

Response to reviewer #1

Thank you for your comments on our manuscript. We hope to have addressed the issues you have raised satisfactorily.

Note that full bibliographic information of the references below is to be found in the manuscript.

Instant equilibration

The presentation of the article is much improved and the authors have provided a good supplementary document with much need details. However, I do not find the explanation they have provided, of why the instantaneous equilibrium is an appropriate approximation, convincing. In my first review I showed that the adsorption and desorption terms were not as fast as the sinking rate for large particles.

After carefully reading the authors response, I returned to this issue and using a single large and single small particle class for Thorium derived 1-D vertical profile solutions. I chose the numbers based on the dominate sinking flux (CaCO_3 for large) and POC for small, their Table 4 and numbers from the supplementary materials. I considered the solutions in the absence of mixing and advection. I chose a very large dissociation value of 4/yr (Note: smaller values will make the problems discussed worse, not better). The profiles obtained are attached.

We see that the large particles are falling so fast, they do not reach equilibrium until at least 2000 m. This means they transport far less Th than estimated by the authors. The dissolved Th and the Th on the small particles are much larger than estimated by the authors.

We agree that it is clear that non-equilibrium scavenging is different from equilibrium scavenging. However, in your calculations there is no comparison with observations, so it does not show that modelling Th-230 and Pa-231 is impossible with an equilibrium scavenging approach.

The model you used (thank you for sending this to us via the editor) is very useful for the purpose of illustration, but the ad- and desorption values are, as far as we can see, quite arbitrary (except of course in that you fixed their ratios to be consistent with our partition coefficients).

More specifically, k_{ads} is on the low side of the values estimated in the shallow waters with ^{234}Th . ^{234}Th data suggests values ranging from 1/20 per day to 1/200 per day. Using these values and maintaining the $k_{\text{ads}}/k_{\text{des}}$ ratio constant, the modelled profile tends towards the equilibrium profile (see figure below).

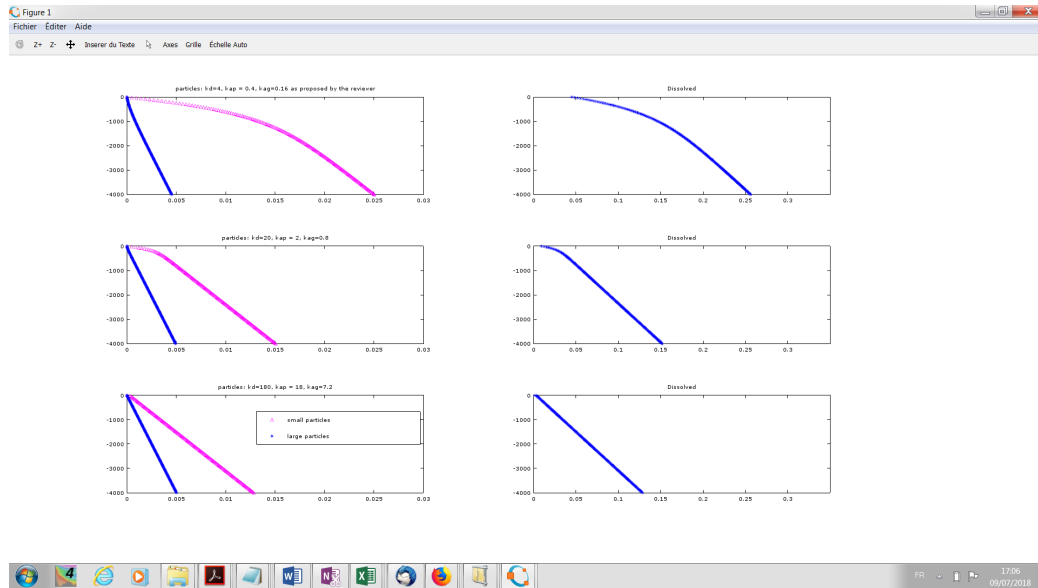


Figure 1:

The upper two panels in the figure are the graphs obtained by using the reviewer's, showing that only from 2000 m downwards the profiles are linear. The centre two panels correspond with the more realistic parameters. There the profiles are linear from 300 m downwards. The lower panels with very high k +/- in good approximation of instant equilibrium.

Furthermore, the reviewer's model (upper panels) assumes a constant particle flux and a constant particle concentration, whereas in the real ocean particle concentrations are higher in the shallow waters: they produce a higher scavenging and a lower dissolved ^{230}Th concentration.

Furthermore, equilibrium scavenging is an approach commonly used in Pa/Th modelling (Siddall et al., 2005; Dutay et al., 2009; Gu and Liu, 2017). It represents the advantage to design the model with partition coefficients that are directly constrained by observations (though admitting that consensus values are still not available, even for partition coefficients). Observations show K values varying (decreasing) with particle flux (Roy-Barman, Chen and Wasserburg, 1996; Chase et al., 2002) that are applied in our simulation.

We do realise that our approach may be imprecise, which raises the question why we do not perform simulations with slow equilibration after all. This would require more model development and simulation time, including the determination of the different k_+ and k_- values; in our opinion this belongs to a different, follow-up study. We maintain that the model as it stands is useful for the community, and, though we cannot be certain at this point, precise enough for for instance deep ocean and sediment studies.

As expressed by the authors in their response, these ratios can be changed by changing the equilibrium constants, $kappa$. However, the other difference the full solution shows is that the dissolved and particulate phases are not straight lines with origins at zero depth. In particular, the dissolved phase has a distinct curvature and intercept. This curvature means, compared with the authors solution, the real difference in the upper waters (0-2000m) and the lower waters (2000-4000m) is much less than occurs for a straight line with origin at zero depth.

On the other hand, observed profiles do not have such a large intercept. This result must mean that particles falling as fast as 50 m/d cannot play as large a role as the authors suggest.

It plays a role in the export of Th and Pa, but we don't think we overemphasise its role. We assign larger K values to small particles, which has as a consequence that much more of the radionuclides are associated with small than with big particles. Indeed, at least in our model which works quite well, the small particles play the dominant role. You may be referring to the fact that we couldn't assign too large values of K for biogenic silica and calcium carbonate. Absolutely, but this is, admittedly, because of the shortcoming of the model that it doesn't have small versions of these particles. As a consequence, at least some of the bulk concentration of biogenic silica and calcium carbonate corresponds to (observed) small particles (in the case of

calcium carbonate the modelled concentration lies in between large and total, as briefly discussed in the paper).

It can not be expected that the results from a model that gets the 1-D profiles incorrect, would be accurate in 3-D. The interpretation of the results, due to the tuning required to correct this model deficit, is uncertain.

We agree with the last sentence: we needed to tune, within a range based on published values, to get better model results, which make interpreting the model somewhat more difficult. However, we cannot agree with the premise of the first sentence. Your model clearly shows a difference between the instant and non-instant 1-D scavenging models, but one cannot infer from this that one or the other is more likely to be correct (or closer to reality). Moreover, we happen to be closer to the instant-equilibration 1-D model.

Other issues

Opal is still used at least once Figure 5c: caption says μM , color bar says nM

We fixed these mistakes.

Response to reviewer #2

Thank you for your comments to our manuscript. We hope to have addressed the issues you have raised satisfactorily.

Additions are denoted in green text in the manuscript.

Scientific Quality

Key points

1. [...] I question the use of the K values for lithogenic material

in this study. For small particles, the values used for both isotopes are much larger than ± 1 standard deviation of the value found by Hayes et al. (2015), the range in Geibert and Usbeck (2004), or the range from other previous studies (Anderson et al., 1992; Chase et al., 2002). The only study I have seen a K value for lithogenic material greater than that reported used this study was by Luo and Ku (2004) ($K = 230 \gg 10^6$ g/g), though this value mostly reflected the variability in K with the % lithogenic composition of sediment trap material from the Southern Ocean and the Equatorial Pacific. Similarly, the source for K for small particle POC is unclear; these values for both isotopes appear to be based on those derived by Hayes et al. (2015), but why was the higher end of the range used for ^{230}Th , and the low end of the range used for ^{231}Pa ? The authors should state explicitly how they arrived at the values of K for both POC and lithogenic material.

The high values that we used for the small lithogenic particles are possibly because we tuned them too high because we are lacking other small particles (e.g. Mn/Fe oxides and calcium carbonate). Hayes et al. (2015) do report higher values for Th than for Pa. (Note that they use different exponents/units for K values for Th versus Pa.) In the supplement we included a table with values that shows we tried to choose reasonable values.

2.

PISCES includes aggregation between small and big POC (Aumont et al., 2015), but in Pa-231 and Th-230 equations 9(b,c) I do not see any terms that represent aggregation of particulate from small to big particles. The authors justify the omission of adsorption and desorption in equations 9(a,b,c) by assuming an instant equilibrium between the dissolved and the two particulate phases, but I do not see a similar argument for the omission of aggregation of POC given. I think the authors need to clarify whether and how aggregation of the particulate radionuclide pools is or is not considered. Additionally, I am curious as to how difficult it would be to include aggregation of the sPOC-bound radionuclide pool in the model, since the aggregation rate can

be derived from eq. (39) of Aumont et al. (2015). For example, could an aggregation term be included in equations 9(b,c):

$$dA_{i,S/B}/dt = \pm\beta A_{i,D}K_{i,POC}P^{POC} \dots,$$

where the aggregation rate represents a loss for radionuclides bound to small particles (S), a source for radionuclides bound to big POC (B), and B is the aggregation rate parameter ($/d$). Including this term in the current setup may not make sense considering the authors already assume instant equilibration with respect to adsorption and desorption, and POC specific aggregation rates may be on the order of adsorption and desorption rates (0.1 to 1 /yr, Murnane (1994a)) or faster (Burd, 2013), but I think it is important to at least make explicit why aggregation of radionuclides in the small POC pool is or is not considered.

We explained in the text now why there is no such aggregation in the model based on the fact that we do have instant equilibration. Here in short, because of the latter, the former would not have any effect.

3. In the conclusion, along with mentioning the potential missing effects of nepheloid layers, Mn (oxyhydr)oxides, and a stronger AMOC on simulated ^{231}Pa and ^{230}Th , I also suggest that the authors mention the sensitivities of these distributions to K for the various particle phases. Although a sensitivity analysis may not be the goal of this study, I think it is at least worth speculating on how changing K values from those used in this study could alter and potentially improve the simulated distributions. Reported K values for any given particle type may vary by up to three orders of magnitude (e.g., $10^{3.98}$ from Guo et al. (2002) vs. up to $10^{6.23}$ from Geibert and Usbeck (2004) for SiO_2), may depend on whether K is derived from field observations or laboratory experiments, and may depend on differences in types of particles used in laboratory experiments (e.g., inorganic vs. biogenic SiO_2 or CaCO_3). Given such large ranges, it is not unreasonable to suspect that a different, yet still plausible, combination of K values could better describe the available data.

We believe that we have given enough details on the effects of different K values, for this study. Anymore would be speculation and just as good a guess for the reader as for us. Therefore, we prefer not to add on this at this point.

Minor comments

1. The authors mention that this model is an improvement of that presented in Dutay et al. (2009). I think this improvement should be shown in the paper. For example, a table showing the root mean square deviation and/or r for dissolved and particulate Th-230 and Pa-231 in the dissolved and small particulate pool (there may not be enough observations to compare the fit to big particles) for both models (the one presented and the one from Dutay et al. (2009)) could be provided. This way, the improvement in fit obtained by the new model, which is one of the key results of this study, is made explicit.

Unfortunately, their model output is not available anymore, so we cannot do this. We have put our most important model output on PANGAEA, so comparing with our study should be possible when future studies want to compare with ours.

2. The authors provide r for the fit between simulated and observed dissolved ^{230}Th at GA02 and GA03. A similar comparison should be presented for ^{231}Pa along both sections, ^{230}Th and Pa-231 in the small particle pool at GA03 (I don't think these particulate radioisotopes have been reported along GA03).

We have added a Table to the supplementary material (Table S4) that lists the r for the dissolved and small particle pools of Th-230 and Pa-231 at GA02, as well as for our sensitivity simulation (Pa–opal affinity decreased).

Presentation quality

1. We have rephrased the sentence according to your suggestion.

2. Names in the figure and caption should now be consistent.
3. We added a comment on different diameter boundaries in the text.
4. We added an extra column; this probably looks just as well as adding it to one of the columns.
5. Yes, rephrased.
6. Thanks, fixed.
7. Done (described consequences of circulation and scavenging changes).
8. Rephrased according to your suggestion.
9. Done.
10. Done.