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_{xs} 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_{xs} stock (µmol 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_{xs}, 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_{xs} stock dataset with all available literature data including data from this study (Figure 4a, Table S3). The mesopelagic Ba_{xs} stock was integrated over the Ba_{xs} 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_{xs} with time, SPF and NPF (Figure 4b and c) is still observed. Mesopelagic Ba_{xs} accumulates at a rate of 0.86 (±0.15) µmol m^{-2} d^{-1}, SPF (R^2 = 0.43, p-value < 0.05, n =

43; Figure 4b), and at 0.88 (±0.20) µmol m^{-2} d^{-1}, NPF (R^2 = 0.41, p-value < 0.05, n = 31; Figure 4c), with no statistically significant difference between the two zones (Welch's t-test = 0.24; p-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 (~ day 310 of the year, i.e., during our study). The mesopelagic Ba_{xs} accumulation over time can, therefore, not be matched with the remotely sensed PP measured during the month of sampling

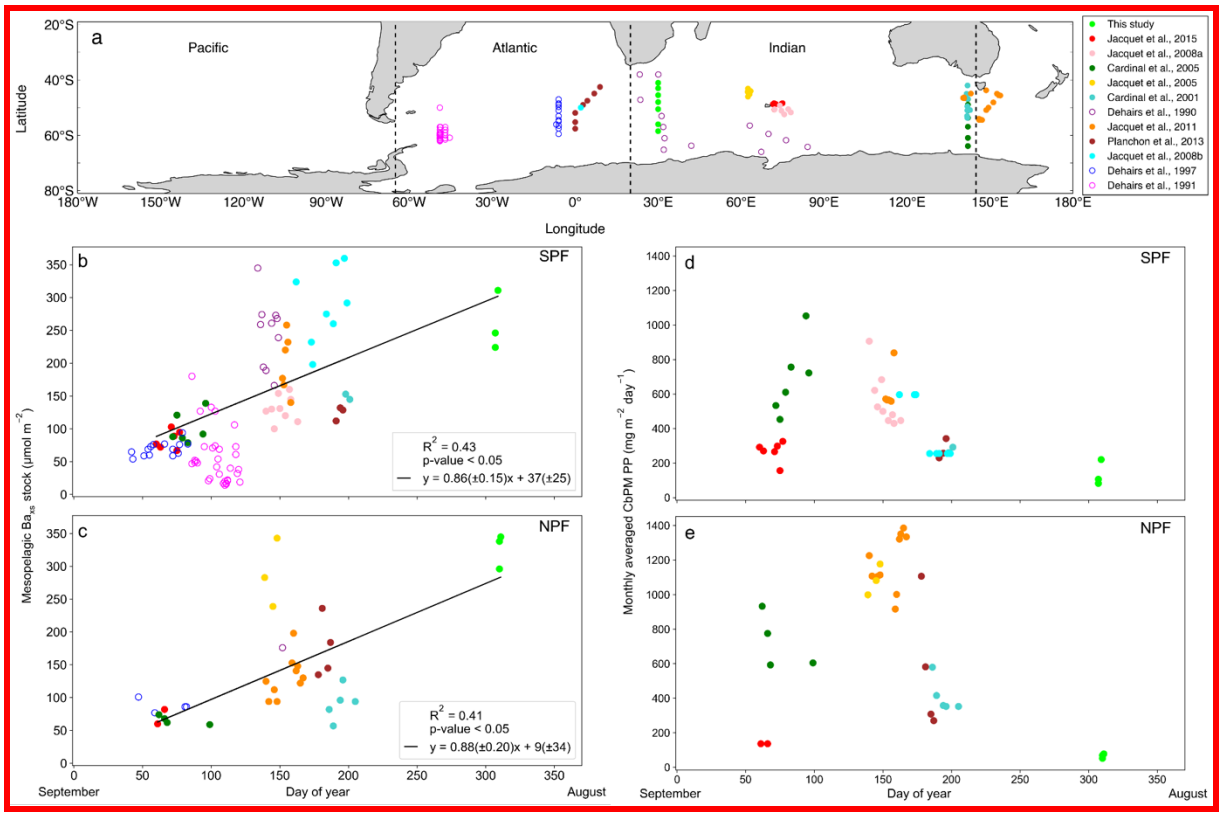


Figure 4: (a) Positions of Ba_{xs} observations compiled from all known SO studies, on a cylindrical equal-area projection of the SO, the three SO basin cut offs are indicated by the dashed black lines, from left to right, Pacific, Atlantic and Indian. Integrated mesopelagic Ba_{xs} stock plotted against 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 Baxs 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 Ba_{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 ~ 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 m d^{-1} that corresponds to an average literature value (50 - 100 m d^{-1}: Riebesell et al., 1991 ; 50 - 430 m d^{-1} around South Georgia: Cavan et al. 2015; ~ 100 m d^{-1} in the Southern Ocean as reviewed in Laurenceau-Cornec et al., 2015; 10 - 150 m d^{-1}: McDonnell and Buesseler, 2010). Assuming a maximum surface current speed of 0.2 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}, ~ 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° upstream longitudinally, and 1° 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°S, approximately 3° (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 Baxs 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 µg/L at the PF and in the SAZ, this taking into account that S.O. Chl values of 1 µg/L can be considered bloom values. Please comment.

Response: Whilst we agree with the reviewer that these Chl-α values are high, these measurements were performed by fluorometry. Fluorometric methods of measuring Chl-α 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-α and Chl-c falsely inflating Chl-α concentrations. This is best demonstrated in the study by Moutier et al. (2018, doi: 10.3390/rs11151793, Table 5) where they show that Chl-α 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-α concentrations by this method.

The issues with the use of fluorometric Chl-α 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-α in the cross-check calibration of remote sensing derived values.

Due to this issue with the Chl-α 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 ~ 2 months prior to the time of sampling.

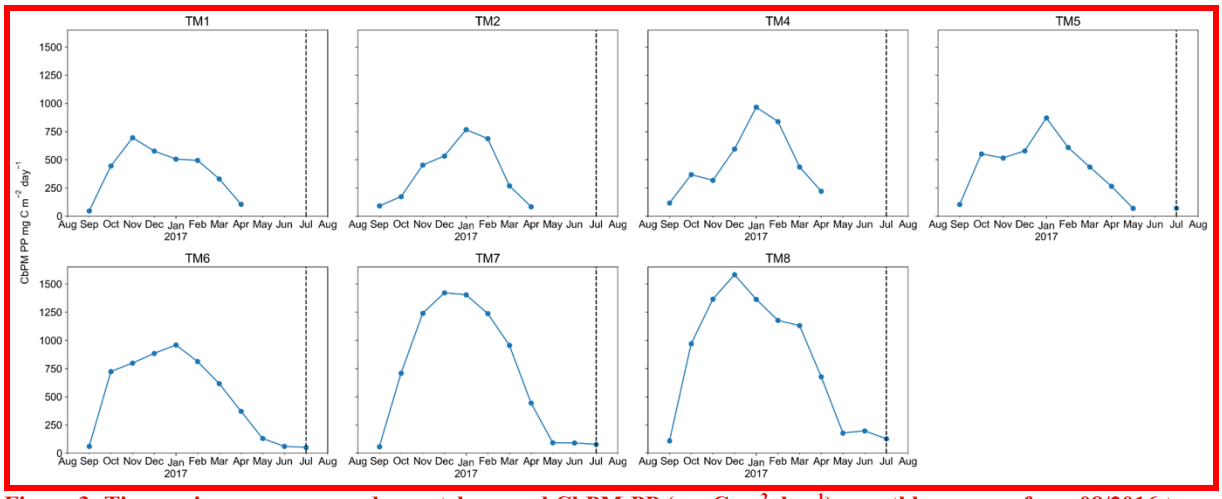


Figure 3: Time series, area-averaged remotely sensed CbPM-PP (mg C m^{-2} day^{-1}), monthly average from 08/2016 to 08/2017, dashed vertical lines indicate sampling date.

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 dehairs 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 234Th activity vs. 238U activity. Specify that 234/238 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}Th activities over ^{238}U activities. When $^{234}Th/^{238}U$ 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 Baxs and diss. O2. Please provide more detail.

Response: We have updated sentences to provide clarity on the gradients observed on the Ba_{xs} and O_2 profiles.

Additionally, decreases observed in dissolved O_2 profiles along the transect were also accompanied by coinciding, increases in Ba_{xs}, 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 Ba 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 ± 15 %, n = 39 and NPF; 10 ± 10 %, n = 29; mean ± SD; t-statistic = 2.75; p-value <0.05; Table S3), was ~ 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 (NH4 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_{xs} 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.

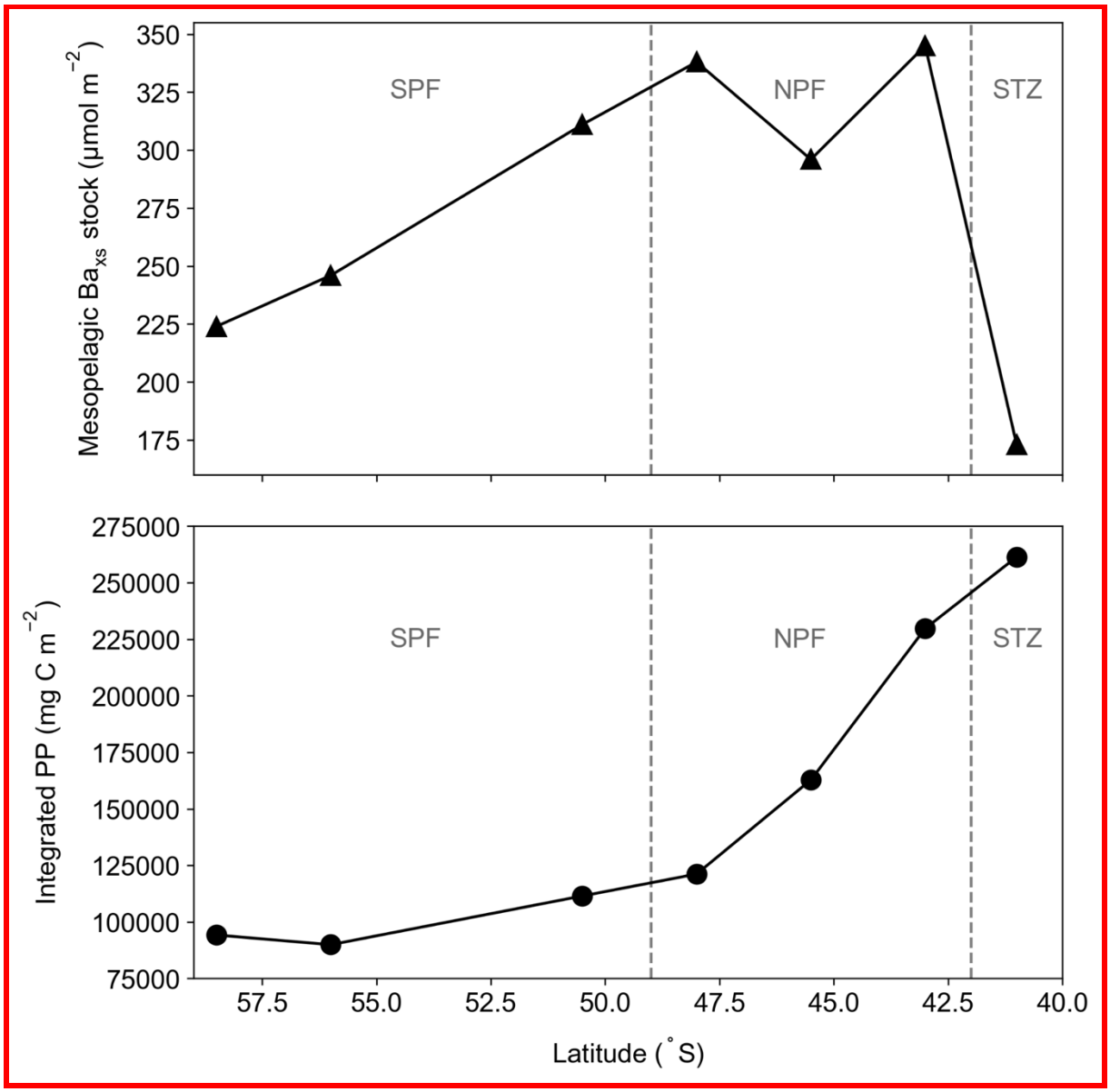


Figure S1: Top panel is the latitudinal trend, south to north, left to right, of winter integrated mesopelagic Ba_{xs} stock concentrations (black triangles). The bottom panel is the latitudinal trend of the corresponding integrated annual remote sensing PP (black circles). Sampling zones are overlaid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

Comment on bg-2021-42

Stéphanie Jacquet (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-RC2, 2021

This manuscript presents a new data set of excess particulate barium (Baxs) concentrations in the Southern Ocean during winter conditions. Correlation with integrated PP and data from literature is interesting. My major comment concerns the conclusion that the Ba proxy would have a longer timescale than previously thought. I don't think that there is a cumulative effect on the Baxs signal for the reasons explained below. I suggest that authors revise their discussion (and reformulate abstract & conclusion).

Response: we thank Dr Stéphanie Jacquet for the review of our manuscript.

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

The hypothesis of this study, that the timescale of Ba_{xs} may be longer than a few days to weeks, has already been suggested by earlier studies, e.g.:

"Significant carry over of Bap between successive plankton growth seasons might occur" (Dehairs et al., 1997)

"The time-delay required to build-up the meso-Ba_{xs} (few weeks) supports the fact that this proxy is not a snapshot (on the contrary of N-uptake for instance) but rather a monthly average of remineralisation." (Cardinal et al., 2005)

We hope that our revised manuscript will be more convincing in this regard. Figure 3 (see below) will be added to the revised manuscript, showing that PP was at a minimum ~ 2 months prior to the time of our sampling. We have also added Figure 4 (see below), showing significant increases of mesopelagic Ba_{xs} from September to July, for all data compiled from the different basins of the Southern Ocean.

Chl a data reported in Figure S1 indicate that stations (northern 50°S) experienced production (even of low intensity). This should be compared with Chl a and Baxs data from other campaigns (e.g., Cardinal et al., 2005; Blain et al., 2007). The winter period appears to be productive in this sector. This would explain why Baxs present similar contents as reported during other seasons.

Response: Whilst we agree with the reviewer that these Chl-α values are high, these measurements were performed by fluorometry. Fluorometric methods of measuring Chl-α 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-α and Chl-c falsely inflating Chl-α concentrations. This is best demonstrated in the study by Moutier et al. (2018, doi: 10.3390/rs11151793, Table 5) where they show that Chl-α 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-α concentrations by this method.

The issues with the use of fluorometric Chl-α 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-α in the cross-check calibration of remote sensing derived values.

Due to this issue with the Chl-α 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 ~ 2 months prior to the time of sampling.

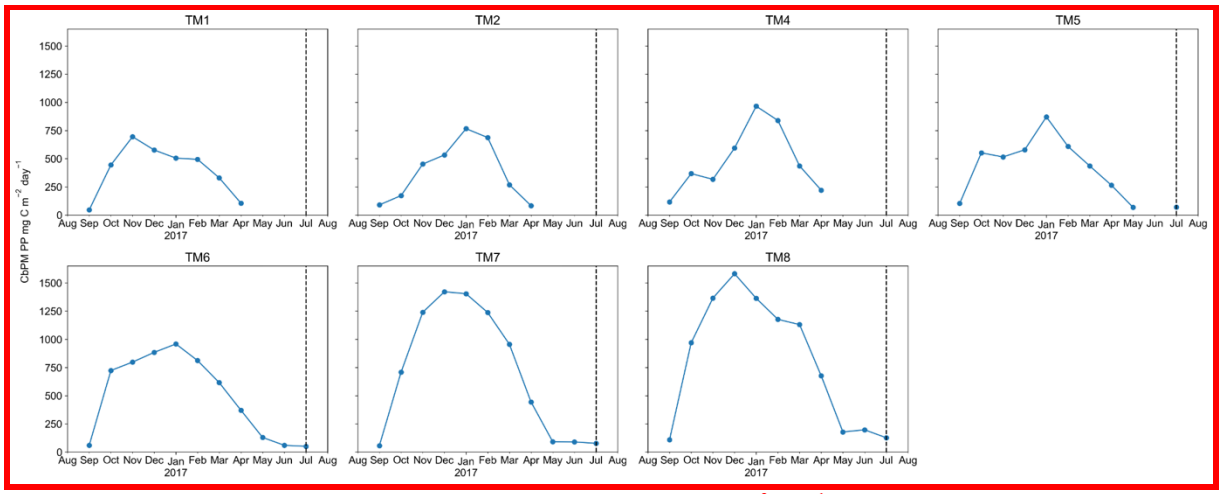


Figure 3: Time series, area-averaged remotely sensed CbPM-PP (mg C m^{-2} day^{-1}), monthly average from 08/2016 to 08/2017, dashed vertical lines indicate sampling date.

Data should be compared to results from the Indigo3, EPO2 and ANTX/6 cruises.

Response: In the initial manuscript, the Ba_{xs} 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_{xs} stock (µmol 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. 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_{xs}, 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_{xs} stock dataset with all available literature data including data from this study (Figure 4a, Table S3). The mesopelagic Ba_{xs} stock was integrated over the Ba_{xs} 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_{xs} with time, SPF and NPF (Figure 4b and c) is still observed. Mesopelagic Ba_{xs} accumulates at a rate of 0.86 (±0.15) µmol m^{-2} d^{-1}, SPF (R^2 = 0.43, p-value < 0.05, n = 43; Figure 4b), and at 0.88 (±0.20) µmol m^{-2} d^{-1}, NPF (R^2 = 0.41, p-value < 0.05, n = 31; Figure 4c), with no

statistically significant difference between the two zones (Welch's t-test = 0.24; p-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 (~ day 310 of the year, i.e., during our study). The mesopelagic Ba_{xs} accumulation over time can, therefore, not be matched with the remotely sensed PP measured during the month of sampling.

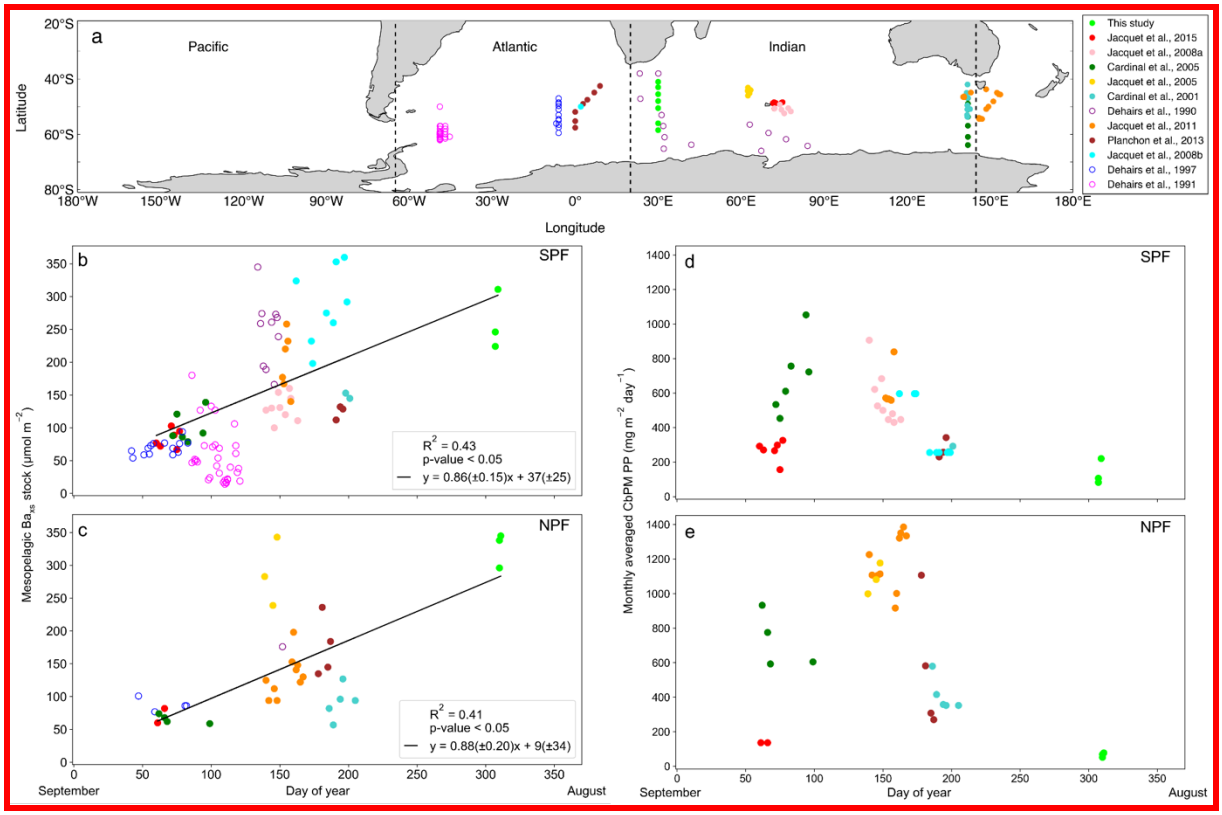


Figure 4: (a) Positions of Ba_{xs} observations compiled from all known SO studies, on a cylindrical equal-area projection of the SO, the three SO basin cut offs are indicated by the dashed black lines, from left to right, Pacific, Atlantic and Indian. Integrated mesopelagic Ba_{xs} stock plotted against 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.

Line 15-19: Please revise the abstract (and part of the conclusion). I don't think it's a question of timescale and cumulative effect. If POC is produced in surface and that remineralization is sustained at mesopelagic depths, Baxs will be produced, independently from the season. There is no clues that POC material could accumulate at mesopelagic depths and conducts to latter (weeks to months after the growth season) remineralization and Baxs

Response: Indeed, we agree that POC may not accumulate in the mesopelagic zone. We are referring to the accumulation of Ba_{xs} in the mesopelagic zone. The barite crystals released in the mesopelagic zone due to remineralisation of POC can become suspended due to its low solubility and slow sinking speeds of ~0.3 m d^{-1} (Sternberg et al., 2008; review comment by Prof. J. Bishop). It has been found that only up to 30% of marine barite could reach the ocean floor due to its low solubility and packaging in fast settling fecal pellets (Paytan and Kastner, 1996). This leaves a minimum of 70% which does not

settle out and will become suspended in the mesopelagic zone, where dissolution and reaggregation would be the main processes controlling the concentration of Ba_{xs}, thereby suggesting accumulation in the ocean interior as more Ba_{xs} is exported from the surface ocean. We have clarified this in the revised manuscript.

A compilation of available SO mesopelagic Ba_{xs} data, including ours, shows a mesopelagic Ba_{xs} accumulation from September to July that correlates with integrated remotely sensed primary productivity (PP), suggesting a possible annual timescale for this proxy.

The integrated mesopelagic Ba_{xs} stock (µmol m^{-2}) over the mesopelagic layer (100 - 1000 m) was calculated from the DWA Ba_{xs} in order to investigate the link between the accumulated Ba_{xs} mesopelagic signal and the corresponding integrated remote sensing primary productivity (PP).

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, and a statistically significant accumulation of mesopelagic Ba_{xs} with time, SPF and NPF (Figure 4b and c) is still observed.

Figure 4: not necessary -it does not add to the understanding. It should be (in-depth) compared to contrasts reported in Jacquet et al. (2011; SAZ-SENSE cruise): diatoms vs. flagellate, PP, EP, Fe depletion or enrichment, type of aggregates. The effect of the contrasts on Baxs and remineralization during SAZ-SENSE was opposite to these reported during KEOPS (Jacquet et al., 2008) and EIFEX (Jacquet et al., 2008) cruises. This should be compared to the present data set.

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

Line 71-82 p11-12 (and Line 90 p17: not clear, please reformulate). Are dissolved Ba and SI available? The SO is globally undersaturated (SI<0.9) or at the equilibrium (0.9<SI<1.1) with respect to barite. Saturation is unusual. Please correct it line 73. Also, in productive situations (and deep POC transfer), it is common that Baxs at 1000 m depths remains larger than the "180 pM" SO reference.

Response: Unfortunately, dissolved Ba was not measured during our study, therefore the SI could not be calculated. We have removed any mention of barite saturation in the revised manuscript as we do not specifically address this topic.

We agree that Ba_{xs} at 1000m can be higher than the SO $Ba_{residual}$ concentration of 180pM due to deep POC transfer, this is the reason for us only using concentrations from depths below 2000m, for the consideration of $Ba_{residual}$ concentrations (line 52, page 6).

Finally, as recently reported in Jacquet et al. (https://doi.org/10.5194/bg-2020-271; Peacetime cruise) remineralization at mesopelagic depths could be restricted to the upper mesopelagic layer or extend up to 1000 m depending the system functioning during a same season. This leads to major differences in the Baxs background reached at 1000 m depths.

Response: We agree fully with this comment and in the paragraph starting on line 51 page 11, we refer to remineralisation and deeper Ba_{xs} peaks NPF due to deep POC export.

Ba_{xs} profiles exhibited similar distributions to those reported throughout bloom seasons in the SO, with distinct peaks observed within the mesopelagic zone across all stations. Earlier in the bloom season peaks mostly occur within the upper half of the mesopelagic zone (100 - 500 m) (Cardinal et al., 2001, 2005; Jacquet et al., 2005, 2008a, 2011, 2015), but as the season progresses, they deepen down towards the bottom half of the mesopelagic zone (500 - >1000 m) (Jacquet et al., 2008b, Planchon et al., 2013). Deepening and widening of the remineralisation depth range can be expected as the season progresses, due to continued remineralisation taking place as particles sink to the bottom of the mesopelagic zone (Lemaitre et al., 2018; Planchon et al., 2013). This is also what we observed during early winter at stations NPF, with a second peak in deeper waters, as observed by Jacquet et al. (2008b) during the iron (Fe) fertilization experiment (EIFEX). The deeper peak could also be linked to relatively larger cells that sink faster as they remineralise, possibly a large bloom early in the season.

Please revise your discussion and conclusion according to these comments.

Response: We have extensively revised the discussion and conclusion of the manuscript to better relay and support our study, and we sincerely hope that our revisions will be more convincing in this regard.

Comment on bg-2021-42

J.K.B. Bishop (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-RC3, 2021

Review. van Horsten et al. "Early winter 1 barium excess in the Southern Indian Ocean as an annual remineralisation proxy".

The authors describe particulate Barium, O2, and potential density profile data from 7 stations in the Southern Ocean along from 59°S to 41°S crossing the Antarctic polar front (51°S) along 30°E south of Africa during GEOTRACES GIPr07 (in early wintertime conditions, June 28-July 13). This is a hard to get and interesting data set. The hypothesis is that since particulate barium should have only a short residence time (days to weeks) in the water column the inventory of particulate Ba would be far lower at times of low productivity that at other times of the year. The authors report particulate Ba concentrations as high as seen in other seasons and infer an active biological carbon pump year-round. The stocks are regressed against annual mean primary production. Comparisons are made with other data sets from the Southern Ocean.

What I like about the work is the heroic effort to achieve sampling in the wintertime and the excellent primary data arising from the expedition. Also, the goal of finding the correct transfer function relating the inventory of particulate barium in the mesopelagic (an indicator of export) to remotely sensed biomass or primary productivity would be a big plus.

That said, the paper falls short of its goals. The regressions in Figure 3, and manuscript discussion provide no insight. The data south of the polar front are aliased by cloud obscured retrievals of surface chlorophyll and primary productivity (See e.g., Ocean color monthly composites) and fall on a different slope than north of the PFZ. The STZ station is an outlier. The discussion does not sufficiently unify these divergent observations.

Response: We thank Pr. Jim Bishop for his review of our manuscript.

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

We agree that remotely sensed PP does have inherent issues, as for any scientific methodology, that being said, we have confidence in our data as we made use of OC-CCI data which integrates all available sensors. This approach increases the chance of accurate measurements compared to a single sensor approach.

We checked the percentage of valid pixels for all stations of the compilation dataset in order to prove that remotely sensed data south of the polar front (82 ± 29 %; mean ± SD, n = 488) is as valid as north of the polar front (90 ± 20 %; mean ± SD, n = 370). This information has been added to the manuscript under section 2.5.

In order to assess the validity of the remotely sensed PP data and demonstrate no meridional bias across the SO, the percentage valid pixels were calculated for data north (90 ± 20 %; mean ± SD, n = 370) and south (82 ± 29 % mean ± SD, n = 488) of the PF.

Reflecting on other reviewer comments, I am convinced that a more comprehensive analysis of the data (now abundant) from multiple projects need to be considered. I am sure that everyone referenced would have data to share.

Response: In the initial manuscript, the Ba_{xs} data were plotted against satellite-derived PP, integrated over months prior to sampling. At the time of previous cruises (e.g., INDIGO 3, ANT X/6 and EPOS 2, as suggested by the two other reviewers), there was no remotely sensed PP data available. The PP data, when available, were measured during the cruise and are not representative of integrated PP over months preceding the study. This is why these data were not initially included in our compilation.

Nevertheless, the mesopelagic Ba_{xs} stock (µmol m^{-2}) is now plotted against day of year sampled (Figure 4, see below) in the revised manuscript, including the INDIGO 3, ANT X/6 and EPOS 2 data. However, as stated in the figure caption and the main text, 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_{xs}, where there are possible significant lithogenic inputs (e.g., close to Antarctica and downstream of the Drake Passage).

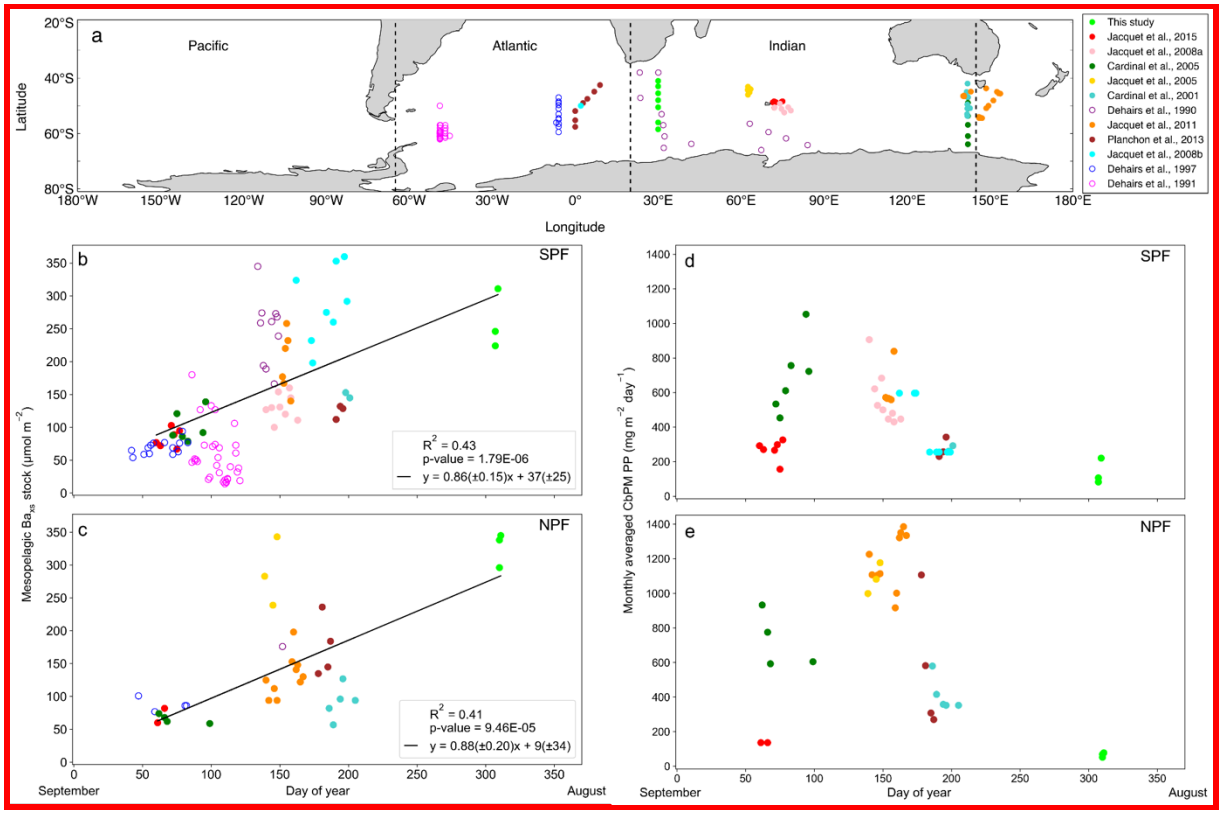


Figure 4: (a) Positions of Ba_{xs} observations compiled from all known SO studies, on a cylindrical equal-area projection of the SO, the three SO basin cut offs are indicated by the dashed black lines, from left to right, Pacific, Atlantic and Indian. Integrated mesopelagic Ba_{xs} stock plotted against 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.

I echo a need for a fuller hydrographic and dissolved phase framework for data interpretation – the supplemental data are very sparse.

Response: The hydrographic data was originally available on an ftp site (address given on page 19, line 30). Unfortunately, we have been made aware of problems with the ftp site and we apologize for that.

Temperature, salinity and nutrient data have now been included in the supplementary as Table S5. Unfortunately, no dBa data are available (nor were samples collected for this parameter).

There are some issues: (1) methodology: bottle sampling and the missing large particle fraction,

Response: We are aware of the differences in sampling systems. Indeed, sampling spigots on Go-Flo bottles are located 4 cm above the bottom of the bottle, which precludes the extraction of water below that level, potentially leaving behind particles that settle below the point of extraction. Strategies to avoid, minimize, or account for these biases have been discussed (e.g., Planquette & Sherrell, 2012) and are recommended in the GEOTRACES cookbook protocols, which we strictly followed.

Moreover, all the data we are comparing have been generated from samples collected with bottles, not in-situ pumps making the comparison less biased in this aspect.

This is now included under section 2.3 of the revised manuscript.

Volumes of 2 to 7 L of seawater were filtered from the GO-FLO bottles onto acid-washed polyethersulfone filters (25 mm diameter, Supor, 0.45 µm pore size), mounted on swinnex filter holders, for pBa and pAl analyses. Filters were mounted in line on the side spigot of each Go-Flo bottle. Furthermore, bottles were mixed 3 times before filtration, as recommended by the Geotraces protocols. Although the large fast sinking fraction of particles may be under sampled by using bottles (Bishop and Edmond, 1976; Planquette and Sherrell, 2012), comparing data that were generated using the same, internationally validated sampling systems and protocols (Cutter et al. 2017) as we do in this study, minimizes the potential biases.

and (2) the hypothesis of expected low wintertime concentrations is premised on particle sinking rates that are far too high (50 m d^{-1}) for the micron sized particles that comprise the bulk of suspended barite (sinking speed ~0.1 m d^{-1}).

Response: The hypothesis of expected low wintertime concentrations was taken from literature (Jacquet et al., 2008b, 2011).

The sinking speed of 50 m d^{-1} was referring to the sinking of aggregates from the surface layer, and not to the sinking speed of suspended barite. This value is within the range of sinking speeds reported in the literature for sub millimetre sized aggregates (50 - 100 m d^{-1}: Riebesell et al., 1991; 50 - 430 m d^{-1} around South Georgia: Cavan et al. 2015; mean of ~ 100 m d^{-1} in the Southern Ocean as reviewed in Laurenceau-Cornec et al., 2015; 10 - 150 m d^{-1}: McDonnell and Buesseler, 2010).

The sinking rates were used to estimate the maximum time needed by sinking aggregates to exit the mesopelagic zone, i.e., 1000m depth:

time = 1000 m / 50 m d^{-1} = 20 days

With a mean current speed of 0.2 m s^{-1} (Ferrari and Nikurashin, 2010), aggregates sinking through the mesopelagic zone (above 1000 m depth) in 20 days would have

been displaced a maximum of 346 km eastward, towards the location of stations sampled for mesopelagic Ba_{xs}:

0.2 m s^{-1} x 3600 x 24 = 17280 m d^{-1}

17280 m d^{-1} x 20 days = 345 600 m = 346 km eastward

This distance was used to define the area of the sampling window where we estimated surface PP that was likely to have formed the aggregates that were further responsible for the release of the mesopelagic Ba_{xs} signal measured within the mesopelagic zone.

The low sinking speed of suspended barite (~0.3 m d^{-1}, Sternberg et al. 2008), once produced in the mesopelagic layer, implies that the residence time of barite is indeed long, as suggested by Pr. Bishop in the last comment of the review. To sink from 300 m depth (~peak of production) to the bottom of the mesopelagic layer (1000 m depth), it would take (1000-300) / 0.3 = 2300 days, i.e., ~ 6 years. This supports our hypothesis, that the Ba_{xs} signal in the mesopelagic layer may represent remineralisation activity over more than a few days to weeks, contrary to what was previously reported in SO studies (Dehairs et al., 1997; Cardinal et al., 2005; Jacquet et al., 2007, 2008a). It also further explains how mesopelagic Ba_{xs} concentrations increase from spring to a maximum in winter (see new Figure 4b and c).

These explanations are now included in the text, and we thank Pr. J. Bishop for this comment that assisted us in clarifying this part.

The seasonal signal of 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 (~ day 310 of the year, i.e., during our study). The mesopelagic Ba_{xs} accumulation over time can, therefore, not be matched with the remotely sensed PP measured during the month of sampling.

This strongly suggests that the Ba_{xs} signal is not directly linked to synoptic measurements of PP at the time of sampling. In order to investigate this hypothesis, for the first time, we compiled a SO mesopelagic Ba_{xs} stock dataset with all available literature data including data from this study (Figure 4a, Table S3). The mesopelagic Ba_{xs} stock was integrated over the Ba_{xs} 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_{xs} with time, SPF and NPF (Figure 4b and c) is still observed. Mesopelagic Ba_{xs} accumulates at a rate of 0.86 (±0.15) µmol m^{-2} d^{-1}, SPF (R^2 = 0.43, p-value < 0.05, n = 43; Figure 4b), and at 0.88 (±0.20) µmol m^{-2} d^{-1}, NPF (R^2 = 0.41, p-value < 0.05, n = 31; Figure 4c), with no statistically significant difference between the two zones (Welch's t-test = 0.24; p-value = 0.80).
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 ~ 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 m d^{-1} that corresponds to an average literature value (50 - 100 m d^{-1}: Riebesell et al., 1991 ; 50 - 430 m d^{-1} around South Georgia: Cavan et al. 2015; ~ 100 m d^{-1} in the Southern Ocean as reviewed in Laurenceau-Cornec et al., 2015; 10 - 150 m d^{-1}: McDonnell and Buesseler, 2010). Assuming a maximum surface current speed of 0.2 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}, ~ 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° upstream longitudinally, and 1° 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.
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 (~ day 310 of the year, i.e., during our study). The mesopelagic Ba_{xs} accumulation over time can, therefore, not be matched with the remotely sensed PP measured during the month of sampling. A possible relationship between Ba_{xs} and surface PP was further investigated by considering longer timescales. Integrated remote sensing PP of the preceding bloom was calculated using the month of September prior to sampling as the start of the bloom. This is in general agreement with previous bloom phenology studies for this region (Thomalla et al., 2011). The PP was integrated up to one month prior to the sampling date of the study, taking into consideration time needed for export, aggregate formation, and barite crystal release through remineralisation (~ 1 month). When remote sensing data was limited due to cloud cover and low sunlight during winter months, specifically at the southernmost stations, all available data was used for the duration of the season.

A couple of issues further complicating review is simply the lack of any access to the more complete data sets from the cruise beyond those used in figure 2 or the partially complete data sets used in figure 3. The cruise data should be available as supplemental data and also submitted to the GEOTRACES archives and DOI traceable.

Response: Data was made available on the SOCCO ftp site (see page 19, line 30 of the preprint) but as stated before, we were made aware of issues with the ftp, and we apologize for this inconvenience. We have now included these data in two tables in the supplementary material, Table S3 for this study and literature data, and Table S4 for nutrients, temperature, and salinity data for this study. Our data will be submitted to the GEOTRACES IDP once published.

I think the fundamental logic flaw (see comments below) lies on page 12 in the discussion of inferred barite residence times in the mesopelagic. I don't see a major advance beyond referenced work and don't support publication of this paper with its present interpretive framework. I encourage the Authors to look again at the results in a larger framework.

Response: Although we agree that further interpretation of data was required to improve the manuscript and support the study, we also believe that this work does go beyond what has been previously published. This is to our knowledge the first Ba_{xs} dataset obtained during winter in the SO and we also use all available SO data and link it to remotely sensed PP, which has not yet been done.

We have included a more extensive assessment of the data in the revised manuscript that we believe to be more convincing.

Figure 4 is not needed. It is out of place. There is room for more figures.... Some detailed comments follow.

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

P4 line 08, R2=0.83... This seems like a bad validation of the O2 results.

Response: The slope (0.94 ± 0.10), intercept (0.07 ± 0.51) and p-value (7×10^{-10}), of the calibration regression indicate that although the correlation coefficient is not as high as could be expected ($R^2 = 0.83$), the calibration is still valid. The sensor had also been calibrated by the manufacturer less than a year prior to the cruise (August 2016).

With this in mind, we do not use any absolute values of dissolved O_2, instead, the shape of the O_2 profiles were used to support evidence of mesopelagic remineralisation and oxygen consumption, and how it is linked to the Ba_{xs} profiles.

This is now clearly stated in the manuscript.

Temperature (°C), salinity and dissolved O_2 (µmol L^{-1}) profiles were measured by sensors (SBE 911plus) which were calibrated by the manufacturer within a year prior to the cruise. At each cast discrete seawater samples were collected and analysed onboard for calibrating sensor salinity (8410A Portasal salinometer, $R^2 = 0.99$) and dissolved O_2 measurements (Metrohm 848 titrino plus; Ehrhardt et al., 1983, $R^2 = 0.83$).

Decreases in dissolved O_2 concentrations at intermediate depths, together with Ba_{xs} concentrations, were used to define the mesopelagic remineralisation depth range.

p 4 line 10. The Python language did not exist in 1982. Please fix sentence.

Response: This sentence has been corrected, with the publication referring to the calculation.

Temperature and salinity measurements were used to calculate potential density (σ_θ; Gill, 1982) to characterise water masses sampled and to identify the mixed layer depth (MLD).

P 5. Lines 18-20. I assume this was an in-line filter, directly connected to the side spigot of the bottle. State what was done. Also, state whether or not the large sinking particle fraction would be sampled.

Response: Indeed, there was an in-line filter (Supor) directly connected to the side spigot of the bottle. Bottles were mixed prior to filtering with the in-line filter as recommended by the Geotraces cookbook. Strategies to avoid, minimize, or account for these biases have been discussed (e.g., Planquette & Sherrell, 2012) and are recommended in the GEOTRACES cookbook. We strictly followed these protocols. This is now clearly stated in section 2.3.

Moreover, all the data we are comparing is generated from samples collected with bottles, not in-situ pumps making the comparison possible with studies included in the compilation dataset. This is also now clearly stated.

Filters were mounted in line on the side spigot of each Go-Flo bottle. Furthermore, bottles were mixed 3 times before filtration, as recommended by the Geotraces protocols.

Although the large fast sinking fraction of particles may be under sampled by using bottles (Bishop and Edmond, 1976; Planquette and Sherrell, 2012), comparing data that were generated using the same, internationally validated sampling systems and protocols (Cutter et al. 2017) as we do in this study, minimizes the potential biases.

p 5. line 29. If varying volumes of water were filtered, the blank will not be a constant value. (Ba(filter)-blank(filter))/volume filtered. to get Ba and error should be the

s.d/filter blanks / volume filtered. Or is this what you did? I think the calculation was done correctly as error bars vary in size. Please clarify methods.

Response: Yes, this is indeed what was done. Unused filters were used to subtract the blank contribution. This is now explained in section 2.3.

Unused blank filters and filters containing the samples were acid reflux digested at 130°C in acid-cleaned savillex vials using a mixture of HF and HNO_3 (both Ultrapure grade, Merck) solutions (Planquette and Sherrell, 2012).

Mean amounts (in nmol) of a given element determined in unused filter blanks were subtracted from the amounts in the sample filter then divided by the volume filtered.

ALSO please state the assumed particle size fraction that has been sampled. There is no evidence that bottles adequately sample the sinking particle fraction.

Response: As stated above, we are aware that bottles may under sample the large fast sinking fraction of particles. There are unfortunately, also other potential sources of discrepancy such as filtration pressure (Gardner et al., 2003; Liu et al., 2005), filter type (Bishop et al., 2012), breakage or leakage of phytoplankton and other cells (e.g., Collos et al., 2014), creation of particles (Liu et al., 2005). Unfortunately, no sampling method is assumed to be perfect. Comparing data that were generated using the same, internationally validated sampling systems and protocols, as we do, minimizes the potential biases

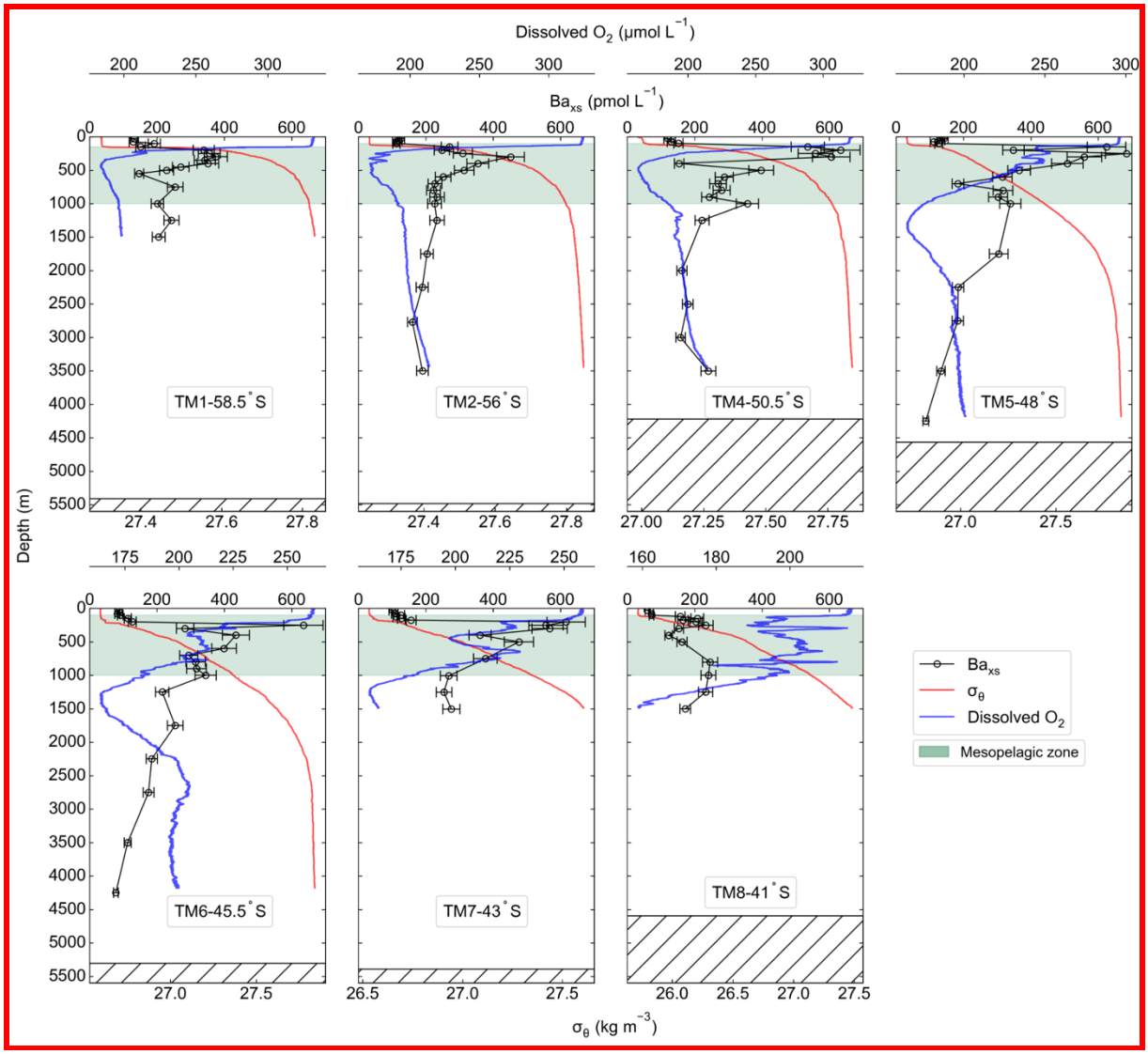
P 6 Line 63. "The data..." Which data?

Response: The integrated remotely sensed PP data. This is now clearly stated in the revised manuscript.

The integrated remotely sensed PP data were regridded to 0.25° spatially, using bilinear interpolation, and averaged monthly.

P9. Fig. 2: O2 scale too compressed to be useful. Authors should provide complete data as supplemental (not just pAl, pBa, Baxs) and submit as soon as possible to GEOTRACES. Include T, S, sigma theta, o2, nutrients, dissolved Ba...

Response: Figure 2 has been amended to widen the dissolved O_2 scale. The temperature, salinity, and nutrient data has now been included in the supplementary (Table S5). We intend on submitting the complete dataset to GEOTRACES IDP once published.



p10... .Lines 31-33. "When taking into account....". There is something wrong with this sentence.

Response: This sentence has been rephrased

A noticeable difference between profiles sampled early in the bloom season (Dehairs et al., 1997; Jacquet et al., 2015) versus those sampled later (Cardinal et al., 2001; Planchon et al., 2013), are the contrasted concentrations of Ba_{xs} in the surface mixed layer.

p 10. Line 34. Very high values can be associated with Rhizosolienia blooms (Bishop, 1988).

Response: We agree that very high values can be associated with Rhizosolienia blooms, but also in most cases when productivity is high, specifically in the SO.

P 12. Lines 84 & 85. Line 94-95... "Residence time of barite in mesopelagic days to weeks. & Particle sinking speeds of 50 m d^{-1}". The large particles comprising the flux do sink that fast; however, the subsurface barite is produced by fragmentation of these particles as they sink. The resulting micron sized barites sink at 0.1 m d-1. Thus, the

premise of decay to background on the time scale of days to weeks is invalid. Barites in the mesopelagic would have a residence time (by sinking) of hundreds of days – if not years. The sink for these barites is dissolution and reaggregation. As grazing is reduced in the wintertime then dissolution and sinking would dominate.

Response: As explained at the beginning of the review, the sinking speed of 50 m d^{-1} was indeed referring to the sinking of aggregates from the surface layer, and not to the sinking speed of barite crystals.

As stated above, the low sinking speed of suspended barite (~0.3 m d^{-1}, Sternberg et al. 2008), once produced in the mesopelagic layer, indeed implies that the residence time of barite is longer than a few days to weeks as generally postulated in the literature for the SO (Dehairs et al., 1997; Cardinal et al., 2005; Jacquet et al., 2007, 2008a). To sink from 300 m depth (~peak of production) to the bottom of the mesopelagic layer (1000 m depth), it would indeed take (1000-300) / 0.3 = 2300 days, i.e., ~ 6 years, without considering time needed for reaggregation and redissolution. This supports our hypothesis that the Ba_{xs} signal in the mesopelagic layer represents remineralisation activity over more than a few days to weeks, as previously reported, and is not directly linked to synoptic measurements of PP during the same cruise. It also further explains how mesopelagic Ba_{xs} concentrations increase from spring to a maximum in winter (see new Figure 4b & c) and suggests that the background value has to be measured at the transition between winter and spring, just before biological activity resumes.

These explanations are included in the text of the revised manuscript.

I've not addressed the detailed discussion further as this point and invalidates the key conclusion of the authors.

Response: We hope that our detailed responses and extensive revisions will convince Pr. Bishop of the validity of our hypothesis and manuscript.

jim Bishop (UC Berkeley).

p.s. have a look at Bishop 1989 (attached - since it may be hard to find). The mapped representation of barite stocks is virtually the same as sampled here.

Please also note the supplement to this comment:

https://bg.copernicus.org/preprints/bg-2021-42/bg-2021-42-RC3-supplement.pdf