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Commentary on: How accurate are the ^{234}Th based particulate residence times in the ocean? by G. Kim, N. Hussain, and T. Church

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1. Introduction

Kim *et al.* (1999) pose the question: "How accurate are the ^{234}Th based particulate residence times in the ocean?" The intent of this commentary is to point out the difficulty one has confirming the accuracy of their ^{234}Th residence time approach when the validity test is a limited comparison between two methods with large uncertainties, namely shallow sediment traps and this new model. Furthermore, we suggest that there is ample evidence to show that the residence time of POC is not the same as the naturally occurring tracer ^{234}Th. As such, the calculation of ^{234}Th ***residence times***, even if accurate, would not provide a direct estimate of POC turnover and export in the upper ocean. Alternative techniques using calculated ^{234}Th ***fluxes*** multiplied by the measured ratio of POC/^{234}Th^{part} do not suffer from these assumptions (as summarized in Buesseler, 1998).

2. Residence Times and Uncertainties

Coale and Bruland (1985) defined the equations which have been commonly used to calculate the residence times of thorium-234. For example, for total ^{234}Th:

$$\frac{\partial A^t_{Th}}{\partial t} = 0 = A_u\lambda - A^t_{Th}\lambda - A^t_{Th}k_t \qquad (1)$$

where A_U and A^t_{Th} are the activities of ^{238}U and total ^{234}Th respectively, λ is the decay constant for ^{234}Th (=0.0288 day^{-1}), and k_t is the first-order scavenging rate constant for total ^{234}Th removal. As such, residence time of total thorium with respect to removal on particles can be calculated from:

$$\tau_t = \frac{1}{k_t} = \frac{A^t_{Th}}{(A_u - A^t_{Th})\lambda} \qquad (2)$$

The accuracy of any ^{234}Th residence time calculation is therefore determined by 1) assumptions made in the formulation of the thorium activity balance (i.e. equation 1), and 2) the accuracy of the ^{238}U and ^{234}Th activity estimates (in particular, the error on $A_U - A^t_{Th}$ in equation 2).

With respect to the model assumptions, Kim *et al.* focus their attention on prior formulations of τ, and suggest that multi-box models of ^{234}Th particulate and colloidal residence times are in error due to a "missing" decay term. Coale and Bruland (1985) define the particulate residence time of ^{234}Th with respect to particle removal only (τ_p=1/k_p, where k_p is the scavenging rate constant for particulate ^{234}Th). Coale and Bruland (1985) also pointed out that the residence times as defined were not additive ($\tau_t \neq \tau_d + \tau_p$; where τ_p and τ_d are the particulate and dissolved ^{234}Th residence times, respectively). Kim *et al.* correctly show that these residence times are only additive if you include a residual term, such that: $\tau_t = \tau_d + \tau_p + \lambda\tau_p\tau_d$ (equation 7 in Kim *et al.*). They add this residual term to the particulate residence time, to define a new τ^*_p, such that $\tau^*_p = \tau_p + \lambda\tau_p\tau_d$ (we use τ^*_p to distinguish Kim *et al*'s formulation of the particulate ^{234}Th residence time, $\tau^*_p = 1/k_p + \lambda\tau_p\tau_d = \tau_t - \tau_d$).

We disagree that τ^*_p is a more "accurate" particulate ^{234}Th residence time. Kim *et al.* contend that residence times must be additive, but in a multi-box model, residence times are only linearly additive in a closed system without radioactive decay. Including this residual term in τ^*_p does not improve our understanding of the true residence time of thorium with respect to particle removal in the ocean.

The uncertainty of τ^*_p can be estimated from error propagation theory (Rutgers van der Loeff and Moore, 1999). In the open Atlantic and Pacific oceans, Chen *et al.* (1986) have shown that the ^{238}U atom abundance is proportional to salinity within a standard deviation of 1%. Thorium-234 activities are directly measured, and the errors associated with this determination are commonly 5-10%, though Kim et al. report a more optimistic 3% error here. Using this 3% error, one can calculate the individual errors of τ_d and τ_p, and hence the propagated error on τ^*_p.

Using this approach, we determine an uncertainty on τ^*_p of 170% (86 ± 148 days) and 100% (154 ± 142 days) for December and June, respectively (same locations and times as the first two North Atlantic values in Table 1; Kim, 1998). This calculation immediately points out the inherent difficulty in using Kim *et al*'s approach. Each of the dissolved and total residence times have a large uncertainty due to the small difference in $A_U - A_{Th}$. In addition, the final particulate residence time is calculated as the difference between these two longer residence times ($\tau^*_p = \tau_t - \tau_d$). As such, the combined error on τ^*_p is subject to an even larger uncertainty than the individual residence times estimates for τ_t and τ_d.

Much of the faith these authors place in the accuracy of the calculated particulate residence times appears to come not from an analysis of how well one can estimate τ^*_p, but from the similarity between these imprecise particulate thorium residence times and similarly unconstrained POC residence time estimates. At best, only two of the four sites where they validated their model have uncertainties <100% (see below).

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3. POC vs. particulate ^{234}Th residence times

If the residence time of particulate Th and POC are the same, then one could use the POC inventory divided by the residence time of particulate Th to calculate POC export. Studies using ^{234}Th as a tracer suggest that these residence times are not similar (e.g. Murray *et al.*, 1989), with the residence time of POC being longer. Kim *et al.* argue that these prior studies are flawed in that they used the Coale and Bruland definition of τ_p in making this comparison. Kim *et al.* go on to show two new analyses of τ_{POC} and τ_p^* from Bermuda, and re-evaluate two Pacific sites where similar comparisons can be made. They conclude that the "difference in residence times of POC and particulate thorium is less than approximately 20%".

One can take issue with this conclusion for at least four reasons. First, in their own work (Kim, 1998), they have a more comprehensive data set on τ_{POC} and τ_p^* than they have chosen to show in this article. These results include variations in τ_{POC} and τ_p^* that are as large as a factor of two (mean τ_p^* / τ_{POC} from additional three months of Bermuda data not shown is 1.75; Table 6.4 in Kim, 1998). The single comparison with a short residence time (Kim *et al.*, Table 1, California Current) is taken from Coale and Bruland (1985), and τ_p^* is 14 days. This compares to a residence time of POC derived from traps of 19-28 days in the original reference (τ_{POC} in Table 5 in Coale and Bruland, 1985). Clearly, more evidence is needed to demonstrate that this new τ_p^* is accurate.

Secondly, the two different residence time estimates may be similar for the wrong reasons. As noted, the uncertainties associated with τ_p^* are substantial, and we argue here that POC residence times calculated from POC inventories/POC trap fluxes are similarly imprecise. There is now ample evidence to suggest that the operational procedures used to determine POC concentrations vary by a factor of two or more (Moran *et al.*, 1999). Furthermore, POC fluxes in shallow sediment traps often have uncertainties greater than a factor of three, as estimated from: a) ^{234}Th trap "calibration" (Buesseler, 1991); b) carbon balance attempts at Bermuda (Michaels *et al.*, 1994); and c) POC flux comparisons between two trap designs (Buesseler *et al.*, 2000).

Our third point involves a time-scale issue that Kim *et al.* do not take into account in making their comparison. The Bermuda trap results are taken from 3-4 day trap deployments, whereas τ_p^* represents a steady-state residence time that is appropriate for ^{234}Th (mean life with respect to decay = $1/\lambda$ = 35 days). Given these first three issues alone, we contend that the agreement between τ_{POC} and τ_p^* in the few examples found in Table 1 is fortuitous.

A fourth argument, and the most direct argument against equal residence times for particulate organic carbon and ^{234}Th comes from field evidence on the ratio of POC/^{234}Th^{part}. Using filtration, the POC/^{234}Th^{part} ratio in the upper 150m decreases by a factor of 2-5 using either 1μm or 53μm nominal pore sized filters in prior studies (summarized in Buesseler, 1998). On particles collected using sediment traps, POC/^{234}Th^{part} decreases by 40% between 150 and 300m (Buesseler *et al.*, 1992). Note that in-situ decay on sinking particles would serve to increase this ratio (assuming no exchange with ambient particles) and that the trap data are from deeper waters than the filtration experiments. If the residence times of the two particulate phases were identical, as argued by Kim *et al.*, there should be no relative change in POC/^{234}Th^{part} with depth. Overall, we can see no geochemical reason nor is there any field data to suggest that the residence time of POC is the same as the particle reactive tracer, ^{234}Th.

4. Conclusion

Kim *et al.* present a variation on prior ^{234}Th studies for calculating ^{234}Th residence times in different phases. The errors associated with using this formulation are quite large, and the limited data presented do not constrain whether this approach is accurate or not. Also, Kim *et al.* have not provided evidence that this residence time of thorium can be directly applied to POC. Existing data showing a decrease in POC/^{234}Th^{part} with depth suggest that particle turnover rates differ for these two elements. Therefore, we disagree with Kim *et al.* that future studies of carbon export would be more accurate using this ***residence time*** approach. We support alternative approaches using calculated ^{234}Th ***fluxes*** multiplied by the measured ratio of POC/^{234}Th^{part} which do not require the unrealistic assumption of identical POC and ^{234}Th residence times (as summarized in Buesseler, 1998).

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