

## Comment on bg-2021-42

Frank Dehairs (Referee)

Referee comment on "Early winter barium excess in the Southern Indian Ocean as an annual remineralisation proxy (GEOTRACES GIPr07 cruise)" by Natasha René van Horsten et al., *Biogeosciences Discuss.*, <https://doi.org/10.5194/bg-2021-42-RC1>, 2021

This manuscript brings much wanted information about the Southern Ocean particulate biogenic Ba (Baxs) distribution during winter conditions. Previous studies in the S.O. were all conducted during spring to autumn conditions, showing a seasonal progress of the Baxs signal but lacking information on winter conditions when plankton activity is at a minimum. The mesopelagic Baxs inventory is gauged against integrated PP covering the growth period preceding the sampling, and these data are combined with literature data revealing an interesting correlation.

Response: We thank Pr. Frank Dehairs for this very positive comment.

Please see below our responses to the revisions and comments (in blue) and the excerpts from the revised manuscript (in red).

I wonder why authors, when comparing their data with literature, have considered data from specific expeditions and not from all available data for the S.O. In particular the Baxs data presented in Dehairs et al. (GBC 1990; INDIGO 3 expedition, 1987) for the same general area as studied by the present authors were not considered. During the INDIGO 3 several stations were occupied along approx. 30°E between 65°S and 57°S. S to N Baxs inventories are similar to values reported in the present ms., confirming indeed that microbial activity in the mesopelagic area is still ongoing during winter period. Further data that have not been included in the Baxs inventory – PP comparison are those from Dehairs et al. (1997) obtained during Polarstern ANT X/6 expedition along 6°W in early season. If possible, these two data sets should be included in the compilation.

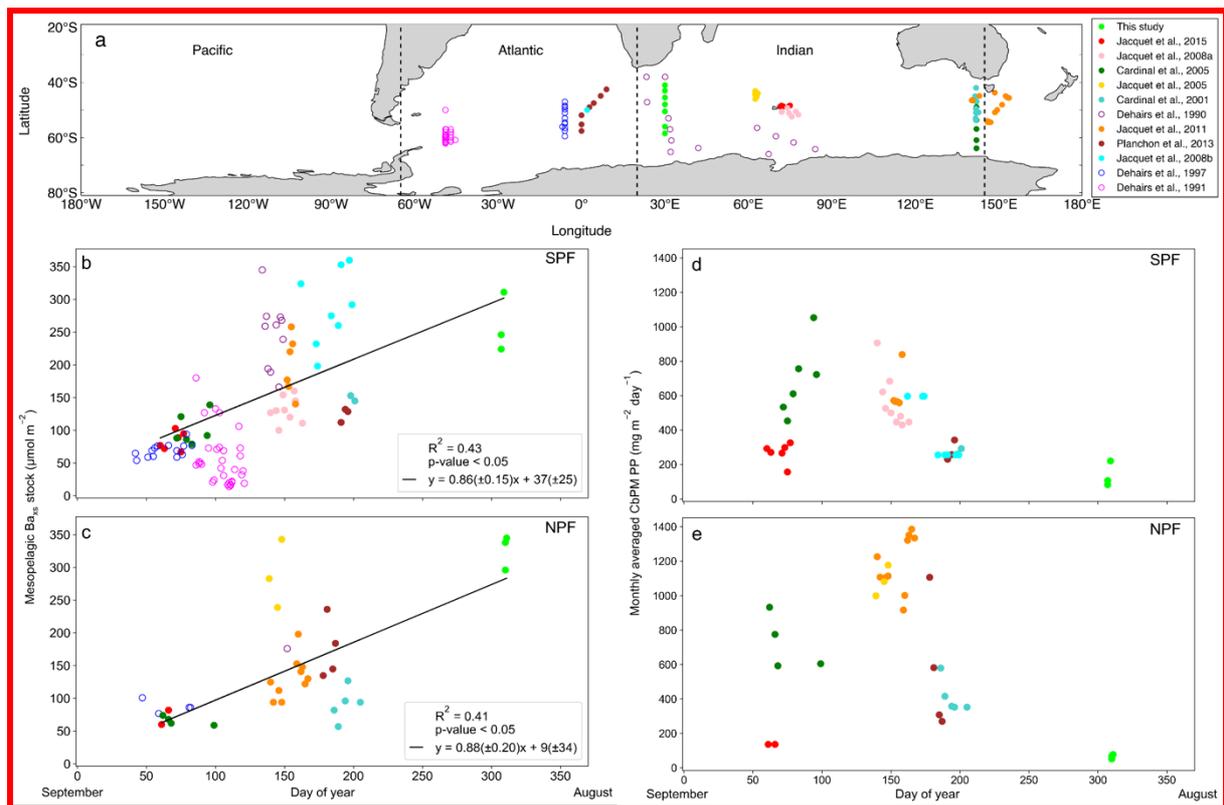
Response: In the initial manuscript, the Ba<sub>xs</sub> data were plotted against satellite-derived PP, integrated over months prior to sampling. At the time of the INDIGO 3 and ANT X/6 cruises, there was no remotely sensed PP data available and the PP data from Dehairs et al. (1997) were measured during the cruise and are not representative of integrated PP over months preceding the study. Therefore, these data were not initially included in our compilation.

Nevertheless, the mesopelagic Ba<sub>xs</sub> stock ( $\mu\text{mol m}^{-2}$ ) is now plotted against day of year sampled (Figure 4b and c, see below) in the revised manuscript, including the INDIGO 3, ANT X/6 and EPOS 2 data (see comment by Stéphanie Jacquet). However, as stated in the Figure caption, these data must be considered with caution because these samples were not digested using HF. This can lead to an underestimation of aluminium concentrations and an overestimation of Ba<sub>xs</sub>, where there are possible significant lithogenic inputs (e.g., close to Antarctica and downstream of the Drake Passage).

In order to investigate this hypothesis, for the first time, we compiled a SO mesopelagic Ba<sub>xs</sub> stock dataset with all available literature data including data from this study (Figure 4a, Table S3). The mesopelagic Ba<sub>xs</sub> stock was integrated over the Ba<sub>xs</sub> peak depth range (as identified in each study). As can be seen on the map of the compilation dataset (Figure 4a), these data points were collected in the three basins of the SO, over 20 years. Despite this diversity, a statistically significant accumulation of mesopelagic Ba<sub>xs</sub> with time, SPF and NPF (Figure 4b and c) is still observed. Mesopelagic Ba<sub>xs</sub> accumulates at a rate of  $0.86 (\pm 0.15) \mu\text{mol m}^{-2} \text{d}^{-1}$ , SPF ( $R^2 = 0.43$ , p-value < 0.05, n =

43; Figure 4b), and at  $0.88 (\pm 0.20) \mu\text{mol m}^{-2} \text{d}^{-1}$ , NPF ( $R^2 = 0.41$ ,  $p\text{-value} < 0.05$ ,  $n = 31$ ; Figure 4c), with no statistically significant difference between the two zones (Welch's  $t\text{-test} = 0.24$ ;  $p\text{-value} = 0.80$ ).

The seasonal signal for PP over the growing season (Figure 4d and e) clearly shows that the highest values occur between January and February (day 125 to 175 of the year), thereafter, steadily decreasing to minimal values in July ( $\sim$  day 310 of the year, i.e., during our study). The mesopelagic  $\text{Ba}_{\text{xs}}$  accumulation over time can, therefore, not be matched with the remotely sensed PP measured during the month of sampling



**Figure 4: (a) Positions of  $\text{Ba}_{\text{xs}}$  observations compiled from all known SO studies, on a cylindrical equal-area projection of the SO, the three SO basin cut offs are indicated by the dashed black lines, from left to right, Pacific, Atlantic and Indian. Integrated mesopelagic  $\text{Ba}_{\text{xs}}$  stock plotted against day of year sampled, with the 1st of September set as day 1, for all available literature data and winter data from this study. Data was split into two zones using the Polar Front (PF) to divide the SO; (b) South of the PF (SPF) and (c) North of the PF (NPF). Monthly averaged remotely sensed PP plotted against day of year, for locations and dates of the SO compilation dataset and winter data from this study; (d) SPF and (e) NPF. Open circles are data points from studies which did not use HF in the particulate sample digestion procedure, regressions did not include these data, there was, however, no significant difference when including these data points.**

Authors do not provide information on how integrated PP was obtained for the compilation of literature data. Figure 1 should differentiate the different  $\text{Ba}_{\text{xs}}$  data sets.

Response: All PP data in the manuscript is satellite derived integrated PP using the CbPM PP algorithm, no in situ PP measurements were taken into consideration as we considered PP prior to the sampling of mesopelagic  $\text{Ba}_{\text{xs}}$ .

The methodology of integrated remotely sensed PP is included under section 2.5 of the original manuscript, with further details on subsampling in the discussion, section 4.2. We have expanded on this in the discussion (section 4.2) to state that this methodology was used for all considered studies in the dataset.

A possible link between the integrated mesopelagic  $Ba_{xs}$  stock and the corresponding integrated remotely sensed PP was assessed for all studies conducted after September 1997, when remotely sensed PP data became available. To do so, we first estimated that sub millimetre sized aggregates, in which barite crystals produced, would take  $\sim 20$  days to sink down to 1000 m (considered as the bottom of the mesopelagic zone, in this study), using a sinking speed of  $50 \text{ m d}^{-1}$  that corresponds to an average literature value ( $50 - 100 \text{ m d}^{-1}$ : Riebesell et al., 1991 ;  $50 - 430 \text{ m d}^{-1}$  around South Georgia: Cavan et al. 2015;  $\sim 100 \text{ m d}^{-1}$  in the Southern Ocean as reviewed in Laurenceau-Cornec et al., 2015;  $10 - 150 \text{ m d}^{-1}$ : McDonnell and Buesseler, 2010). Assuming a maximum surface current speed of  $0.2 \text{ m s}^{-1}$  (Ferrari and Nikurashin, 2010), it was estimated that these aggregates would have originated, 346 km west from the station that was sampled for mesopelagic  $Ba_{xs}$ ,  $\sim 20$  days prior. Using this distance, the dimensions of the sample area were set with the southernmost station (TM1) of this study, where degrees of longitude cover the smallest area. For the sake of consistency this sampling area was applied to all sampling locations of the considered dataset. The integrated remotely sensed PP (see section 2.5) was then averaged spatially, positioned  $6^\circ$  upstream longitudinally, and  $1^\circ$  latitudinally centred around each sampled station, in order to capture the surface PP that is assumed to translate to the mesopelagic remineralisation and  $Ba_{xs}$  stock.

An additional map has been included to identify the location of studies in the compilation dataset (Figure 4a).

Authors do not provide any information on sea ice extent relative to position of the southernmost station.

Response: This information is now included in the revised manuscript.

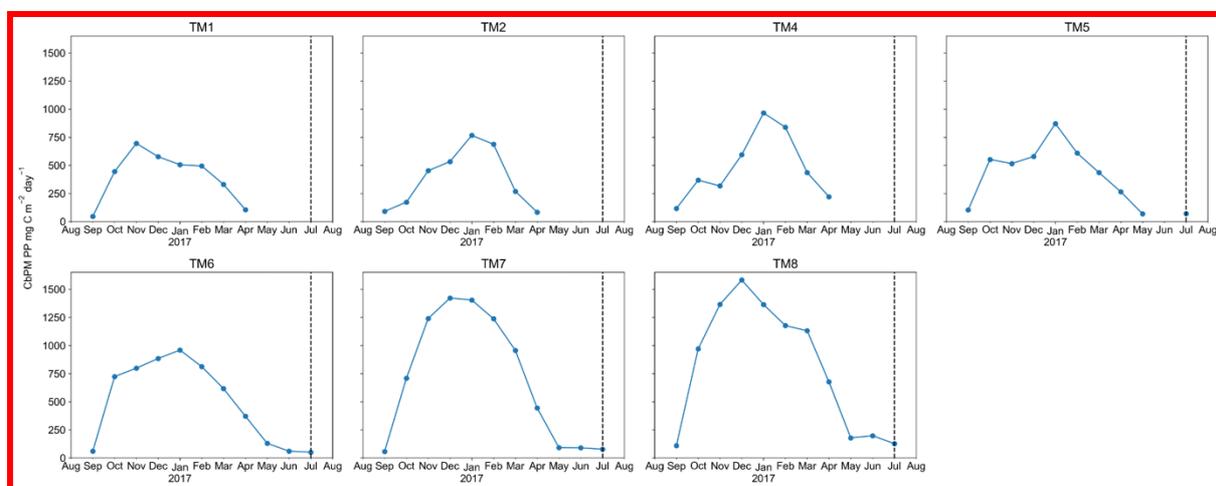
The marginal ice zone, identified as the position of 30% ice cover, was positioned at  $61.7^\circ\text{S}$ , approximately  $3^\circ$  (356km) south of the southernmost station (de Jong et al., 2018). Therefore, a potential sea ice influence on our study area can be disregarded.

While it makes sense to compare  $Ba_{xs}$  inventories with PP intensity in the months preceding the sampling, the coinciding Chlorophyll data shown in Fig. S1 still are relatively elevated reaching about  $0.5 \mu\text{g/L}$  at the PF and in the SAZ, this taking into account that S.O. Chl values of  $1 \mu\text{g/L}$  can be considered bloom values. Please comment.

Response: Whilst we agree with the reviewer that these Chl- $\alpha$  values are high, these measurements were performed by fluorometry. Fluorometric methods of measuring Chl- $\alpha$  are prone to errors, particularly in areas where there are high concentrations of diatoms. This is due to the presence of high Chl-c pigment concentrations in diatoms, and the spectral overlap between Chl- $\alpha$  and Chl-c falsely inflating Chl- $\alpha$  concentrations. This is best demonstrated in the study by Moutier et al. (2018, doi: 10.3390/rs11151793, Table 5) where they show that Chl- $\alpha$  determined by fluorometry can be almost double that as measured by HPLC. Unfortunately, no HPLC samples were collected during this study, so we do not have access to Chl- $\alpha$  concentrations by this method.

The issues with the use of fluorometric Chl- $\alpha$  have been reported by many studies (Pereira et al., 2018; Marrari et al., 2006; Gibbs, 1979; Welschmeyer, 1994; Roesler et al., 2017; Kumari, 2005; Lorenzen, 1981; Trees et al., 1985; Bianchi et al., 1995; Dos Santos et al., 2003). It is for this very reason that NASA only uses HPLC derived Chl- $\alpha$  in the cross-check calibration of remote sensing derived values.

Due to this issue with the Chl- $\alpha$  measurements, we have removed them from the revised manuscript, and we have instead added time series, area-averaged remotely sensed CbPM PP plots for each station sampled, indicating that PP was at a minimum  $\sim 2$  months prior to the time of sampling.



**Figure 3: Time series, area-averaged remotely sensed CbPM-PP ( $\text{mg C m}^{-2} \text{ day}^{-1}$ ), monthly average from 08/2016 to 08/2017, dashed vertical lines indicate sampling date.**

Not sure Figure 4 adds to the understanding. This figure could be omitted.

Response: As the three reviewers agree on this point, we have decided to remove this figure from the revised manuscript.

Specific comments

Line 67, page 3: Dehairs et al. 1980 more appropriate as ref. here than dehairst et al. 1997.

Response: This reference has been modified.

It is defined as the "biogenic" portion of particulate Barium (pBa) as barite crystals, formed by the decay of bio-aggregates below the surface mixed layer (Bishop, 1988; Dehairs et al., 1980; Lam and Bishop, 2007; Legeleux and Reyss, 1996; van Beek et al., 2007).

Lines 58-59: Surface export is set by the deficit (not excess) of  $^{234}\text{Th}$  activity vs.  $^{238}\text{U}$  activity. Specify that  $^{234}\text{Th}/^{238}\text{U}$  ratios  $>1$  can occur below the upper 100m, or so, reflecting remineralisation.

Response: This has been corrected.

Surface export is set by the deficit of  $^{234}\text{Th}$  activities over  $^{238}\text{U}$  activities. When  $^{234}\text{Th}/^{238}\text{U}$  ratios are larger than 1, below the surface mixed layer, this can reflect remineralisation processes, integrating processes over a 2 to 3 week period (Buesseler et al., 2005; Planchon et al., 2013).

Lines 26-28 page 10 and lines 75-76 page 16: Sample numbers  $n=39$  (SPF) and NPF ( $n=31$ ) pertain to what? Table S1 shows only data from the present study and not the compilation data set.

Response: The n values were referring to the number of observations in the compilation dataset for which there is remotely sensed PP available, i.e., studies after September 1997, split between two zones, SPF and NPF respectively.

Section 3.4 (lines 26 - 28, page 10) has been removed and this information has been added to the discussion under section 4.3 in the revised manuscript, after the compilation dataset has been properly introduced.

The compilation dataset has also now been included as supplementary Table S3 and in-text references to the supplementary table have been corrected.

Lines 46-47 page 11: Opposite gradients of  $B_{axs}$  and  $O_2$ . Please provide more detail.

Response: We have updated sentences to provide clarity on the gradients observed on the  $B_{axs}$  and  $O_2$  profiles.

Additionally, decreases observed in dissolved  $O_2$  profiles along the transect were also accompanied by coinciding, increases in  $B_{axs}$ , in line with  $O_2$  consumption due to remineralisation within the mesopelagic zone (Figure 2) (Cardinal et al., 2005; Jacquet et al., 2005, 2011).

Lines 65-79 page 16: These sentences are confusing. If there is no significant difference in relative amount of POC remineralized relative to PP (all stations except STZ), then there is no difference in response of  $B_a$  relative to PP at the different stations.? Only the STZ site behaves differently.

Response: We agree that this section of the discussion was indeed confusing, and therefore we took a closer look at our data and became aware of two outliers, both being much higher than 100%, which completely altered the mean and variance of the % POC remineralised of the NPF data. We have excluded these two outliers from the % POC remineralised data, as they both fell outside the limit of acceptance of three times the standard deviation of the dataset. This results in a significant difference in the % POC remineralised, between the two zones (NPF and SPF). Making a lot more sense, as this highlights the difference in surface export efficiency between the two regimes.

The physics at the time of sampling for the two outliers (Jacquet et al., 2004), reveals that these locations were more affected by physics than was the case for the rest of our dataset. Specifically, the southern edge of a subtropical Tasman Sea eddy, coinciding with the STF, to the north, and a cold core eddy from the SAF to the south, creating a highly dynamic region between the STF and SAF (Jacquet et al., 2004). These physical factors would affect the mesopelagic signal, thereby masking the surface to mesopelagic relationship usually seen when physics is not the dominating process, as was the case for the rest of our dataset.

We thank Pr. Frank Dehairs for bringing this error to our attention. We have rewritten the discussion to rectify this.

The percentage of mesopelagic POC remineralisation as calculated from estimated POC remineralisation fluxes over integrated remote sensing PP and determined for the SO compilation dataset (SPF;  $19 \pm 15$  %,  $n = 39$  and NPF;  $10 \pm 10$  %,  $n = 29$ ; mean  $\pm$  SD; t-statistic = 2.75; p-value <0.05; Table S3), was  $\sim 2$  fold higher SPF than NPF, revealing the higher surface carbon export efficiency SPF.

Also, high productivity, low export can be associated with large particles in the surface layer (see Lam & Bishop, 2007). High surface water productivity associated with low export has also been described in Jacquet, Lam, Trull, Dehairs, DSR II, 2011. The possibility that high phyto biomass attracts more grazing and is more depending on recycled production (NH<sub>4</sub> based) and thus results in smaller export (more surface water recycling) and possibly lower mesopelagic Ba, is reported also in Dehairs et al., 1992.

Response: The discussion on HPLE regions has been expanded to include this information.

HPLE regimes (High Productivity Low E-ratio, e-ratio referring to the ratio between export production and net primary productivity, Fan et al., 2020) are indeed characteristic of large areas of the SAZ. They are mainly due to surface POC accumulation caused by non-sinking particles, tending towards less efficient export of smaller cells (Fan et al., 2020). Even when large particles are abundant in HPLE surface layers, a complex grazing community may prevent the export of large particles (Dehairs et al., 1992; Lam and Bishop, 2007). This can explain the higher surface carbon export efficiency that we estimate in the AZ compared to the SAZ. Export efficiency has also been linked to bacterial productivity, when most of the water column integrated bacterial productivity is restricted to the upper mixed layer, efficient surface remineralisation limits surface POC export (Dehairs et al., 1992; Jacquet et al., 2011).

Line 76 page 16: "... are comparable to surface export efficiency obs. In this region ..." which region?

Response: We were referring to the SO. The sentence has been amended to clearly state that.

Line 88 page 17: this sentence is unclear. Similar latitudinal trend (of what?); higher values NPF (values of what?)

Response: We were referring to the latitudinal trend of mesopelagic Ba<sub>xs</sub> concentrations. The sentences have, however, been removed from the revised manuscript.

Line 90 page 17: saturated vs undersaturated: specify saturation for dissolved Ba.

Response: Unfortunately, there was no dBa measured during our study. Any mention of Ba saturation has been removed from the conclusion as this was not specifically discussed in our manuscript.

Table S2: Add lat. position for each site

Response: This has been added to Table S2.

Figure S1: top panel indicate AZ, PFZ, SAZ. Why is the STZ station not reproduced here?

Response: We have overlaid the zones on the figure. The STZ station was included at 41°S.

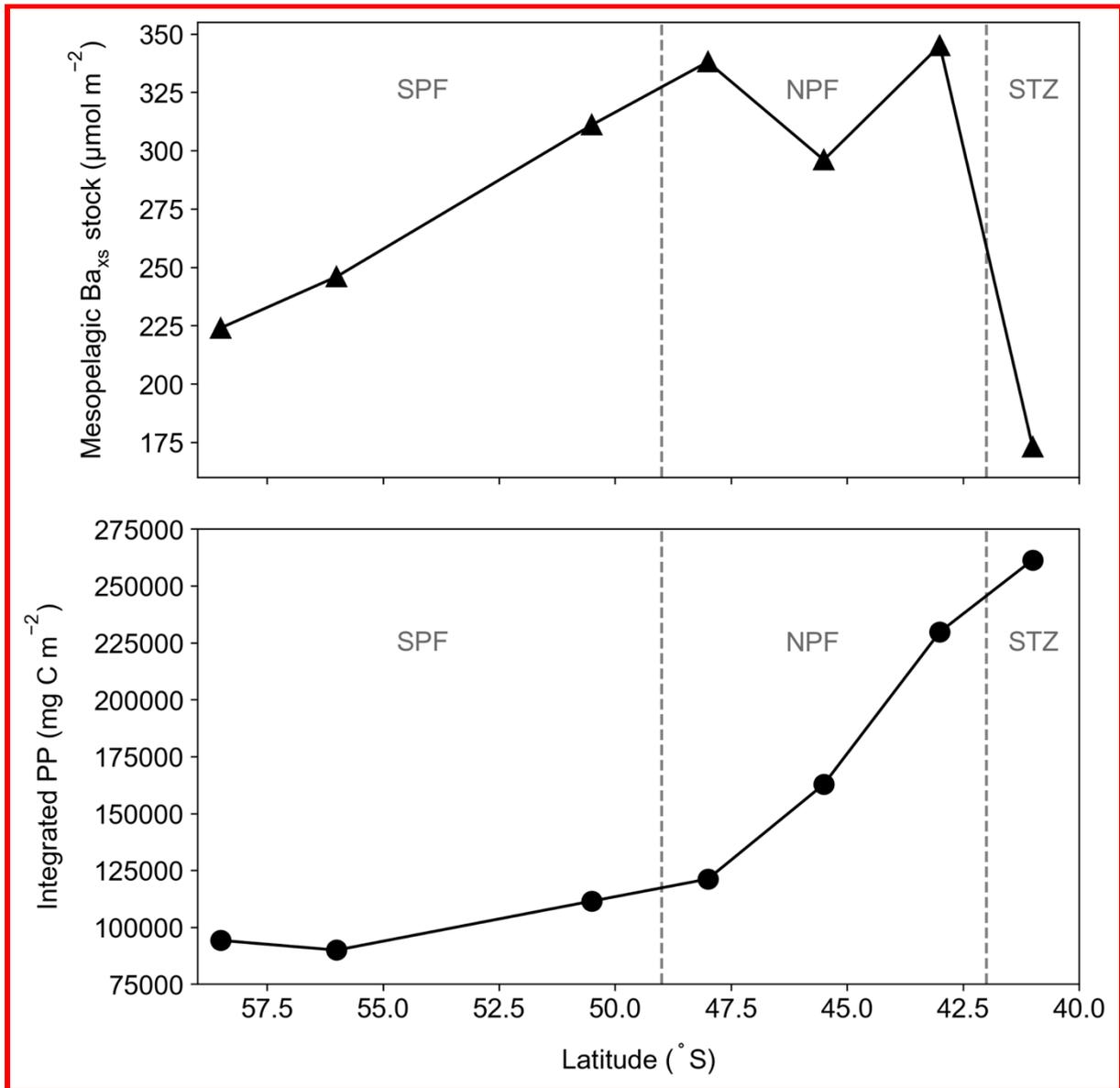


Figure S1: Top panel is the latitudinal trend, south to north, left to right, of winter integrated mesopelagic  $Ba_{xs}$  stock concentrations (black triangles). The bottom panel is the latitudinal trend of the corresponding integrated annual remote sensing PP (black circles). Sampling zones are overlaid in grey, namely SPF, NPF and STZ.

Table S3: Add the Lat-Long range for the basin regions

Response: This has been added to Table S3, which has also been updated to include all data pertaining to the compilation dataset.