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

Ken O. Buesseler and Matthew A. Charette

Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, U.S.A.

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^{part} 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:

$$\frac{\partial A_{Th}^{t}}{\partial t} = 0 = A_{u}\lambda - A_{Th}^{t}\lambda - A_{Th}^{t}k_{t} \qquad (1)$$

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:

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

The accuracy of any ^{234}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}U and ^{234}Th activity estimates (in particular, the error on $A_U - A_{Th}^t$ 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; 1987) define the particulate residence time of ^{234}Th with respect to particle removal only ($\tau_p = 1/k_p$, 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 between Kim *et al*'s formulation of the particulate ^{234}Th residence time, $\tau_p^* = 1/k_p + \lambda\tau_p\tau_d = \tau_t - \tau_d$, and Coale and Bruland's definition, $\tau_p = 1/k_p$).

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. 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 τ_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 τ_p^* will be due to the propagation of ^{234}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}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 τ_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}U and daughter ^{234}Th activities. 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%. Hence in prior studies, ^{238}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

Geophysical Research Letters, vol. 27, no. 13, p1939-1940 (2000).

3

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 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.

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 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 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 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, rather than the more optimistic 20% (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 data comparison with a short residence time (Kim *et al.*, Table 1, California Current) is taken from Coale and Bruland (1985), and the calculated 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 above, 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" 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 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 cannot be used to argue that τ_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

Geophysical Research Letters, vol. 27, no. 13, p1939-1940 (2000).

5

(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^{part} decrease, but this general finding of a decrease in POC/^{234}Th^{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^{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).

References

Bacon, M.P., J.K. Cochran, D Hirschberg, T.R. Hammar and A.P. Fleer (1996). Export Flux of Carbon at the Equator During the EqPac Time-Series Cruises Estimated from ^{234}Th Measurements. *Deep-Sea Research II,* **43***,* 1133-1154.

Buesseler, K.O. (1991). Do Upper-Ocean Sediment Traps Provide an Accurate Record of Particle Flux? *Nature*, **353**, 420-423.

Buesseler, K.O., M.P. Bacon, J.K. Cochran and H.D. Livingston (1992). Carbon and Nitrogen Export During the JGOFS North Atlantic Bloom Experiment Estimated from ^{234}Th:^{238}U Disequilibria. *Deep-Sea Research I*, **39 (7/8)**, 1115-1137.

Buesseler, K.O. (1998). The de-coupling of production and particulate export in the surface ocean. *Global Biogoechemical Cycles*, **12 (2)**, 297-310.

Buesseler, K. O., L. Ball, J. Andrews, C. Benitez-Nelson, R. Belastock, F. Chai and Y. Chao (1998). Upper Ocean Export of Particulate Organic Carbon in the Arabian Sea derived from Thorium-234. *Deep-Sea Res. II, Arabian Sea Volume*, **45 (10-11)**, 2461-2487.

Buesseler, K.O., D.K. Steinberg, A.F. Michaels, R.J. Johnson, J.E. Andrews, J.R. Valdes and J.F. Price (1999). A comparison of the quantity and quality of material caught in a neutrally buoyant versus surface-tethered sediment trap. *Deep-Sea Research I*, in press.

Charette, M. A., and S.B. Moran (1999). Rates of particle scavenging and particulate organic carbon export estimated using ^{234}Th as a tracer in the subtropical and equatorial Atlantic Ocean. *Deep-Sea Research II*, **46(5)**:885-905.

Chen, J.H., R.L. Edwards and G.J. Wasserburg (1986). ^{238}U, ^{234}U

and ^{232}Th in Seawater. *Earth Planet Sci. Lett.*, **80**, 241-251.

Clegg, S.L. and M. Whitfield (1990). A generalized model for the scavenging of trace metals in the open ocean-II. Thorium scavenging. *Deep-Sea Research*, **38**: 91-120.

Clegg, S.L. and M. Whitfield (1993). Application of a generalized scavenging model to time series ^{234}Th and particle data obtained during the JGOFS North Atlantic Bloom Experiment. *Deep-Sea Research*, **40**: 1529-1545.

Coale, K.H. and K.W. Bruland (1985). ^{234}Th: ^{238}U Disequilibria within the California Current. *Limnol. Oceanogr.*, **30 (1)**, 22-33.

Coale, K.H. and K.W. Bruland (1987). Oceanic Stratified Euphotic Zone as Elucidated by ^{234}Th:^{238}U Disequilibria. *Limnol. Oceanogr.*, **32 (1)**, 189-200.

Dunne, J.P., J. Murray, J. Young, L. Balistreiri and J. Bishop (1997). ^{234}Th and particle cycling in the central equatorial Pacific. *Deep-Sea Res. II,* **44 (9-10)**, 2049-2083.

Gustafsson, Ö., K.O. Buesseler, W.R. Geyer, S.B. Moran and P.M. Gschwend (1998). On the Relative Significance of Horizontal and Vertical Transport of Chemicals in the Coastal Ocean: Application of a Two-Dimensional Th-234 Cycling Model. *Cont. Shelf Res.* **18**, 805-829.

Kim, G (1998). Atmospheric Inputs and Upper Ocean Biogeochemistry of Trace Elements and Radionuclide Tracers in the Atlantic. Univ. of Delaware, Ph.D. thesis. 214pp.

Kim, G., N. Hussain, T.M. Church (1999). How accurate are the ^{234}Th based particulate residence times in the ocean? *Geophys. Res. Letts.*, **26(5),** 619-622

Michaels, A.F., N.R. Bates, K.O. Buesseler, C.A. Carlson and A.H. Knap (1994). Carbon-Cycle Imbalances in the Sargasso Sea. *Nature*, **372**, 537-540.

Moran, S.B., M.A. Charette, S.M. Pike, and C.A. Wicklund (1999). Differences in seawater particulate organic carbon concentrations in samples collected using small-volume and large-volume methods: the importance of DOC adsorption to the filter blank. *Marine Chemistry*, in press.

Murnane, R. J., J. K. Cochran, K. O. Buesseler, and M. P. Bacon (1996). Least-squares Estimates of Thorium, Particle, and Nutrient Cycling Rate Constants from the JGOFS North Atlantic Bloom Experiment. *Deep-Sea Research I,* **43(2)**, 239-258.

Murray, J.W., J.N. Downs, S. Strom, C.-L. Wei and H.W. Jannasch (1989). Nutrient Assimilation, Export Production and ^{234}Th Scavenging in the Eastern Equatorial Pacific. *Deep-Sea Research*, **36 (10)**, 1471-1489.

Murray, J.W., J. Young, J. Newton, J. Dunne, T. Chapin and B. Paul (1996). Export Flux of Particulate Organic Carbon from the Central Equatorial Pacific Determined Using a Combined Drifting Trap-^{234}Th Approach. *Deep-Sea Research II*, **43,** 1095-1132.

Rutgers van der Loeff, M.M. and W.S. Moore (1999). "Determination of natural radioactive tracers". Chapter 13 in Methods of Seawater Analysis, edited by K. Grasshoff, M. Ehrardt and K. Kremling, Verlag Chemie, Weinheim. (in press).

K.O. Buesseler and M.A. Charette, Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, MS 25, Woods Hole, MA, 02543 (kbuesseler@whoi.edu; mcharette@whoi.edu).