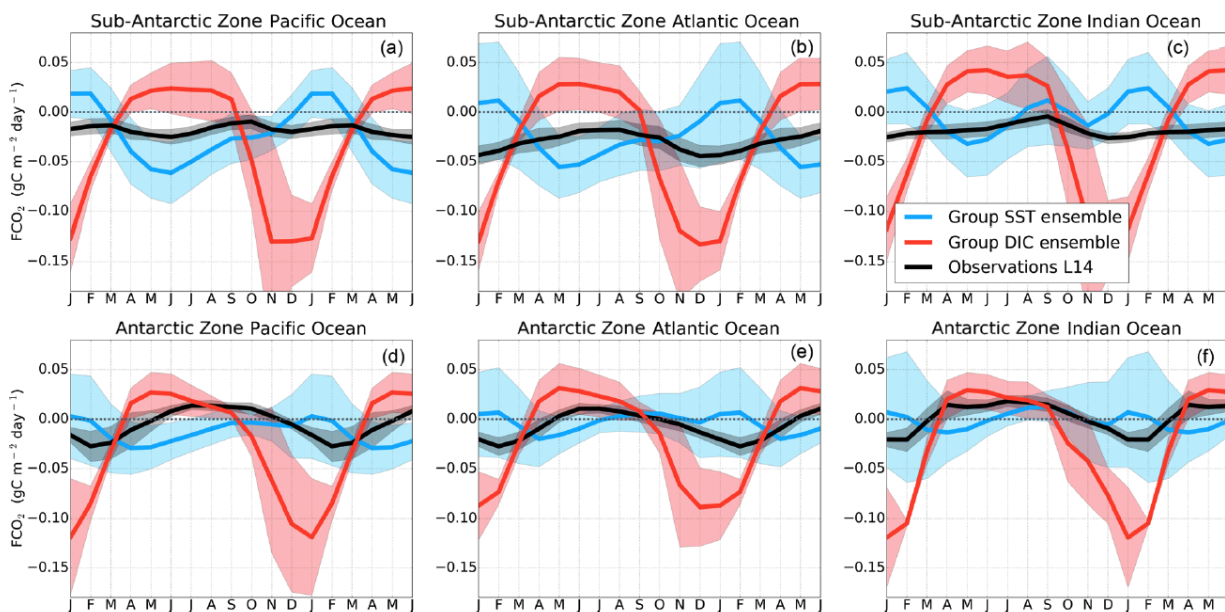
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Figure R1: Seasonal cycle of the CO_2 flux between the Southern Ocean surface and the atmosphere in all three major ocean basins; positive (negative) values of FCO_2 indicates that the Southern Ocean is a CO_2 sink (source). The red lines show the modelled biological component of the flux while the blues lines show the modelled physical component (means of numerous models; see Mongwe et al (2018) for details). The black lines show the mean of the observations from Landschützer et al. (2014). [Figure from Mongwe et al. 2018].

The data presented for the early winter period (May – July 2019) by Sutton et al. (2021) that was referenced by the Reviewer show the same thing – that the wintertime Southern Ocean is a net source of CO_2 to the atmosphere while in the summer, it is a sink. We note that the Sutton et al. (2021) dataset is showing the net (i.e., biological + physical) CO_2 flux and does not, therefore, directly relate to our argument about the biological flux. Further, Sutton et al. (2021) do not explicitly show spatial variation between the Southern Ocean sectors in winter (or indeed, summer) since their sampling track covers 196 days (i.e., the dominant mode of variability is seasonality). Nonetheless, we have changed "…for half of the year…" to "…in autumn and winter…" in the abstract (line 36), since we cannot know the exact period over which the Southern Ocean is a biological CO_2 source, and to avoid the insinuation that during the other half of the year, the Southern Ocean is a CO_2 sink.

Finally, we have amended the discussion text to clarify our meaning as follows –

> "In net, the Southern Ocean mixed layer is a biological source of CO_2 to the atmosphere in autumn and winter (Mongwe et al., 2018). The persistence of elevated NH_4^+ concentrations across the polar Southern Ocean between late summer and winter implies that this biological CO_2 production occurs not only because NO_3^- drawdown is weak relative to NO_3^- supply at this time (e.g., Gibson & Trull, 1999; Gray et al., 2018; Hauck et al., 2015; Mongwe et al., 2018; Shadwick et al., 2015), but also because the ambient conditions allow for NH_4^+ accumulation."

Methods:

Some care and clarification needed in presentation of methodological details.

L192-200: It is not clear from the method description that the authors conducted size-fractionated N uptake experiments though this is indicated later on L269-270, L420-421 etc. Nor is it clear from the description whether the authors split the duplicate 1L bottles to obtain the size fractions in each bottle i.e. 500 ml per fraction or whether they used 1 replicate for the bulk and the second replicate for the nanoplankton fractions. A minor detail, but please clarify the methods used.

Response: We have added to the sentence at L199 –
"Incubations **and filtration** were carried out as for NPP**, although 500 mL was used per size fraction**."

L248: Heading for section 3.2.4 indicates that only bulk POC, PON and d15N measurements were collected. Text on L406-408 implies size-fractionated POC and PON data exist. If the latter is true please amend section 2.3.4 with the analytical details.
Response: We have amended the methods sentence to the following –
"Duplicate seawater samples (4 L) were also gently vacuum-filtered through combusted 47 mm-diameter, 0.3 µm GF-75 **and 2.7 µm Grade-D** filters for POC and PON concentrations and δ^{15}N-PON."

L357: Typo - NH4 consumption rate is not defined in equations 6- 8. Please check and correct
Response: We have fixed the typo to the intended term as in equation 8 –
"Where, $NH_4^+{}_{\text{removal rate}} = \rho NH_4^+ + NH_4^+{}_{\text{ox}}$."

Results:

L467 & Fig 7: Figure 7 could be improved by merging the two subplots such that the "% of particles" is reflective of the actual proportions observed (i.e. contribution to the total particle count, photo + hetero + detrital). Currently, the approach used is a little confusing, with Fig7a indicating that heterotrophic cells represent ~30% of particles (photo + hetero) (or as described in the text the % of small cells L465), and Fig 7b suggesting heterotrophic cells represent ~<10% of particles (hetero + detrital). Given the presentation of results on L467, would it not be clearer to state the proportion of each particle type in a single figure where the % contribution is the contribution to the total particle count (photo + hetero + detrital)? The real value of Fig 7a and 7b only appears in the discussion (L698-701) and not really in the results section.
Response: We have heeded the suggestion of the Reviewer and combined Figure 7a and 7b (see Figure R2 below). We have moved the previous version of Figure 7 to the supplement as Figure S5.
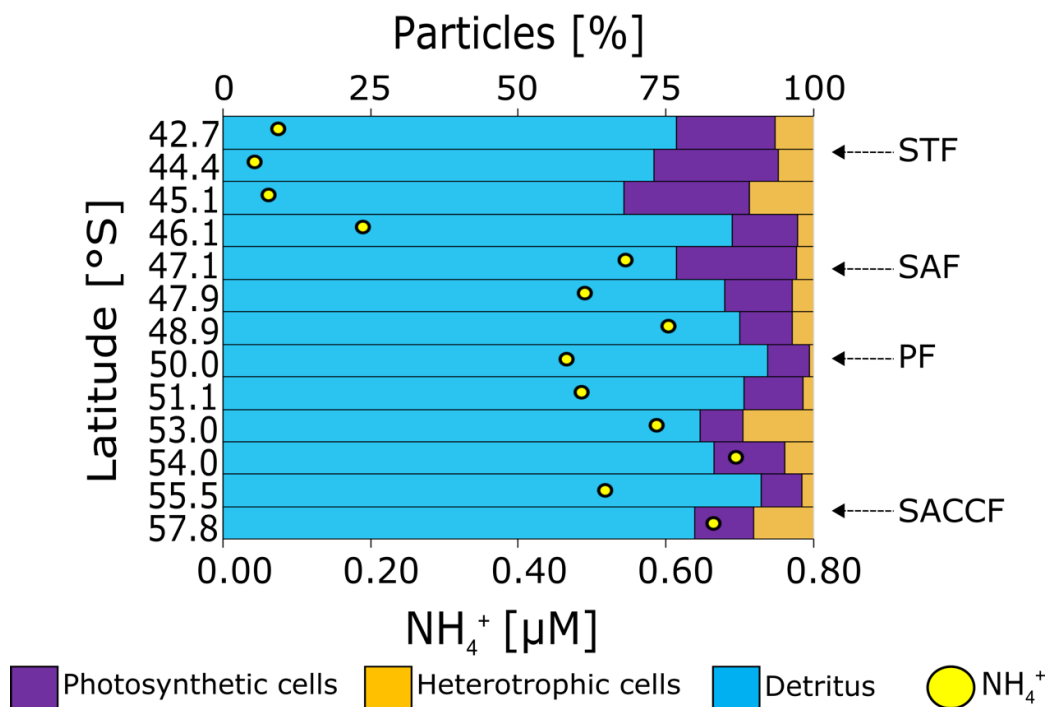

Figure R2 (Figure 7 in main manuscript): Relative contributions of photosynthetic, heterotrophic bacterial, and detrital particles to

the total flow cytometry counts at the surface during leg S. The coincident NH_4^+ concentrations are shown as yellow dots. Abbreviations are as in Figure 1.

Section 4.7 & L523: To be fair to your intended readership can the authors add their estimates of NH4 residence times north of the SAF to the text for completeness

Response: We have changed the results paragraphs in section 4.7 to include the results from north of the SAF as follows –

"The $NH_4^+{}_{residence\ time}$ in winter 2017, computed using Eqn 5, ranged from 10 to 38 days (median of 21 days) south of the SAF and **from 0 to 6 days (median of 2 days)** north of the SAF. These values were estimated using wintertime measurements only and as such, may not be representative of the transition from summer to winter. To refine our estimates, we used average ρNH_4^+ and NH_4^+ concentration measurements. South of the SAF in late summer, $\rho NH_4^+ = 50.6 \pm 24.0$ nM day^{-1} and the NH_4^+ concentration $= 0.81 \pm 0.92$ µM (Deary, 2020), which together yield an $NH_4^+{}_{residence\ time}$ of 2 to 27 days (median of 5 days). **The $NH_4^+{}_{residence\ time}$ north of the SAF, calculated using $\rho NH_4^+ = 20.7 \pm 8.6$ nM day^{-1} and NH_4^+ concentration $= 0.16 \pm 0.45$ µM (Deary, 2020) was 1 to 17 days (median of 14 days).**

The $NH_4^+{}_{production\ rate}$ south of the SAF, calculated using Eqn 8 and an $[NH_4^+]_{decline}$ of 330 nM (i.e., the difference between late summer and winter 2019; 810 nM – 480 nM), t of 141 days, and $NH_4^+{}_{removal\ rate}$ of 50.6 ± 24.0 nM day^{-1} (here, the average late-summer ρNH_4^+ south of the SAF is used to approximate $NH_4^+{}_{removal\ rate}$), was 52.9 ± 25.0 nM day^{-1}. **Similarly, north of the SAF (using an $[NH_4^+]_{decline}$ of 20 nM, i.e., 160 nM – 140 nM, and $NH_4^+{}_{removal\ rate}$ of 20.7 ± 8.6 nM day^{-1}), the $NH_4^+{}_{production\ rate}$ was 50.7 ± 9.3 nM day^{-1}.** If we instead use the average $NH_4^+{}_{removal\ rate}$ and NH_4^+ concentration measured in winter 2017 south (21.4 ± 0.6 nM day^{-1} and 520 ± 110 nM) **and north (18.4 ± 0.8 nM day^{-1} and 80 ± 10 nM)** of the SAF, the $NH_4^+{}_{production\ rate}$ was 23.4 ± 6.6 nM day^{-1} **and 18.5 ± 6.6 nM day^{-1}**, respectively. Using the range of $NH_4^+{}_{removal\ rate}$ estimates and the average ambient NH_4^+ concentration measured south of the SAF in winter 2017 (16.7 to 31.2 nM day^{-1} and 520 nM) and late summer 2019 (22.6 to 98.6 nM day^{-1} and 810 nM), we calculate that over the late-summer-to-winter transition, the $NH_4^+{}_{production\ rate}$ ranged from 18.8 to 100.9 nM day^{-1} **(compared to 6.3 to 28.8 nM day^{-1} north of the SAF)**."

Discussion:

L712-722: The role of zooplankton in NH4 production is certainly important in some studies (see Hernandez-Leon et al 2008; Priddle et al 1997 etc) but this section presents a rather limited assessment of its significance due to the acknowledged limitations of the dataset. It remains an interesting interpretation (already modified by the authors) but perhaps one that should still be strengthened with some literature support.
S. Hernández-León, C. Fraga, T. Ikeda, A global estimation of mesozooplankton ammonium excretion in the open ocean, Journal of Plankton Research, Volume 30, Issue 5, May 2008, Pages 577–585.
Priddle et al., (1997). Diurnal changes in near-surface ammonium concentration – interplay between zooplankton and phytoplankton. J. Plankton Res, 19(9), 1305-1330.

Response:

We have no doubt that at times, zooplankton make a potentially significant contribution to the mixed-layer NH₄ pool in the Southern Ocean. However, in response to the first round of review of the manuscript, we have tried to keep speculation in this regard to a minimum, particularly given our limited dataset (as noted by the Reviewer). That said, for the wintertime Southern Ocean, we do not think it is unreasonable to suggest a higher contribution to the NH_4^+ supply by heterotrophic bacteria than zooplankton given the low biomass concentrations (i.e., low food supply) and low zooplankton abundances that we observed during our sampling. It is likely that the zooplankton contribution to the NH_4^+ flux is far more significant in (late) summer and near the fronts (i.e., in response to elevated phytoplankton biomass following the growing

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season and driven by frontal upwelling, respectively). Indeed, our late summer and spring 2019 datasets appear to show evidence of both these scenarios.

We have thus added the following sentence and relevant references –

> "That said, it is possible that the contribution of micro- (and/or macro-) zooplankton to the NH_4^+ pool surpasses that of heterotrophic bacteria under certain conditions (Koike et al., 1986; Priddle et al., 1998), such as in (late) summer and near regions of frontal upwelling in response to elevated rates of phytoplankton biomass accumulation."

We also allude to this possibility at L850 –

> "By late summer, the NH_4^+ concentrations increased (Fig. 8b) presumably due to elevated heterotrophic activity (i.e., bacterial decomposition and zooplankton grazing) following the accumulation of algal biomass (Mengesha et al., 1998; Le Moigne et al., 2013)."

We feel that we cannot make any more conclusive statements than the above given that previous studies have shown a highly variable contribution by zooplankton to the NH_4 pool in the Southern Ocean (i.e., <0.5 – 82%; Alcaraz et al., 1998; Atkinson & Whitehouse, 2001; Hernández-León et al., 2008; Whitehouse et al., 2011).

Reviewer 2: Anonymous

Referee comment on "Biogeochemical controls on wintertime ammonium accumulation in the surface layer of the Southern Ocean" by Shantelle Smith et al., Biogeosciences Discuss., https://doi.org/10.5194/bg-2021-149-RC2, 2021

General comments

The authors have done an excellent job of updating their manuscript following the previous reviewer's comments. I have two minor comments on this version to be considered for revision.

Response: We appreciate the comments from the Reviewer regarding our efforts on the revised manuscript.

Specific comments

Methods:

1. In the Methods Sec 3.1 there is no mention of how the NH4+ samples were taken on the 2018/19 voyages. Were they taken following the same method in L161-169 and were they underway or CTD samples?

Response: We have added the following sentence to the paragraph at L161-169 –

> "During the 2018-2019 cruises, NH_4^+ samples were collected every two hours from the ship's underway system."

Discussion:

2. In the Discussion Sec 5.2 the authors attribute that changes in the NH4+ concentration in late summer were "due to" (L758) a range of biological processes. However, they can only support this hypothesis by the literature, as these measurements were not made in this study. I suggest a slight change in the wording here to reflect that.

Response: We have changed the wording here to "…presumably due to…" to indicate our reliance on the literature as opposed to measurements made during the study.

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