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

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

Due to this issue with the Chl-ɑ 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.

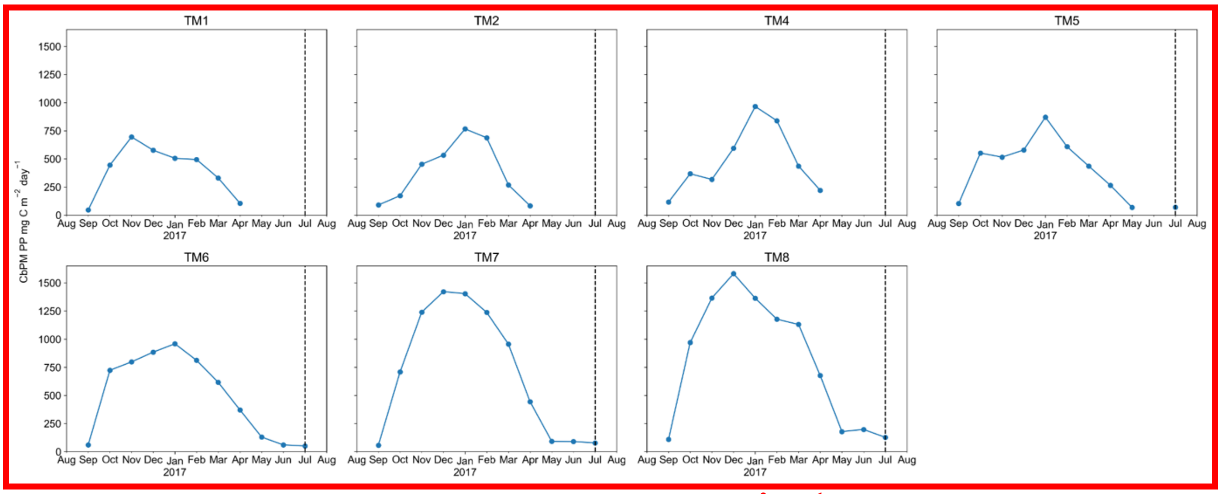

Figure 3: Time series, area-averaged remotely sensed CbPM-PP (mg C m^{-2} day^{-1}), monthly average from 08/2016 to 08/2017, dashed vertical lines indicate sampling date.

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.

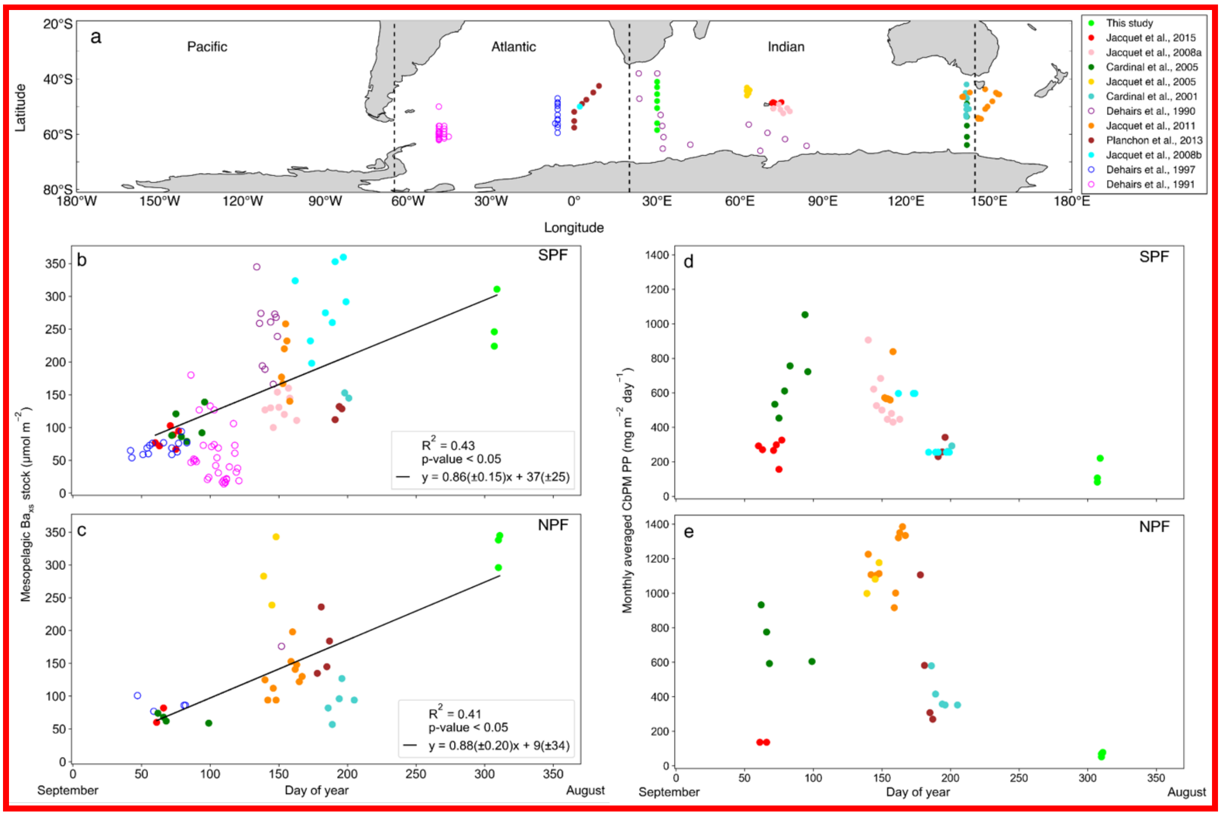

Figure 4: (a) Positions of Ba_{xs} observations compiled from all known SO studies, on a cylindrical equal-area projection of the SO, the three SO basin cut offs are indicated by the dashed black lines, from left to right, Pacific, Atlantic and Indian. Integrated mesopelagic Ba_{xs} stock plotted against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