Interactive comment on "Effects of 238 variability and physical transport on water column 234Th downward fluxes in the coastal upwelling system off Peru" by Ruifang Xie et al.

Anonymous Referee #1

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Xie et al. present new data of 234Th export fluxes from the coastal upwelling system off Peru, associated with an oxygen minimum zone (OMZ). The aim of this research is to investigate the effects of 238U variability and physical processes on the 234^{Th} fluxes. The authors found a poor correlation between measured (by isotopic dilution) and calculated (from salinity) 238U activities. Even though only small variations were observed between measured and calculated 238U activities, this difference leads to significant underestimation of 234Th fluxes. 238U activities are usually not measured, as this represents additional work and the linear relationship with salinity is generally assumed. However, the current study clearly shows the need for measuring 238U activities in non-open ocean systems. The impact of physical processes, such as advection and diffusion, was evaluated by using ADCP, current velocities, satellite wind stress and in situ microstructure measurements. Unlike horizontal diffusion and advection, vertical diffusion and advection were found to significantly modify the 234Th export fluxes at shelf stations. Again, most studies neglect the impact of physics on 234Th fluxes and rare are those considering vertical/horizontal advection and diffusion effects on 234Th fluxes. Finally, the authors investigated the 234Th residence time and found a large temporal variation across the Peruvian upwelling zone, warning future studies to take into account these temporal changes while evaluating carbon export efficiencies. Overall, the manuscript is well written and represents an important effort. In most studies the influence of the 238U variability and physical processes are assumed to be negligible. The findings of this study are therefore highly valuable for the community. With some reorganisation and some more details on the calculations, this manuscript will be a good fit for publication in Biogeosciences.

We thank the reviewer for his/her constructive comments. We've listed our point-by-point response in bold below.

1. Specific comments.

1-Results section. Details are missing to really understand the choices made in the Discussion. I propose to add a "Results" section that would moreover make the discussion clearer for the reader. This new section could present: 1) Total 234Th and 238U activities: basically what is written between the beginning of Section 3 and before the beginning of Section 3.1. 2) Export fluxes of 234Th: - Please give more details on the relevance of estimating fluxes at different horizon depths. First, clearly mention in the Methods that you calculate the export fluxes at 100m and below the mixed layer (ML). Then, in this new Results section, you could explain why you calculate the fluxes at 2 different depths. Why is it relevant to discuss fluxes at 100m or at the base of the ML for the purpose of this work? Also, explain why you estimate the fluxes "below" the ML and not simply at its base? - Steady state versus non-steady state (it should not be part of the sub-section dedicated to "dynamic advective and diffusive 234Th fluxes").

Response: We have now added a new Results section to the manuscript that include details on the 234Th and 238U profiles, export of 234Th fluxes at 100 m and base of the ML (and why we used these two different depths), and comparison of the steady state versus non-steady state models. Please refer to the manuscript for more details.

Due to sampling logistics, we did not sample at the base of the ML, but 5-20 m below the ML. This depth corresponded closely to the EZ depth used in Black et al. (2018) in the same study area. For the purpose of comparison with earlier studies which reported 234Th fluxes at 100 m, we also calculated 234Th fluxes at 100 m in this study.

2-More details on the physical processes. Methods, section 2.3: For each physical process (horizontal advection, vertical advection, horizontal diffusion and vertical diffusion), please give details on how the 234Th fluxes due to these processes are calculated. For example, lines 180-182, how do you use the daily wind stress to estimate the upwelling velocity? Lines 180-182 and lines 189-191: In addition to the cited references, please, briefly explain how VmADCP and in situ microstructure profiler measurements work and how you obtain current velocities or diffusivities from them?

Response: We have now expanded the Methods section to include detailed descriptions of how upwelling rates, VmADCP -derived current velocities and microstructure-derived diffusivities were calculated.

Table 1: As not significant processes, you do not present the 234Th fluxes due to horizontal advection and diffusion. Please, give the values in Table 1 for comparison.

Response: We grouped stations within a 1° by 1° grid and calculated the average 234Th for the top layer, and large scale (1° apart) horizontal 234Th gradients were calculated based on this grouping. We then used average alongshore current velocities and eddy diffusivities for the flux estimation due to horizontal advection and diffusion. These estimations are correct to the first order. As these values were rough estimates, we feel that we should not include them in Table 1. We now explained these in more details in the manuscript.

Discussion, section 3.2: Please, explain in more details how you calculate the vertical and horizontal 234Th gradients. Explanations about the vertical gradient are for example given by

Black et al. (2018) and are useful for the reader. Moreover, lines 326-329, please, clearly say how you determine the horizontal 234Th gradient. What does "larger spatial scale" mean?

Response: We now specified these details on how we calculated the vertical and alongshore 234Th gradients in the Results section (new subsection 2.3.4).

3-Greater 238U activities in suboxic environment. I am very surprised by these results as I would have expected the opposite, i.e., less U in anoxic/suboxic waters. This is very interesting and I did appreciate reading your possible explanations. I however have some questions about them:

- Lines 265-267: If Fe reduction was going on, it would definitely be associated with U removal to the sediment. Is there enough U adsorbed on oxyhydroxides to outpace U removal?

- Could an oxygenation event such as the one described by Rapp et al. (2020) during the 2015 El Niño be responsible of high U concentrations? Assuming a dynamic OMZ and assuming Uranium needs some time to equilibrate, would it be possible to measure high concentrations in low oxygen waters?

Response to both comments: The presence of high content of organic matter in the Peruvian sediments greatly influence U mobility and promote U sorption onto mineral surfaces, such as Fe hydroxides. However, the reviewer is correct that U reduction and removal should occur when sedimentary Fe reduction took place. This was indeed what was observed on the Peruvian shelf by an earlier study (Scholz et al. 2011). We now significantly toned down the discussion on Fe reduction being the main additional U source to the water column, as we cannot accurately quantify the amount of remobilized adsorbed-U vs. U removal.

The same study by Scholz et al. (2011) further showed considerable diffusive U fluxes out of the sediments along the Peru shelf where both Fe reduction and U reduction took place. This remobilization of U was attributed to ENSO-related transient U re-oxidation and recycling. It was suggested that a minute increase in bottom water oxygen concentration was sufficient to shift the U(VI)/U(IV) boundary by a few centimeters and remobilize authigenic U. The coastal El Niño developed preceding to and during our sampling campaign could induce an oxygenation event large enough to remobilized authigenic U along the Peruvian shelf. We now added this discussion to our manuscript.

We would also like to point out that we have significantly modified the discussion on the U-salinity relationship. We now acknowledged that poor U-salinity correlations were also observed in other open ocean basins, and explored possible explanations for this poor correlation in our study area.

- Lines 270-273: Uranium enhancement related to flooding, strong rainfall and landslide would also come with freshwater. Don't you think this would also affect salinity?

Response: This is a fair point. Flooding likely affected both U and salinity in coastal waters. The addition of freshwater and riverine U may draw the datapoints up and down the conservative mixing line (as shown in Owens et al. 2011). However, this was not the case in our study where majority of the U data points fall above the S-U line defined by Owens et al. (2011), indicative of other governing processes other than conservative mixing. We have disregarded the discussion of coastal flooding being one of the main causes of the poor U-salinity correlation.

4-Residence times of 234Th. Lines 371-372: Please, explain how you estimate the residence times.

Response: We now specified in the Methods section the formulation and details on how we calculated the residence times.

2. Line notes.

Line 97, line 104, line 113 and line 676: Keep similar wording all along the text and use "shelf-offshore transect" instead of "shelf-normal" or "shore-normal" transect.

Response: We now used the wording "shelf-offshore transect" instead of the technical term "shore-normal transect".

Line 42: add "e.g." at the beginning of the citation list. There are many more studies.

Response: fixed

Lines 119-120: Please, give the deep ocean average 234Th/238U ratio in your study.

Response: We now added this average 234Th/238U ratio in the Results section

Lines 167-168: Please, mention that fluxes are also estimated at 100m. You should also explain the reason of calculating fluxes at both 100m and at 5-20m below the ML for the relevance of this study – as justified for EZ and ML.

Response: We now specified in the Results section why we chose two different depths for the flux calculation.

Line 183: “the depths correspond to 5-20m below the base of the ML”, please mention that this is the reason why you calculate export fluxes at this horizon depth.

Response: fixed

Line 203: would yield a maximum.., instead of would a yield maximum..

Response: fixed

Lines 203-206: Maybe to move to the new “Results” section.

Response: fixed

Lines 217-219: Please, provide the number of replicates for the IAPSO standard seawater: “3.24 ± 0.06 ng/g, 1SD, n=?”.

Response: fixed

Lines: 249-254: “The consequence of this notable difference in 238U to 234Th flux according to Eq. (2) is neither linear nor straightforward, because the vertical gradients of both 238U and 234Th strongly affects the impacts of 238U variations on 234Th fluxes. In this study, 234Th fluxes at 100 m derived from S-based 238U lead to significant underestimation of 234Th fluxes by an average of 20% and as high as 40% (Table 2). These differences in 234Th fluxes will have direct consequences for 234^{Th} derived elemental fluxes such as C, N, P and trace metals.” This is a conclusion of the all section. I would thus move these sentences to the end of Section 3.1.

Response: fixed

Line 260: S>12?

Response: It should be S > 10 as stated in the original text. McKee et al. (1987) and Swarzenski et al. (2004) looked at two different salinity thresholds in terms of the 238U-S linear correlation.

Lines 276-277: Shepherd et al., 2017 is not listed in the section "References".

Response: fixed

Line 308: For comparison, please give also the fraction of upwelled 234Th fluxes compared to the total fluxes for the offshore stations.

Response: The fraction of upwelled 234Th fluxes compared to total fluxes is now quoted in text.

Line 308: Cite Figure 5.

Response: quoted

Line 322: Mean 234Th "activities" in the top layer.. ?

Response: fixed

Line 322: Please precise what does "top layer" exactly mean. Like in the caption of Figure 6 and Table 3..

Response: fixed

Line 355: cruises

Response: fixed

Lines 380 and 382: Maybe change the 234Th activities into 234Th/238U ratios, as it might be easier to realise the magnitude of the deficit.

Response: The reviewer provided a very good suggestion here, but we unfortunately cannot proceed for one important reason: the activities of 238U in Black et al. (2017) were not measured nor are they reported in the available GEOTRACES database.

Lines 411-412: And 7Be isotopes, as you mention line 351.

Response: added

Line 696: Error bars "are" (instead of were) indicated. Shelf instead of nearshore (to keep the same wording all along the manuscript).

Response: fixed

Figure 2: It is difficult to see the small variations. Please, decrease the size of the 234Th data points and make the lines thinner. Add the error bars. If they are already indicated but too small to be seen, please mention it in the caption. The x axes are always the same, please, keep the O2 values only on the top of the figure and the 234Th, 238U, fluorescence values only on the bottom of the figure. By doing so, you can slightly increase the size of each graph. Please, keep your colour legend of Figure 1 and indicate the shelf to offshore transect by an arrow (maybe by writing W and E, like in Figure 5). Like in Black et al., 2018: indicate the depth of the mixed layer and the start of the Oxygen deficient zone.

Response: Figure 2 was modified according to most of these comments. The depth of the mixed layer is now indicated by a red dashed line. The start of the oxygen deficient zone is where oxygen diminishes. We did not use color legend from Figure 1 to keep Figure 2 clean and easy to read.

Figure 3: Please indicate the error bars. If it is too much for the figures, I recommend to at least, indicate the size of the average error bar on a corner of the plot. Indicated the O2 concentrations in Figure 3c as well. This would confirm that the poor relationship does not depend on O2 concentrations.

Response: We now added error bars, which are smaller than symbols. We also added oxygen concentrations in Figure 3c.

Figure 4: There is no need to write the depths for each plot. Write the values only on the left side of the figure. The legend has to be fixed and "fluorescence" has to be added on the bottom x axis of Figure 4c. In the legend of Figure 4a, define that the black dotted line corresponds to salinity and that the black solid line corresponds to temperature.

Response: We fixed the vertical axes and Figure 4c horizontal axis (now Figure 5). It is not correct regarding reviewer's comment on the dashed and solid lines. We specified in the caption that the dashed lines corresponded to temperature and dashed lines corresponded to salinity.

Figure 5: I do like this Figure: it is clear. Please modify the caption and write “5-20m below ML” instead of “base of the ML. In the legend, please write “Final total 234Th flux” for the white dots to keep the same wording than in Table 1.

Response: Fixed

Table 1: Please modify the caption and the top line of the 2nd column: “234Th flux 5-20m below the ML” instead of “below the ML” or “at the base of the ML”.

Response: Fixed