Response to reviewers: Seasonal cycles of biogeochemical fluxes in the Scotia Sea, Southern Ocean: A stable Isotope approach

Response to reviewers: Reviewer 1

Review Biogeosciences Discussion (June 2023)/2nd round
Seasonal cycles of biogeochemical fluxes in the Scotia Sea, Southern Ocean: A stable Isotope approach
Belcher et al.
The revised version is significantly improved. However, I still have some minor comments, that needs to be addressed before publication.

Reply: Thank you for taking the time to review the manuscript, we have addressed the points you have raised below. Line numbers refer to the marked up version of the text.

L205: The authors give the delta notation only for carbon and nitrogen isotopes, but not for silicon isotopes. I see that the silicon method description is given in another paragraph, but the authors could at least refer to the delta notation, as it is the same for all three stable isotopes (C, N, Si).
Reply: We have added the following text to the methods (line 231 -234)
"Stable Si isotopic compositions are presented in standard delta notation (δ30Si), as for δ13CPOC and δ15NPN according to Equation 2, where R is 30Si/28Si. These compositions are checked against δ29Si (where R is 29Si/28Si) for mass dependence."

L393: Other organisms were observed, but not counted? Do the authors have a rough idea of how much of the sediment trap material was diatoms compared to other (non-siliceous) organisms)? This has some implications for the interpretation of δ13C and δ15N. See also my comment below (L.474). In line 395, the authors say "with a dominance of diatoms". What exactly does that mean? More than 50% or 90%? The following paragraph only gives information about the diatoms and a few silicoflagellates in each sample. How many dinoflagellates do the authors observe? Does "other" in Figure 4 refers to other taxa, like dinoflagellates? Or other diatoms? Please clarify in the text and the figure caption.
Reply: Other organisms were indeed counted, as detailed in the methods, but we focus the results on the organisms that dominated the sediment trap material (as can be seen in figure 4). Figure 4 displays the phytoplankton that dominated by abundance as well as biovolume and it is clear from this that diatoms are dominant. In most samples diatoms were >90% but all were greater than 85% (by abundance and biovolume); we have added this into the text at line 411. The dinoflagellates *prorocentrum* spp. and *pronoctiluca* spp. are shown to have >5% abundance in Figure 4, and the silicoflagellate *Dictyocha* has >5% contribution by biovolume. 'Others' refers to all other taxa counted to sum to 100%, so this encompasses any taxa that were counted but comprised <5% of the sample. We have amended the caption to explain this.

L429: It is very interesting to see the comparison to other flux measurements in the region. However, I miss some kind of interpretation here. Why are POC and BSi fluxes generally higher, but much lower compared to Closset et al. (2015)? Any major changes in the area, that are causing this. Why does the sampling location from Closset et al. (2015) have more than 10x higher fluxes compared to this study?
Reply: There are a number of interacting factors impacting the magnitude of export flux, including species composition, nutrient limitation and level of zooplankton grazing, and this, combined with the high interannual variability in export flux in these high latitudes, makes it difficult to give the exact cause of the differences between the two region. Comparing our study to that of Rembauville

highlights the high variability in the Scotia Sea, and where as Closset et al. 2015 measured very high fluxes, Trull et al. 2001, measured much lower fluxes in the same region in a different year.
We have added the following additional text lines 479-486.
"Interannual variability in export flux can be high due to the complexity of processes controlling the magnitude of export flux, such as community structure, nutrient limitation and zooplankton activity. Closset et al. (2015) measured very high fluxes (>700 mg SiO_2 m^{-2} d^{-1}) of BSi south of the Sub-Antarctic Front in the Australian sector of the Southern Ocean at 2000 m, and similarly high fluxes have been observed in other sectors (Fischer et al., 2002; Honjo et al., 2000). A study by Trull et al. (2001) measured fluxes of BSi in the range of 30- 160 mg SiO_2 m^{-2} d^{-1} during the productive season in the same region as Closset et al. (2015), again highlighting the high interannual variability."

L469: Please check the sentence. Something is odd. "This could be achieved if cells are large through large".
Reply: We have added in a comma to correct this sentence

L474: I think, this is not even a "broadly" similar trend in Figure 5b. I think the authors should rather discuss, why they do not see a linear trend between δ13CPOC and δ30SiBSi. Even though the particulate ratios show a strong relation between POC and BSi (except for 3-4 points above the line), the less pronounced or not present relationship in the isotopes can have several reasons.

1. more variation and a higher range in the fractionation factor for δ13C compared to δ30Si (e.g. Brandenburg et al., 20221), which can also include different trophic levels.
2. non-siliceous organisms or organic material (dinoflagellates, microzooplankton). Whereas δ30Si is measured mainly in diatoms, δ13C, as well as δ15N, is measured in other materials/organisms as well
3. different remineralization for organic carbon and silicon in the frustule

Reply: We have edited the text to reflect that though significant, the R2 is low. Thank you for the valuable insight here and suggestions of reasons to explain the weaker relationship between the Si and C isotopes. We have added this information in, as below, lines 513-519.

"Despite the strong relationship between particulate fluxes of POC and BSi, the relationship between the δ13CPOC and δ30SiBSi isotopes signatures is less pronounced (linear regression: $R2 = 0.452$, $p<0.001$; Figure 5). This may relate to greater variation in the fractionation factor for δ13C compared to δ30Si (Brandenburg et al., 2022), as well as differences in remineralisation of organic carbon and silicon in the frustule. Additionally, whereas most of the δ30Si signal is from diatoms, the δ13C signal in the sediment trap material is also impacted by the presence of other organic material, e.g. zooplankton faecal pellets."

1 Brandenburg, K. M., Rost, B., Waal, D. B. V. de, Hoins, M. & Sluijs, A. Physiological control on carbon isotope fractionation in marine phytoplankton. *Biogeosciences* **19**, 3305–3315 (2022).

L476: The authors state that they do not find significant relationships between δ13CPON, δ13CPOC, and δ30SiBSi. It would be good if the authors could either show the figures in the supplement or report the r2 and p levels here for comparison. I am a bit surprised, that the relationship in Figure 5b is significant. Did you include the error? Please check again.
Reply: We have added in the p values of the non significant relationships as requested but do not give the R2 since these are 0 so do not provide useful information. We have double checked and the relationship in figure 5b is significant, we base the relationship on the mean values of Si and C isotope ratios from the replicated available.

L487: This is more of a general comment. Do the authors take the sinking velocity of particles into account, when discussing the sediment trap data? And if yes, what is the sinking velocity they assume?

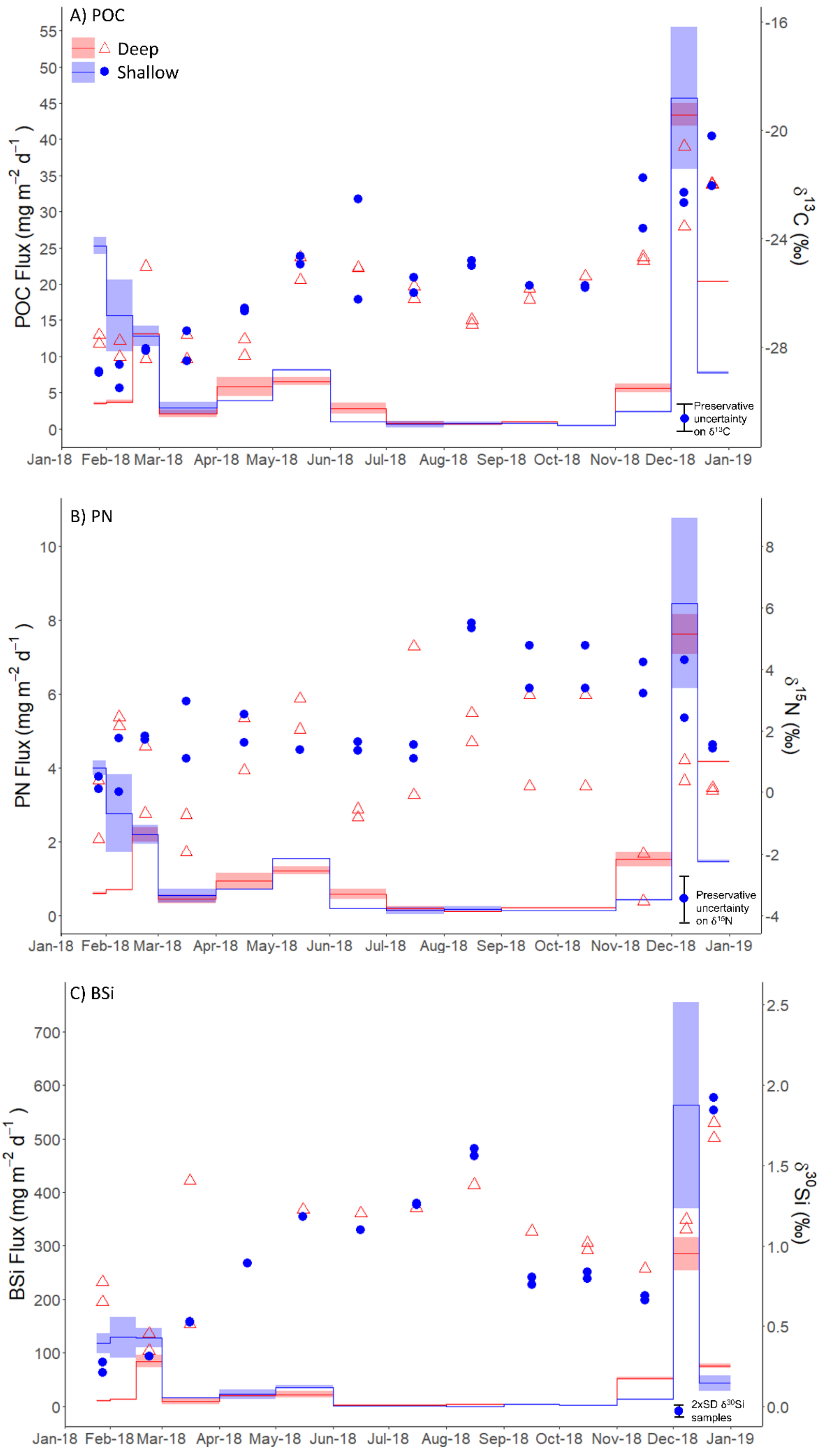
Reply: We do not directly measure sinking rates since material can aggregate together in the sediment trap cup, and therefore particles cannot be presumed to be in the same state that that they were on entering the trap. We are able to make some inferences on sinking velocity based on lags between isotopic shifts in the shallow and deep sediment traps (e.g. see lines 343-349).

L493: "BSi: POC ratios were elevated at the start of productive period 1, suggesting that phytoplankton were heavily silicified…..this statement can only be made if the ratio of siliceous to non-non-siliceous plankton is not changing over time. Here the authors need to give more information about the amount of dinoflagellates in their samples (see also statement above). And if the statement is "true", why should a more intense silicification is observed?

Reply: Thank you for this observation, we have amended the text here as follows:
"BSi:POC ratios were elevated at the start of productive period 1, which may suggest that phytoplankton were heavily silicified. The contribution of non-siliceous phytoplankton was low during the periods analysed for phytoplankton composition (<2%, with the exception of the shallow trap in the late January sample where the contribution was 6.7%), though we cannot rule out higher contributions of non-siliceous phytoplankton during other periods which could account for the lower BSi:POC ratios at these times."

Figure 3: The figure did improve significantly. Maybe it is possible to additionally add the legend to the figure for the deep (red) and shallow (blue) sediment traps.

Reply: We have added the legend as below and amended the caption accordingly.



A) POC
Deep
Shallow
POC Flux (mg m^{-2} d^{-1})
δ^{13}C (‰)
Preservative uncertainty on δ^{13}C
Jan-18 Feb-18 Mar-18 Apr-18 May-18 Jun-18 Jul-18 Aug-18 Sep-18 Oct-18 Nov-18 Dec-18 Jan-19
B) PN
PN Flux (mg m^{-2} d^{-1})
δ^{15}N (‰)
Preservative uncertainty on δ^{15}N
C) BSi
BSi Flux (mg m^{-2} d^{-1})
δ^{30}Si (‰)
2xSD δ^{30}Si samples

Figure 4: Maybe the authors could either highlight it in the figure or in the figure caption, how does the assemblage data fit to their different time periods? The abundance data at the end of the sampling campaign (Dec./Jan.) fit within the productive period 2, but the first was already in the winter hiatus.

Reply: We have added shading for the two productive periods as per figure 2

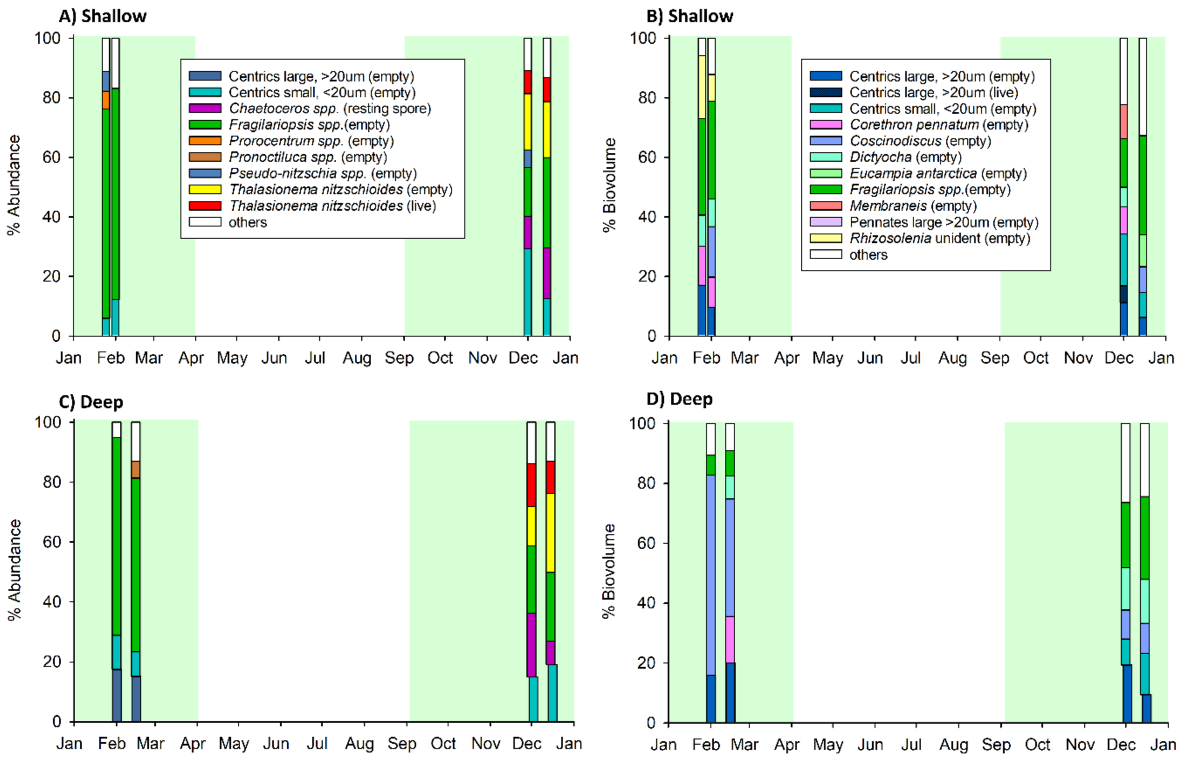
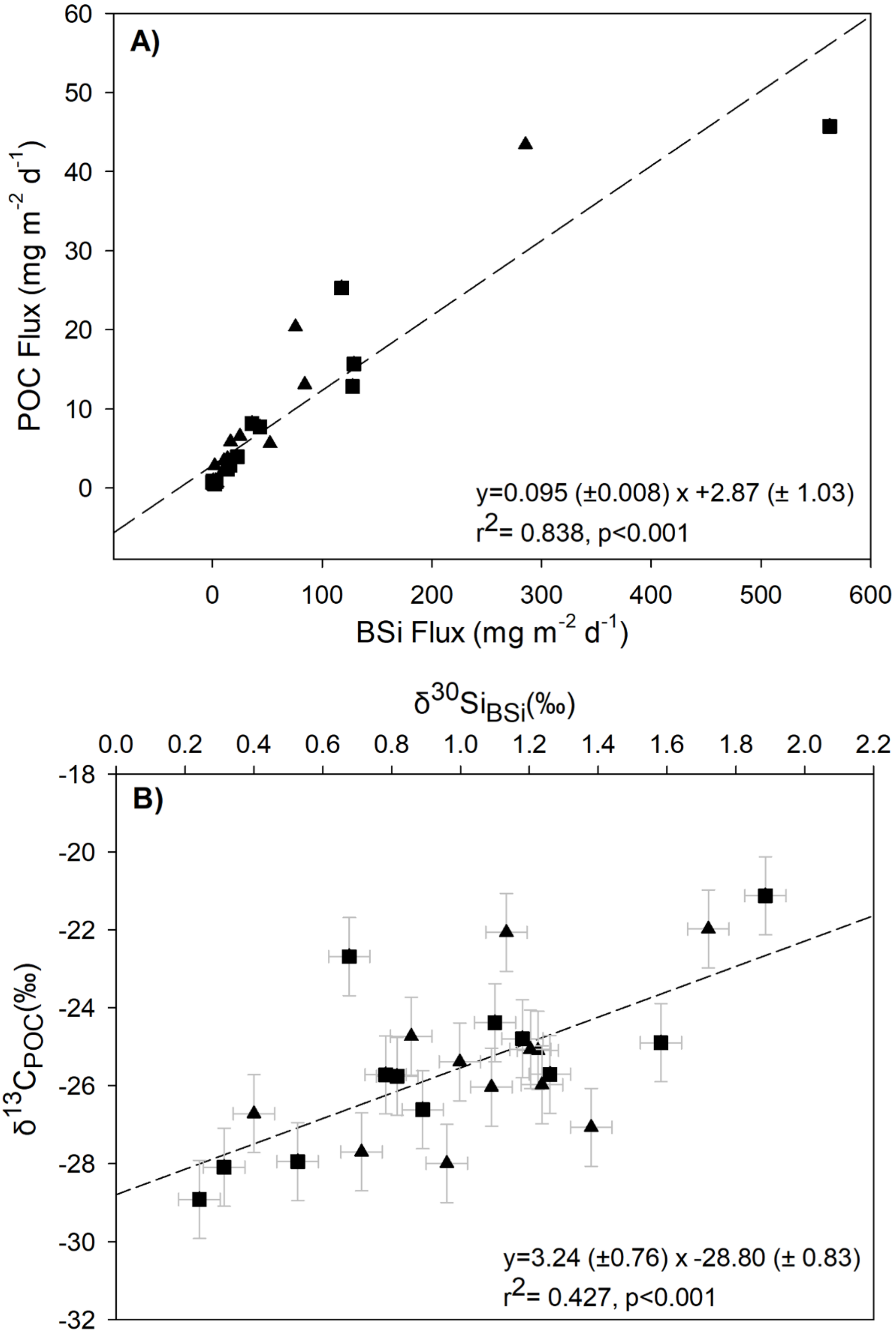


Figure 5: Please add error bars for the isotope data in 5b.

Reply: we have added error bars as per the error bars in figure 3, based on preservative uncertainty and analytical uncertainty for δ13CPOC and δ30SiBSi respectively.


A)
POC Flux (mg m-2 d-1)
BSi Flux (mg m-2 d-1)
y=0.095 (±0.008) x +2.87 (± 1.03)
r2= 0.838, p<0.001
δ30SiBSi(‰)
B)
δ13CPOC(‰)
y=3.24 (±0.76) x -28.80 (± 0.83)
r2= 0.427, p<0.001

Response to reviewers: Reviewer 2

General comments

In "Seasonal cycles of biogeochemical fluxes in the Scotia Sea, Southern Ocean: A stable isotope approach", Belcher et al. present a study investigating the seasonal variations of organic matter (POC and PON) and biogenic silica fluxes from two sediment traps located north-West of South Georgia in the Scotia Sea (Southern Ocean). Using stable isotope approaches the authors examine the origin and some of the processes controlling the fluxes they have observed in the traps.

They investigated the differences between two productive events (in February 2018 – summer season – and December 2018 – spring season) and the coupling of C, N and Si fluxes during these events. Their main results are: Particulate fluxes and isotopic compositions were similar in the deep and shallow trap suggesting that most of the remineralization occurred in the upper layer of the water column. Despite a very noisy d15N signal, the synchronicity if the d30Si and d13C signals highlight the coupling between these two elements and the significant role of diatoms in the export of C (and BSi) in the area. Based on the estimation of isotopic baselines associated with the two productive events, they also suggested a change in the source region of the material coming into the sediment traps.

Having reviewed the first version of this manuscript, I greatly appreciate authors' efforts to improve the reading by carefully re-organizing the different sections. The introduction is clear and describes all the background needed to fully appreciate the manuscript. New elements have been added to the discussion and greatly improve the manuscript. Some minor points will still benefit to be clarified and, although they have already greatly improved the figure, I am personally not convinced that figure 3, which is the most important figure in the manuscript, is not presented in the clearest/smartest possible way (but this is my personal taste, the data are currently there).

I detail these points below and, although I recommend publication of the manuscript after minor revisions, I am convinced that this paper will be a great addition to "Biogeosciences".

Thank you for taking the time to look at the manuscript for a second time and for the enthusiasm about the manuscript. Thank you for the minor points raised to further improve the manuscript, which we have addressed as detailed below. Line numbers refer to the marked up version of the text.

Methods

* L238: Pioneer ref is Cardinal et al. 2003

Reply: Reference added in

* L249-253: A 0.12‰ offset in δ^{30}Si value might be an order of magnitude lower compared to the seasonal signal, however it is significant regarding the magnitude of δ^{30}Si variations measured in the study (and could potentially be higher than the error calculated on duplicates or using standards). I am aware that this offset is the wort case scenario, and I am convinced about the quality of the isotopic measurements and the assessment of the error and potential bias in this study. However, I think that few sentences explaining why contamination by lithogenic material has the potential to bias the signal, and most importantly why this potential contamination is unlikely, or small, in this study is missing here. Is there any data from other studies that could support the fact that LSi is not a problem here?

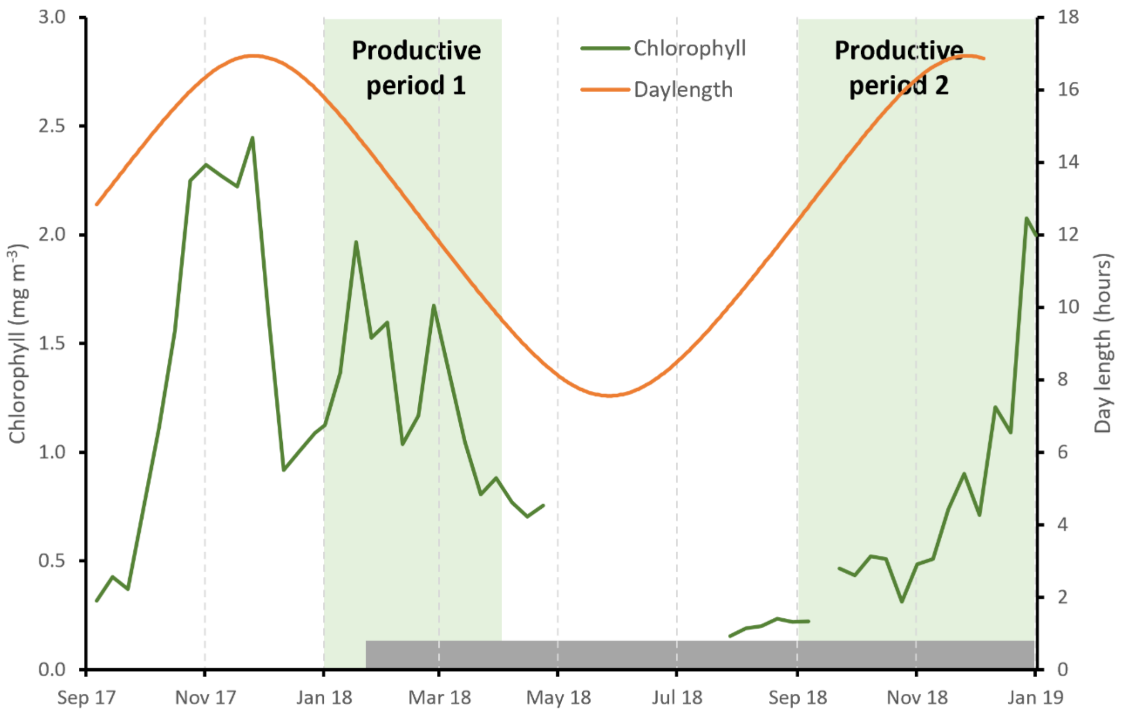
Reply: The text here has been amended as follows:

"A lithogenic correction (e.g., Closset et al., 2015) was not carried out on these samples given the high percentage of biogenic silica present in the samples (mean percentage BSi as SiO_2 of 17 %). BSi extraction methods show lower variability for marine sediments with BSi > 15-20 % and do not show evidence for significant leaching of lithogenic material through time (Conley, 1998). Furthermore, even an extreme scenario of variable lithogenic contamination of 1-5 % of isotopically light marine clays (with δ30Si of -2.3 ‰; Opfergelt and Delmelle, 2012) would only result in a potential systematic offset of 0.12 ‰, which, although this is larger than the uncertainty on an individual datapoint, is an order of magnitude smaller than the observed seasonal signal."

Results

* Figure 2: Just an idea like this… adding a dark horizontal bar along the x axis to visualize the sampling period by the sediment trap.

Reply: Thank you for the excellent suggestion, we have added this in and amended the caption accordingly.



* Figure 3: As I mentioned earlier, I am still not convinced that using the min/max this is the smartest way to present the isotope values, especially when refereeing only to the mean value in the text. I actually had to manually draw a line going through what should be the mean value for all the δ13C, δ15N and δ30Si panels to be able to properly follow authors' discussion (see picture below). I personally think that, as it is, the figure kind of work but does not easily help supporting the text and that it will greatly benefit by plotting one symbol for the mean value (as this is the one authors used in the discussion) and perhaps a vertical line representing the range between the min and max (if authors want to keep this information on the figure).

Reply: We believe that figure 3 is now a good representation of the data, as agreed by the first reviewer. Since there are a few isotope values where the range is large between sample splits we think that showing the max and min more fairly represents the heterogeneity of sediment trap material. In these cases, the mean line (without max and min) is not a fair representation. We therefore keep figure 3 as is, adding the legend as requested by reviewer 1.

L361: "flux-weighted" sounds odd, perhaps use "integrated"

Reply: This is common terminology in sediment trap papers and is descriptive in terms of what has been used to weight the isotope values, so we keep this.

Table 1: Having an additional line with winter values will be useful as authors mention these winter values in the text.

Reply: We have added this in as suggested.

L383: "[…] were globally/more or less similar […]"
Reply: Amended to 'quite similar'

L388-391: I don't see quite steady isotopic values in winter in the shallow trap. They vary from 1‰ to 1.5‰ which is a significant variation when considering δ30Si values.
Reply: We have amended the sentence to reflect the increase of 0.38 per mille in the shallow trap : "Isotopic values in the deep trap were then quite steady over winter compared to the rest of the record, with an increase of 0.38‰ in the shallow trap between May and August."

L410: Since Dictyocha is not a diatom, do we have an idea of the range of δ30Si of these organisms and how they could potentially affect (or not) the isotopic signal measured in the traps?
Reply: To the best of our knowledge there have not yet been any studies investigating the range in δ30Si of *Dictyocha* or indeed other silicoflagellates so we are not able to constrain the impact this of organism on our measured values. This would be a useful area of further research. We have added the following sentence to make it clear that we cannot assess the impact of this organism, though since the % contribution by abundance was <5% and diatoms were dominant (>85% - this information has been added to the manuscript), their isotopic signature would need to be vastly different from that of diatoms to have an appreciable impact on our results.
"Since there has been little known work on the δ^{30}Si of *Dictyocha* or indeed other silicoflagellates, we are not able to constrain the impact of this organism on our measured values. However, since the contribution by abundance was <5 % and diatoms were dominant (>85 %), their isotopic signature would need to be vastly different from that of diatoms to have an appreciable impact on our results."

Discussion
* L436-439: This could be more elaborated even briefly. For example, what kind of source? what are the different degradation states and how do they affect the δ15N signal in the particles?
Reply:

Reply: We have expanded this argument, so that it is clear what we mean, as follows:

The lower POC:PN ratios measured in the deep trap between August and October, compared to the shallow trap are consistent with a divergence in $\delta^{15}N_{PN}$ ratios, and could indicate that material arriving at the two traps is not necessarily sourced from the same region and time period in surface waters. Given the slower sinking speeds at this low-productivity time of year, it is possible that material reaching the deep trap is sourced from upstream of where material reaching the shallow trap is sourced in the regional circulation system. Different source regions are likely characterised by different phytoplankton assemblages with different nutrient stoichiometry, and the time taken for source material to reach each of the traps may well lead to differences in degradation state of organic matter, which could also lead to variations in POC:PN.

To ensure that the reviewer's comment is addressed comprehensively, we have also added to the related argument in Section 4.2.2 (lines 591-602), as follows.

"$\delta^{15}N_{PN}$ in the shallow trap showed a slight progressive decrease from April to July, before increasing in August to 5.42 ‰. The progressive decrease is consistent with the propagation of the surface signal of phytoplankton growth and fractionation, with a longer time lag than during spring and summer due to slower sinking rates during the low-productivity period. Decreasing $\delta^{15}N_{PN}$ reflects the increasing influence of ammonium uptake, either in the same locale or upstream in the regional circulation system, which leads to lower $\delta^{15}N_{PN}$ than nitrate uptake in the slowly-sinking flux. The large range in $\delta^{15}N_{PN}$ in the deep trap in July makes it difficult to determine with certainty a trend in $\delta^{15}N_{PN}$ in the deep trap between July and October. Dissimilar trends in $\delta^{15}N_{PN}$ between the two traps over the winter period also support the argument that material reaching these two traps may have a different source region or time period in surface waters (Section 4.1)."

* L467: please change "algal" by "phytoplankton"
Reply: Changed

* L474-476: If it is only "broadly similar trends", and regarding the R2, I would not use "close coupling of carbon and silicon cycling processes."
Reply: We have amended this section in response to this comment and a related comment from reviewer 1, as follows:
"Despite the strong relationship between particulate fluxes of POC and BSi, the relationship between the $\delta^{13}C_{POC}$ and $\delta^{30}Si_{BSi}$ isotope signatures is less pronounced (linear regression: $R^2 = 0.452$, $p<0.001$; Figure 5). This may relate to greater variation in the fractionation factor for $\delta^{13}C$ compared to $\delta^{30}Si$ (Brandenburg et al., 2022), as well as differences in remineralisation of organic carbon and silicon in the frustule. Additionally, whereas most of the $\delta^{30}Si$ signal is from diatoms, the $\delta^{13}C$ signal in the sediment trap material is also impacted by the presence of other organic material, e.g. zooplankton faecal pellets."

* L508: Please remove "with no significant difference between deep and shallow" as deep trap data seem more variable compared to shallow trap data.
Reply: Deleted

* L520: I would not qualify this as a slight increase (it just increases)
Reply: Deleted word slight

* L563-566: Could it be also associated with a shift in community with for example a little bit more silicoflagellates?
Reply: Although species related shifts in silicon isotopes have been observed in the laboratory, the evidence for this is lacking in the field (e.g.Closset et al., 2015; Egan et al., 2012), and thus we do not speculate about this here. We mention this in lines 587-591 and 697-699, and do not think it needs repeating here. We have no constraints on Si isotope fractionation by silicoflagellates.

* L599 and few other times later in the discussion: "flux-weighted" sounds odd, perhaps use "integrated"
Reply: As above, this is common terminology in sediment trap papers and is descriptive in terms of what has been used to weight the isotope values, so we keep this.

Conclusion
L704-706: Without changing the sentence too much, I think this study does not really highlight how, but perhaps more "the importance of conducting a more detailed mechanistic understanding of the drivers of POC flux […]"
Reply: Amended as follows:
"Our results highlight the need for more detailed mechanistic understanding of the drivers of POC flux and biogeochemical cycling, to improve estimates of the current and future strength of the biological carbon pump and the ocean's role as a CO_2 sink."

NB: The data were not available at the time of the review

Reply: The data DOI are in progress and data will be housed with the Polar Data Centre, as per the data availability statement.