

Response to Reviewer #1 comments on “Radium-228-derived ocean mixing and trace element inputs in the South Atlantic” by Hsieh et al. (bg-2020-377)

Reviewer’s comments are shown in black.

***Authors’ responses are highlighted in blue.

Hsieh et al (2020) use radium-228 to derive vertical and horizontal mixing rates of trace elements in the South Atlantic. These calculations improve our understanding of trace metal cycling in this part of the ocean, and this manuscript is therefore an important contribution to the field. However, the manuscript could be improved by clarifying when and where certain model assumptions are applied, and by considering some suggested changes/clarifications to the box model calculation. Additionally, I have concerns about the curve fits used to calculate the vertical mixing rates that should be addressed before publication. My comments and suggestions are detailed below, divided by section.

***We thank the reviewer for their positive feedback and constructive comments. We respond to all the comments point by point below and explain how we will address the issues in the revised manuscript. In particular, we have addressed the issue of the curve fit when using the linear regression in Excel. This fit was performed mistakenly assuming that (by default) the TE concentration (x-axis) is the dependent variable and that the depth (y-axis) is the independent variable, but it should be the other way round. This issue has now been corrected. Most of the gradients stay the same (except for Zn, slightly steeper), and hence the changes in the TE fluxes are insignificant. We will update the figures and results in the revised manuscript.

Introduction:

The introduction shifts back and forth from talking about the Southern Atlantic to talking about nutrient limitation more generally. The authors may wish to re-organize the text so that it starts more broadly and then focuses on the South Atlantic to introduce this specific study. In particular, I recommend moving the second paragraph (lines 41-48) farther down (perhaps making it the second to last paragraph instead), so that there are not two separate “In this study. . .” statements.

***We will follow the reviewer’s suggestion and rewrite the introduction.

Line 68: the first reference for continental shelf inputs should be “Rutgers van der Loeff et al.”, not “van der Loeff et al.”

***We will make the correction in the revised manuscript.

Methods:

It is not clear where each of the cruises started and stopped. Both are described as following a 40 deg S transect, but it is not clear how much overlap there was. It would be helpful to color code the lines on Figure 1a to show each of the cruise tracks (perhaps one color to show JC068 and another color or dashed line to show overlapping sections?).

***In the revised Fig. 1a, we will add different colour lines (Red: JC068; Green: D357) to show the cruise tracks.

Line 80: What about the trace metal data? Were all elements measured on both legs?

***All the trace elements have been measured on both legs, and most of the trace element data have been published (Wyatt et al., 2014 and 2020; Browning et al., 2014; Clough et al., 2016). We will add more details to clarify that in the revised manuscript.

Line 103: The authors mention that a separate sample is collected for Ra-226 measurements, but do not explain why the larger volume samples cannot be used for this measurement. Please add an explanation of cartridge collection efficiencies and the reason for a separate Ra-226 aliquot.

***As the reviewer is already aware of the collection efficiency issues when using the Mn-fibre cartridges, the direct use of large volume samples requires the recovery correction to obtain accurate concentrations of each Ra isotope. The cartridge efficiency can vary hugely, depending on the conditions of fibre coating and the pump flow rates. For example, the efficiency ranges from 70 to 128% in some of the samples in this study (comparing the RaDeCC and MC-ICP-MS Ra-226 results, Geibert et al., 2013).

Moreover, depending on the instrumentation, other recovery issues may also occur during the sample preparations. For example, MC-ICP-MS requires the purification of Ra from sample matrices prior to the analysis (e.g. fibre leaching and ion chromatography), but these processes could introduce an additional loss of Ra (i.e. 70-90% yield, Hsieh and Henderson, 2011) and hence contribute a large uncertainty in Ra concentrations when using the Ra counts directly from these large volume samples.

Isotope ratios (or isotope dilution) provide the advantage of being able to correct for the recovery issues, making the valid assumption that recovery does not change the isotope ratios. Thus, the isotope dilution (Ra-228 spike) was used in separate Ra-226 samples to get accurate Ra-226 concentrations in this study. For the large volume samples, we then only need to focus on measuring Ra-228/226 ratios without being concerned with the recovery issues. We will add more information in the revised manuscript to clarify the reason for and advantage of using a separate Ra-226 aliquot.

Three different collection Ra methods are described. Was any intercalibration between methods conducted? (e.g. collecting samples at the same depth using different methods?)

***There is no direct intercalibration between the three sampling methods in this study. However, the samples collected by pump (fish), CTD and SAP within the mixed layer at each station show consistent Ra results. We will add a few sentences to clarify this in the revised text.

Line 121: The authors explain that the Ra-226 aliquots are spiked with Ra-228. How large is the spike, how can you be sure that no seawater Ra-228 contributes to the “spike” signal?

***We usually added ~70 attomol Ra-228 spike to ~250mL seawater. The contribution of seawater Ra-228 is < 0.05 attomol (< 0.1% of the spike signal).

The authors mention that chemical blanks are monitored throughout the procedures, but it is not clear whether this is a seawater sample or a Milli-Q blank. I understand chemical blanks to be reagents only, not including seawater background activities.

***The procedure blanks were carried out in the same way as the samples except there was no added seawater. It is similar to a Milli-Q blank as the reviewer has described, but it also includes all the reagents and procedures that were involved in the sample preparation. We will add some information to clarify this in the revised manuscript.

Line 128: The comma after CRM-145 is unnecessary and can be deleted

***We will make the correction.

Line 138: If using a global dataset, why not include more recent GEOTRACES data as well? Alternatively, did the authors consider using an Atlantic-specific trend rather than a global trend? The Ra-226 – Si relationship can vary by basin.

***Follow the reviewer's comments, we have included more recent GEOTRACES data from the North Atlantic (GA03) and removed the non-Atlantic data. As the non-Atlantic data were only 126 out of 3392 data points (< 4%), the trend slope and interception remain similar to our previous estimates. The difference in the corrected Ra-226 is less than 3%. We will update the data in the revised manuscript.

Line 159: Change “on the decade timescales” to “on decadal timescales”

***We will make the change.

Line 165: The authors state here that vertical mixing could affect horizontal distributions of Ra-228, but that the sample resolution is not good enough to account for this input, and they therefore ignore vertical mixing. This is at odds with the section of the paper where they explicitly use the vertical distribution of Ra-228 to calculate vertical mixing rates. It is not clear to me how they can argue that vertical mixing is insignificant in one case, and the main control on Ra in the second case.

***These model assumptions are justified under different conditions, depending on the mixing time scales and the sources of Ra-228 at the defined sections of the ocean. For example, vertical mixing is typically 5 to 8 orders of magnitude smaller than horizontal mixing. Therefore, the vertical term is often ignored in the Ra-228 horizontal mixing model. In the Ra-228 vertical mixing model, surface waters need to be assumed as the dominant source of Ra-228 to the waters below the mixed layer with no significant horizontal inputs at depths. Hence, the Ra-228 depth gradient is mainly driven by vertical mixing. In the upper ocean, horizontal Ra-228 largely comes from the continental margins (shelf and slope sediments). There is also no direct evidence suggesting that the Ra-228 profiles are affected by the horizontal input below the mixed layer (Fig. 7). Therefore it is not unreasonable to assume that, at least in the top 600 m depth, the vertical gradient of Ra-228 is mainly set by the surface Ra-228 values and downward mixing.

To a certain degree, the Ra-228 background correction in the vertical profiles has considered the horizontal Ra-228 signal at depths. However, this does not mean that all the additional Ra-228 inputs at depths can be corrected. For example, the elevated Ra-228 signals can still be seen at depths in the Argentine Basin and this has led to unreasonably high vertical mixing coefficients. Thus, we do not use the vertical mixing results in these stations.

We acknowledge the fact that these mixing results may only provide upper or lower bound estimates because of the restrictions in these assumptions. Nevertheless, the consistent results shown between this study and previous studies suggest that these assessments are still valuable and can improve our understanding of the trace element budgets in the South Atlantic. We will clarify these assumptions and explain their limitations in the revised manuscript.

Line 173: This sentence is confusing as written (too many commas) and should be re-phrased.

***We will rewrite the sentence.

Line 176: Why is the Ra-228 background determined from the mid-water column? If this is being used to calculate horizontal mixing at the surface, a more appropriate Ra-228 background activity would be the surface water activity in the central South Atlantic (perhaps the ANT XV/4 surface activities? Or GEOTRACES data from the central North Atlantic could also provide a comparison)

***In this study, the Ra-228 background is determined by the average value from both the mid-water column and the surface waters (ANT XV/4) far away from shores, because the background correction is applied to both horizontal and vertical mixing. In fact, the Ra-228 background in the mid-water column (1000-3000 m) is not zero (~ 0.2 dpm/100L) and similar to the remote surface waters (~ 0.2 dpm/100L), suggesting that there may be an advective Ra-228 background in the mid-water column and that this should be corrected for in the vertical mixing calculation.

For comparison, we select the surface water data (< 100 m) from the GEOTRACES central North Atlantic (GA03, between station 12 and 20). The data show significantly higher Ra-228 concentrations (2.23 ± 0.41 dpm/100L) than the values observed in the central South Atlantic (< 0.3 dpm/100L; Hanfland, 2002, ANT XV/4). Moore et al. (2008) have found a similar distribution of Ra-228 between the North and South Atlantic. This value is more than 2/3 of the highest value (3.22 dpm/100L) observed in the shelf water of the Cape Basin in this study. Therefore, this is not a suitable background value for the South Atlantic waters. In contrast, the mid-water data from GA03 (1000-3000 m depth, between station 12 and 20, and 1000 m above seafloor) show a very similar background value (0.16 ± 0.1 dpm/100L) to this study. Thus, we prefer to use the low background value to reflect the Ra-228 level in the South Atlantic. In the revised manuscript, we will add the comparison between the data in the North and South Atlantic.

Line 185: This sentence states that the two scenarios (mixing only, diffusive only) are used to bracket the range of estimates. However, it is stated in line 193 that the diffusive only case is used nearshore, and the mixing only case is used past the shelf- break. Throughout the methods section, it is confusing which assumptions are applied in which environments (e.g.

when vertical mixing is ignored, or when advection is ignored)- perhaps it would help to structure the methods section by geographic region rather than by the individual assumptions? I am not entirely convinced that an advection-only scenario is valid. In other words, what is the basis for ignoring diffusive mixing? Are there other studies that have used Ra-228 in this way before? To the best of my knowledge, most other Ra-based studies ignore advection rather than diffusion.

***We agree with the reviewer. The advection-only scenario is unlikely to be valid. We only do this as an example for comparisons. In this study, it has only been applied to the data in the Argentine Basin after the shelf-break where the advection signal is strong. We will rewrite the relevant section to clarify that in the revised manuscript.

Results:

Line 214-215: delete “with expectations based on” so the sentence reads “are consistent with GEOSECS and TTO observations. . .”

***We will make the change.

Line 213: Are the authors specifically comparing the vertical profiles with Southern Atlantic GEOSECS and TTO stations here, or the entire Atlantic? If the entire Atlantic, the Charette et al (2015) North Atlantic GEOTRACES data should also be referenced.

***The comparison is only for the South Atlantic. We will clarify this in the revised manuscript.

Discussion: Vertical mixing:

Does the exponential curve fit for Ra include any of the data in the surface layer, or does the curve fit start below the mixed layer (Figure 6)?

***The exponential curve fit starts from below the mixed layer but includes the average value in the mixed layer at the bottom of the layer. We will explain this with more details in the revised figure caption.

Station 2 does not have sufficient Ra data (only one point) below the mixed layer to fit a curve. This station should be removed from the vertical mixing analysis.

***We agree with the reviewer that Station 2 does not have sufficient Ra data below the mixed layer. However, the mixing result is consistent with the adjacent stations in the Cape Basin. Therefore, we prefer to keep the mixing results for comparison in Fig. 6, but we will remove the Stn2 vertical TE flux calculations and explain the limitation due to the insufficient Ra data.

Some of the linear regressions on the trace element vertical profiles start below the mixed layer, while others do not (Figure 4). Why does this vary from station to station? In particular, the Zn data has particularly poor linear fits, and it is not clear whether all the data were included in the fit (the deepest sample at all three stations are below the end of the dashed line).

***As mentioned in the beginning, we used the function for linear regression in Excel to fit all the available TE data in the top 600 m. By default, this fit mistakenly assumed that the TE concentration (x-axis) is the dependent variable and that the depth (y-axis) is the independent variable, but it should be the other way round. This issue has now been corrected. Most of the gradients stay the same (except for Zn, slightly steeper), and hence the changes in the TE fluxes are insignificant. We will update the figures and results in the revised manuscript.

Box model/trace element inputs:

Why are the calculations of Ra/TE fluxes put in an appendix? I recommend moving these into the main text, as they form the basis for the conclusions of the paper.

***We agree with the reviewer that the TE flux calculations form the basis for the conclusions of the paper, but think that they would also obstruct the flow of discussion in their current form. Thus, we will move the basics of the calculations into the main text by adding a new section in the methods (2.5) to introduce these approaches and equations. We will keep the calculation details in the appendix to avoid any potential obstruction in the discussion.

Line 305: change “may not be unreasonable” to “are reasonable” Lines 309 – 311 are repetitive with line 299-301

***We will make the change.

Line 319: delete “in fact” so the sentence reads “which is very close..”

***We will delete this.

Line 321: I recommend saying that the Fe fluxes are “slightly lower than” previously reported fluxes, instead of saying that they “compare well with” these other estimates, as they are an order of magnitude lower.

***We will make the change.

Line 328: I don’t understand why these estimates must represent a lower bound for what is expected in the South Atlantic. If the concentrations of Zn are lower in the Southern Atlantic, wouldn’t a lower flux be expected, making these reasonable estimates rather than lower bounds?

***We will rewrite the sentence in the revised manuscript.

Line 335-340: The Southern Ocean Fe fluxes reported by Dulaiova et al (2009) are almost exactly equal to the winter mixing Fe fluxes in the North Atlantic reported by Achterberg et al (2018). However, the authors state that the Fe fluxes they calculated are similar to Dulaiova but lower than Achterberg.

***We will correct the statement in the revised manuscript.

Line 363: stating that the integrated timescale is “relatively short” makes it seem like the half life of Th-234 is too short to capture changes in POC flux. It could be the opposite, that the biology is changing faster than the Th. I suggest removing “the integrated timescale is relatively short” so the sentence reads “given that the mean life of Th is 35 days”. This way both possible conditions are accounted for.

***We will make the change.

The loss via sinking out of the surface box is estimated using ²³⁴Th-based POC fluxes, and TE/C uptake ratios in phytoplankton. As I understand it, using the TE/C ratios in phytoplankton aims to isolate the flux from biology. Why not estimate the total flux? The box model sources include inorganic inputs, so the total source from sinking particles should be considered, not just the organic flux. This can be done by multiplying TE/²³⁴Th ratios by Th fluxes, rather than adding the extra step of converting to C in the middle. TE/²³⁴Th ratios are available for the North Atlantic (Hayes et al., 2018) and South Pacific (Black et al., 2019). If it is not possible to find TE/²³⁴Th ratios for all metals, perhaps this can at least serve as a comparison to the biology-based fluxes for the metals where data is available.

In Hayes et al. (2018), the total Fe flux is significantly smaller than the biological flux estimated here; perhaps the lab-based Fe/C ratios over-estimate the actual ratios in this region?

***We agree with the reviewer that the total TE fluxes (biological uptake + particle scavenging) are more appropriate to represent the total output. However, it is not unreasonable to assume that biological uptake is the major output for the chosen trace elements in the open ocean primary productivity zone. Particle scavenging may become more important in certain areas of the surface ocean (e.g. continental margins or high dust plume regions), but fluxes of micronutrients metal in the region in this study is likely to be dominated by biological uptake.

Although the direct comparison of TE/²³⁴Th ratios between this study and Hayes et al. (2018) or Black et al. (2019) is currently not available, the comparison of the pFe export fluxes between this study and Hayes et al. (2018) actually shows relatively good agreement - 445 nmol/m²/day (this study) vs 274 ~ 2740 nmol/m²/day (0.1 ~ 1 mmol/m²/yr, the results of the ²³⁴Th approach between the longitude 24.5W and 66.5W shown in the Fig. 8c in Hayes et al., 2018). Likewise, the estimates of pCo flux between this study and Hayes et al. 2018 show similar level results (15 nmol/m²/day vs 0.27 ~ 6.8 nmol/m²/day, converted from 0.1 ~ 2.5 umol/m²/yr). We will add this comparison in the revised manuscript.

The depth horizon for the surface box is not mentioned in the text, but is noted as 50 m in Figure 8. Why was this depth chosen? Please add an explanation to the text in addition to noting the depth in the figure. Particle fluxes can vary greatly depending on the depth chosen- see Buesseler et al. 2020 for example.

***The depth of 50 m was initially chosen as an average depth of the mixed layer in this region, and it was only used (to get the vertical section area) in the calculations of the net TE fluxes from the continental shelf to the defined surface box in the open ocean. We agree with the reviewer that the ²³⁴Th particle fluxes can vary with the integration depths. The ²³⁴Th flux is usually integrated to the ²³⁴Th-²³⁸U equilibrium depth (e.g. Thomalla et al., 2006) or to the 1% light depth (e.g. Owens et al., 2015). Thus, we compare the ²³⁴Th POC fluxes

around the 40S Atlantic from Thomalla et al. (2006) (7.0 ± 2.2 mmol/m²/day, CTD05, integration depth: 101 m) and Owens et al. (2015) (6.4 ± 3.3 mmol/m²/day, DT6, integration depth: 88 m). Despite the difference in the integration depths, the two independently assessed POC fluxes are relatively consistent in this region.

To reflect the integration depth of the removal flux in the euphotic zone in the box model, we will change the depth of the surface box to 100 m and correct the shelf-ocean TE fluxes accordingly. We will provide more details in the revised manuscript.

In the conclusion (line 383) and abstract the authors mention that particle inputs may need to be accounted for to close gaps in the mass balance. What are some examples of these possible particle sources? Is dust deposition not considered a particle source? It seems like some particle inputs and outputs are considered in the box model but not others.

***The particles here mainly refer to the laterally transported particles from the continental margins. Rijkenberg et al. (2014) have suggested that laterally transported particles from the offshore export waters may release Fe to the upper ocean in this region. However, it is not possible to evaluate this flux with our current dataset. We will clarify this in the revised manuscript.

Figures:

Figure 1a: It would be helpful to add “Cape Basin” and “Argentine Basin” to the map, as these locations are referenced throughout the text.

***We will add the ocean basin names to the revised map.

Figure 1a: “GEOSEC” should be changed to “GEOSECS”

***We will make the correction.

Figure 1b: The colorbar extends over a much larger range than necessary; as far as I can tell, there are no samples with a salinity below 34. Shorten the range of the colorbar (e.g. 34 – 36) so that changes in the study area can be more clearly seen. I also recommend using a different color scale- this one has non-linear changes in both hue and brightness that make some gradients appear sharper than others (and will not print well as black & white). The highest peach values can also be misconstrued as orange (falling lower on the color scale between yellow & red, as opposed to being read as the highest values).

***We will make the change in the revised manuscript.

Figure 4: The caption says that dashed lines show linear regression trends with the uncertainty. It’s not clear how the uncertainty is shown- should there be shading around the line? Or are the authors referring to the equations next to the lines?

***The uncertainty refers to the slope in the equation. We will clarify this in the revised caption.

Figure 4: Why do some of the lines not extend through all of the data? (e.g. panels g and j)

***As mentioned above, the Excel linear regression was performed mistakenly assuming that the TE concentration (x-axis) is the dependent variable and the depth (y-axis) is the independent variable, when it should be the other way round. This will be corrected in the revised manuscript.

Tables:

Table 1: On my PDF, it appears as if half the caption is above the table and half is below. I am not sure if the authors intended to put some information at the end (information about extrapolated Ra-226 activities & errors), but this should be included in the top caption.

***The information at the end of the table is the footnotes. We will label and clarify this.

Appendix

D:

Line 400: The end of this sentence is missing.

***There should be a colon symbol in the end of this sentence. We will correct this.

Line 444: What two surfaces are the authors referring to?

***In Fig 8, the two surfaces refer to the surface of the shelf horizontal plane (brown) and the surface of the shelf vertical section (red). We will clarify this in the revised manuscript.

References:

Buesseler et al. 2020. "Metrics that matter for assessing the ocean biological carbon pump." Proceedings of the National Academy of Sciences. DOI: 10.1073/pnas.1918114117

Hayes et al. 2018. "Flux of Particulate Elements in the North Atlantic Ocean Constrained by Multiple Radionuclides." Global Biogeochemical Cycles. <https://doi.org/10.1029/2018GB005994>

Black et al. 2019. "Insights From the ²³⁸U-²³⁴Th Method Into the Coupling of Biological Export and the Cycling of Cadmium, Cobalt, and Manganese in the Southeast Pacific Ocean" Global Biogeochemical Cycles. <https://doi.org/10.1029/2018GB005985>

***Other references cited in the response:

Browning et al. (2014) Nutrient regimes control phytoplankton ecophysiology in the South Atlantic, *Biogeosciences*, 11, 463-479.

Clough et al. (2016) Measurement uncertainty associated with shipboard sample collection and filtration for the determination of the concentration of iron in seawater, *Anal. Methods*, 8, 6711-6719.

Geibert et al. (2013) ²²⁶Ra determination via the rate of ²²²Rn ingrowth with the Radium Delayed Coincidence Counter (RaDeCC), *Limnology and Oceanography Methods*, 11, 594-603.

Hanfland (2002) Radium-226 and Radium-228 in the Atlantic sector of the Southern Ocean, PhD thesis, AWI Bremerhaven Germany, 135pp.

Hsieh and Henderson (2011) Precise measurement of ²²⁸Ra/²²⁶Ra ratios and Ra concentrations in seawater samples by multi-collector ICP mass spectrometry, *Journal of Analytical Atomic Spectrometry*, 26, 1338-1346.

Moore et al. (2008) Submarine groundwater discharge revealed by ^{228}Ra distribution in the upper Atlantic Ocean, *Nature Geosciences*, 1, 309-311.

Owens et al. (2015) Thorium-234 as a tracer of particle dynamics and upper ocean export in the Atlantic Ocean, *Deep Sea Research, Part II*, 116, 42-59.

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Wyatt et al. (2014) Biogeochemical cycling of dissolved zinc along the GEOTRACES South Atlantic transect GA10 at 40°S , *Global Biogeochem. Cy.*, 28, 44-56.

Wyatt et al. (2020) Seasonal cycling of zinc and cobalt in the Southeast Atlantic along the GEOTRACES GA10 section, *Biogeosciences Discuss.*, in review.