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?” Kim et al. present their newly derived calculation of particulate $^{234}$Th residence times and provide some examples of how these rates vary in space and time. They compare these residence times to estimated particulate organic carbon (POC) residence times and find apparent agreement. Using only four samples as evidence, these authors conclude that their calculations of particulate $^{234}$Th residence times are accurate and provide an improved approach for estimating POC residence times and hence, fluxes.

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 do not suffer from these assumptions (as summarized in Buesseler, 1998).

2. Residence Times and Uncertainties

Coale and Bruland (1985; 1987) defined the equations which have been commonly used to calculate the residence times of total, dissolved and particulate thorium-234. Mathematically, these formulations are equivalent to those used by Kim et al., and have in common the production of $^{234}$Th from $^{238}$U, and losses due to in-situ decay and removal of thorium on sinking particles. For example, for total $^{234}$Th, the activity balance requires that in steady-state:

$$\frac{\partial A_{\text{th}}}{\partial t} = 0 = A_{\text{u}} \lambda - A_{\text{th}} \lambda - A_{\text{th}} k_1$$

where $A_{\text{u}}$ and $A_{\text{th}}$ are the activities of $^{238}$U and total $^{234}$Th respectively, $\lambda$ is the decay constant for $^{234}$Th ($=0.0288$ day$^{-1}$), and $k_1$ 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:
\[ \tau_i = \frac{1}{k_i} = \frac{A_{Th}^i}{(A_u - A_{Th}^i)\lambda} \]  

(2)

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

With respect to the model assumptions, Kim et al. focus their attention on prior formulations of \(\tau\), and suggest that multi-box models of \(^{234}\text{Th}\) particulate and colloidal residence times are in error due to a “missing” decay term. Coale and Bruland (1985; 1987) define the particulate residence time of \(^{234}\text{Th}\) with respect to particle removal only (\(\tau_p = 1/k_p\), where \(k_p\) is the scavenging rate constant for particulate \(^{234}\text{Th}\)). Coale and Bruland (1985) also pointed out that the residence times as defined were not additive (\(\tau_p \neq \tau_d + \tau_p^*\); where \(\tau_p\) and \(\tau_d\) are the particulate and dissolved \(^{234}\text{Th}\) residence times, respectively). Kim et al. correctly show that these residence times are only additive if you include a residual term, such that: \(\tau_p = \tau_d + \tau_p^* + \lambda \tau_p^* \tau_d\) (equation 7 in Kim et al.). They add this residual term to the particulate residence time, to define a new \(\tau_p^*\), such that \(\tau_p^* = \tau_p + \lambda \tau_p^* \tau_d\) (we use \(\tau_p^*\) to distinguish between Kim et al.’s formulation of the particulate \(^{234}\text{Th}\) residence time, \(\tau_p^* = 1/k_p + \lambda \tau_p^* \tau_d = \tau_p^* - \tau_d\), and Coale and Bruland’s definition, \(\tau_p = 1/k_p\)).

We disagree that \(\tau_p^*\) is a more “accurate” particulate \(^{234}\text{Th}\) 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. If one does attempt to add these residence times, then Kim et al.’s residual term is mathematically correct. However, including this residual term in \(\tau_p^*\) does not improve our understanding of the true residence time of thorium with respect to particle removal in the ocean.

In addition to these assumptions in the formulation of the residence time model, the uncertainty in \(\tau_p^*\) will be due to the propagation of \(^{234}\text{Th}\) measurement errors. Before we look at these errors, we should also note that Kim et al.’s model, like most others, assumes steady-state and ignores horizontal processes in the \(^{234}\text{Th}\) activity balance. Prior studies suggest that while these assumptions can be made in non-bloom open ocean conditions, they may not be valid in all of the sites reviewed by Kim et al. in Table 1 (Buesseler et al., 1992; 1998; Gustafsson et al., 1998).

The uncertainty of \(\tau_p^*\) can be estimated from error propagation theory (Rutgers van der Loeff and Moore, 1998). For any individual residence time, the error is determined by our ability to measure the difference between the parent \(^{238}\text{U}\) and daughter \(^{234}\text{Th}\) activities. In the open Atlantic and Pacific oceans, Chen et al. (1986) have shown that the \(^{238}\text{U}\) atom abundance is proportional to salinity within a standard deviation of 1%. Hence in prior studies, \(^{238}\text{U}\) has been estimated from salinity. Thorium-234 activities by contrast are directly measured, and the errors associated with this determination are considerably higher. At a minimum, radiochemists must use counting statistics to determine the
probability that a decay event of a given type will be detected during a given measurement interval. In addition, detector calibration, yield determinations and initial volume/weight estimates all add to the associated uncertainties. On any given $^{234}$Th activity measurement, these errors are commonly 5-10% using the procedures of Kim et al. In the thesis work of Kim (1998), dissolved and total $^{234}$Th activities at the sites presented here have reported errors of only 2 to 5%, with a mean error of 3%. Assuming this uncertainty is correct, one can calculate the individual errors of $\tau_d$ and $\tau_p$, and hence the propagated error on $\tau^*_p$.

Using this approach, we determine an uncertainty on $\tau^*_p$ 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 $\tau^*_p$ is subject to an even larger uncertainty than the individual residence times estimates for $\tau_t$ and $\tau_d$.

Coale and Bruland (1987) and others have discussed error propagation in their $^{234}$Th models, but Kim et al. did not. Kim et al. do state that with a thorium $\tau > 300$ days, there are “large errors” in the calculation, but they do not define large, and none of the examples shown in Table 1 have such long residence times. Arguably, only precision can be estimated from measurement error alone, but with such a large inherent uncertainty in the predicted residence times, it is difficult to answer the question posed by the title of this article. 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 $\tau^*_p$, 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 against sediment trap derived POC fluxes have uncertainties <100% (see below).

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

Eppley (1989) suggested that if the residence time of particulate Th and POC are the same, then one should be able to 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 due to preferential remineralization of POC. Kim et al. argue that these prior studies are flawed in that they used the Coale and Bruland definition of $\tau_p$ in making this comparison. Kim et al. go on to show two new analyses of $\tau_{POC}$ and $\tau^*_p$ 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 $\tau_{POC}$ and $\tau_p$ than they have chosen to show in this article. These results include variations in $\tau_{POC}$ and $\tau_p$ that are as large as a factor of two, rather than the more optimistic 20% (mean $\tau_p$ / $\tau_{POC}$ from additional three months of Bermuda data not shown is 1.75; Table 6.4 in Kim, 1998). The single data comparison with a short residence time (Kim et al., Table 1, California Current) is taken from Coale and Bruland (1985), and the calculated $\tau_p$ is 14 days. This compares to a residence time of POC derived from traps of 19-28 days in the original reference ($\tau_{POC}$ in Table 5 in Coale and Bruland, 1985). Clearly, more evidence is needed to demonstrate that this new $\tau_p$ is accurate.

Secondly, the two different residence time estimates may be similar for the wrong reasons. As noted above, the uncertainties associated with $\tau_p$ 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” studies (Buesseler, 1991; Buesseler et al., 1994; Murray et al., 1996); b) carbon balance attempts at this Bermuda site (Michaels et al., 1994); and c) POC flux comparisons between two trap designs at the same depth (Murray et al., 1996; Buesseler et al., 1999). These trap uncertainties are not restricted to low or high POC flux environments, but appear to be related to hydrodynamic interferences related to ambient flow conditions and the sinking speed of the particles, and/or swimmers, small animals that may be collected by a trap while still alive.

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 $\tau_p$ 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 $\tau_{POC}$ and $\tau_p$ in the few examples found in Table 1 cannot be used to argue that $\tau_p$ is an accurate POC flux tracer.

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 between 20m and 150m decreases by a factor of 2-3 using either 1µm or 53µm nominal pore sized filters in the Arabian Sea (Buesseler et al., 1998), by a factor of 3-5 using 53µm filters in the Equatorial Pacific (Bacon et al., 1996), and by a factor of 2-5 on either filter size in the Southern and Equatorial Atlantic (Charette et al., 1999). If the residence times of the two particulate phases were identical, as argued by Kim et al., then there should be no relative change in POC/$^{234}$Th$_{part}$ with depth. On particles collected using sediment traps, POC/$^{234}$Th$_{part}$ decreases by 40% between 150 and 300m during the North Atlantic Bloom Experiment (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. Overall, there are variations in the rate of POC/\(^{234}\)Th\(^{\text{part}}\) decrease, but this general finding of a decrease in POC/\(^{234}\)Th\(^{\text{part}}\) with depth on all particle types strongly suggests that POC is preferentially remineralized relative to particulate \(^{234}\)Th. Finally, papers by Clegg and Whitfield (1991; 1993), Murnane et al. (1996) and Dunne and Murray (1997) show that to model thorium adsorption-desorption and remineralization, the rates of particulate thorium and POC turnover must differ.

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 can be directly applied to POC. Existing data showing a decrease in POC/\(^{234}\)Th\(^{\text{part}}\) 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\(^{\text{part}}\) which do not require the unrealistic assumption of identical POC and \(^{234}\)Th residence times (as summarized in Buesseler, 1998).

Acknowledgements. We are grateful for feedback provided by M. Bacon, C. Benitez-Nelson, L. Rasmussen and two anonymous reviewers on this commentary.

References


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(Received: April 20, 1999; Revised: September 15, 1999; Accepted: October 08, 1999)