COMMENT

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Uncertainty versus variability in upper ocean carbon flux estimates

The recent article written by Moran et al. (2003) (herein referred to as M2003) poses the question whether thorium-234 (^{234}Th) provides an accurate record of particulate organic carbon (POC) export from the upper ocean. Although there is little argument that ^{234}Th : ^{238}U disequilibrium can be attributed to particle flux, we agree that there are still many unknowns regarding the factors that control the ratio of POC to ^{234}Th among various particle size classes. However, we argue that the M2003 article misapplies POC : ^{234}Th ratios and confuses ''natural range and variability'' with ''uncertainty'' in the ^{234}Th technique to support its hypothesis. Rather than clarifying how the ^{234}Th technique should be applied, the M2003 article clouds the issue. We feel that its narrow focus and interpretation do not reflect the ^{234}Th community's current understanding and application of the ^{234}Th method for deriving export. Thus, it is misleading to the rest of the oceanographic community.

In seawater, highly particle reactive ^{234}Th is produced from its conservative parent ^{238}U. The basis for the ^{234}Th technique is straightforward: disequilibrium between measured and expected concentrations of ^{234}Th in seawater can be directly attributed to removal by scavenging onto sinking particles. ^{234}Th fluxes are converted into other elemental fluxes by simply multiplying the ^{234}Th flux by the ratio of a particular element (i.e., POC) to ^{234}Th on sinking particles at the base of the depth range of interest. The M2003 article focuses on only a subset of issues associated with the ^{234}Th technique: depth-integrated ^{234}Th fluxes and POC : Th ratios collected by in situ pumps.

POC fluxes, POC : ^{234}Th ratios, and ^{234}Th disequilibria

Fluxes of POC decrease with increasing depth due to remineralization (Suess 1980; Betzer et al. 1984; Pace et al. 1987). As such, care must be taken when comparing fluxes across different depth horizons. First and foremost, in the M2003 article, ^{234}Th-derived POC fluxes from 0 to 50 m are compared with fluxes determined from 0 to 250 m within each station to imply that there is a large uncertainty in the POC export flux. This is deceptive and confuses uncertainty with real decreases in POC export with depth, as indicated by decreasing POC concentrations.

The M2003 article is equally misleading by incorrectly applying deeper POC : ^{234}Th ratios with shallow ^{234}Th disequilibria in obtaining POC flux. The POC : ^{234}Th ratio changes with depth, mainly driven by decreasing POC concentrations (e.g., Buesseler 1998). This is not surprising, since thorium and C are two different elements with differing geochemistries (e.g., Murray et al. 1989; Guo et al. 2002; Quigley et al. 2002). Thus, integrating POC : ^{234}Th ratios over a large depth horizon, as is done in the M2003 article, is inappropriate and adds a false source of uncertainty to POC-derived ^{234}Th fluxes. For example, 0- to 50-m integrated particulate POC : ^{234}Th ratios look almost identical to 0- to 100-m integrated POC : ^{234}Th ratios simply because the POC : ^{234}Th ratio is dominated by both high POC and ^{234}Th in the upper 50 m (*see table 3 in M2003*). In the M2003 article, the POC : ^{234}Th ratios measured at 50 and 100 m are often less than half of the 0- to 50-m and 0- to 100-m average POC : ^{234}Th ratio (*see table 2 in M2003*). Thus, they do not represent what is actually sinking out of the upper ocean, and their use to determine ^{234}Th-derived POC fluxes at a given depth is inappropriate.

Mismatching depth horizons and flux intervals also do not incorporate any preferential removal of POC during remineralization and add an erroneous source of uncertainty to POC flux calculations. For example, using a POC : ^{234}Th ratio from 100 m to compute a POC flux at 250 m may result in an overestimation of the true value. Likewise, using a 250-m POC : ^{234}Th ratio to compute a POC flux at 50 m, as was done in the M2003 article (*see table 2 in M2003*), will be an underestimation. The key to the ^{234}Th : ^{238}U disequilibrium technique is to measure the POC : ^{234}Th ratio at the base of the depth interval of interest, with integrated ^{234}Th disequilibrium fluxes determined over that same depth interval.

Although we agree with M2003 that the method of integration of ^{234}Th disequilibria should also be clarified, again, no guidance is given as to the best method. In fact, as shown in M2003, there is no statistical difference between using a trapezoidal and a depth-averaged ^{234}Th disequilibria. Nonetheless, we argue that if given sufficient sample collection, the trapezoidal method described in detail by Buesseler et al. (1992) should always be used, as it most accurately reflects the range in ^{234}Th disequilibria measured within a depth profile. If sample integration, such as that performed with in situ pumps, is used, then one must ensure that depths and sample volumes are either equally distributed to the integration depth of interest or depth weighted accordingly (e.g., Buesseler et al. 1995, 1998). Otherwise, there is a risk of sample bias. Furthermore, if the depth horizon to which the in situ pumps integrate is significantly below the depth of any ^{234}Th disequilibria, there will be an associated increase in the calculated flux error due to a decreasing difference between two large numbers.

Upon closer examination of the presented M2003 data with the above caveats, a different pattern in the POC export uncertainty emerges. We have limited our discussion to the integrated ^{234}Th fluxes versus the depth-averaged ^{234}Th fluxes, as there is no significant difference between the two methods of integration at this study site. When the

POC : ^{234}Th ratio is applied correctly, the only source of uncertainty, as presented in table 2 of M2003, is whether one uses the POC : ^{234}Th ratio measured on particles 10–53 μm or >53 μm in size across a specified depth horizon. Using these ratios, POC fluxes at 100 m show little difference at Sta. 9 (5.9 ± 0.3 mmol C m^{-2} d^{-1}) and a factor of 4.6 and 2.3 at Sta. 18 (13.1 ± 11.9 mmol C m^{-2} d^{-1}) and Sta. 25 (11.1 ± 6.9 mmol C m^{-2} d^{-1}). As a result, the total variability in POC flux is almost 50% less than that reported in M2003.

Variability versus uncertainty

In table 1 and fig. 1 of M2003, POC : ^{234}Th ratios range over several orders of magnitude. It should be explicitly stated that much of this variability is likely due to a number of natural processes associated with location (open vs. coastal ocean), depth, season, primary and secondary production, plankton speciation, etc. (Murray et al. 1989; Buesseler 1998; Guo et al. 2002; Quigley et al. 2002). This natural variability should not be confused with real uncertainty in the collection and measurement of POC : ^{234}Th ratios. That POC : ^{234}Th ratios may vary within an individual study does not imply that the POC fluxes are uncertain by a similar magnitude as stated on page 1025 in M2003.

For example, in table 2 and figs. 3 and 4, the M2003 article determines POC export with depth at three different sites in the Labrador Sea. The range in POC export within each site is large and reflects not only differences in integration techniques, but also real variability in POC remineralization from 50 to 250 m and across the different sites. As presented in M2003, this real variability in POC export is difficult to distinguish from the uncertainty of the integration methods. For example, in table 2, ranges in POC export within each station are shown from 50 to 250 m, rather than across a single depth horizon. In fig. 3, each profile has had a mean line drawn that averages across all three disparate sites. In fig. 4, the real uncertainty as proposed in M2003 is again compared across all three sites rather than just within a single station. Thus, although these figures and tables may have been combined to save space, they imply an uncertainty that is much larger than actuality.

We would further argue that much of the current uncertainty in ^{234}Th-derived POC flux does not stem from issues associated with depth averaging and applying mismatched POC : ^{234}Th ratios to ^{234}Th flux horizons, as argued in M2003. That the most significant uncertainty in the POC : ^{234}Th ratio in M2003 is derived from the choice of particle size leads to issues only peripherally addressed in M2003, but these issues are in many ways the most critical and problematic for the accurate application of ^{234}Th: how should sinking particles, and their POC : ^{234}Th ratio, be identified and collected? As mentioned in M2003, the particulate ratios of POC : ^{234}Th at a specified depth horizon are currently collected using water bottles, large-volume pumps, and sediment traps (Murray et al. 1996; Buesseler 1998; Buesseler et al. 1998; Benitez-Nelson et al. 2001*a*). All have inherent biases and issues associated with them to the extent that it remains controversial which method is the most accurate (e.g., Buesseler et al. 1998). While sediment traps potentially suffer from hydrodynamic effects and swimmers, in situ pumps and bottles may have filtration artifacts (Moran et al. 1999; Gardner et al. 2003); also, they may collect particles that may be more representative of the suspended pool than of the sinking particle pool. It is the difference in the POC : ^{234}Th ratio measured using these various methods of particle collection that now drives the largest uncertainties associated with determining upper ocean POC : ^{234}Th ratios and hence ^{234}Th-derived POC fluxes (e.g., Quay 1997). POC : ^{234}Th ratio collection techniques are still controversial.

While we concur with the M2003 authors that all ^{234}Th-derived POC fluxes must include a statement regarding the assumptions and methodologies used and that a standardized method of ^{234}Th application is needed, we disagree with the manner in which the M2003 article supports its arguments. Indeed, many of the literature examples that the M2003 article uses to argue its case deviated from the trapezoidal ^{234}Th integration and POC : ^{234}Th depth horizon approach that we describe herein because of limited data sets. The large changes in POC fluxes cited within each study further reflect, at least in part, real seasonal variability. Understanding oceanic C uptake and the depth to which POC fluxes should be integrated is not just a ^{234}Th community issue, but also an issue for the oceanographic community as a whole. These two communities need to work together to determine the appropriate depth intervals over which POC export should be determined beyond the depth of the euphotic zone or artificial depth horizons determined by the placement of sediment traps.

There is much work to be done regarding ^{234}Th speciation and POC and particulate ^{234}Th dynamics in the ocean, and this area of research is still in its infancy. Nonetheless, we feel that the many advantages of the ^{234}Th technique (as outlined in M2003) greatly outweigh the uncertainties. To answer the question whether ^{234}Th-derived POC fluxes are accurate, we need to compare particulate ^{234}Th and POC collection methodologies as well as ^{234}Th-derived POC fluxes over seasonal and annual timescales with independent estimates of POC flux derived from new and net production, nutrient inventories, oxygen balances, and deep ocean POC fluxes. The results thus far look much more encouraging than that implied in M2003 (Quay 1997; Buesseler 1998; Buesseler et al. 2000; Benitez-Nelson et al. 2001*a*). With new small-volume (∼2–4 liters) techniques for ^{234}Th analysis in seawater (Benitez-Nelson et al. 2001*b*; Buesseler et al. 2001) and the development of neutrally buoyant sediment traps (Buesseler et al. 2000), we are at a very exciting crossroads in the application of ^{234}Th studies to the ocean C cycle.

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