

Future Applications of ^{234}Th in Aquatic Ecosystems

Preface

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One of the outstanding questions in oceanography is how particles that form in the surface ocean are subsequently transported to the seafloor. Issues of size and density fractionation, aggregation and disaggregation, remineralization and scavenging are embedded within this central question. Sinking particles are the ultimate removal pathway of many biologically and particle active elements from marine systems, including atmospheric CO_2 (which is converted to particulate matter during biological production), macronutrients, trace metals, organic compounds and contaminants. Yet the magnitude and temporal and spatial variability of sinking particle fluxes remain elusive. The particle reactive radionuclide, thorium-234 ($t_{1/2} = 24.1$ days), has been increasingly used to examine sinking particle fluxes from the surface ocean on timescales of days to weeks. In aquatic systems, ^{234}Th is produced via the decay of its dissolved conservative parent, ^{238}U . In principle, differences between dissolved ^{238}U and total ^{234}Th (the $^{234}\text{Th}/^{238}\text{U}$ activity ratio) should reflect the net rate of removal of ^{234}Th on sinking particles.

The first measurement of ^{234}Th in marine systems occurred almost 40 years ago. As with many new ideas, these first analyses were unplanned. On May 29, 1967, one of us (WM) was talking with Rama (who has no first name) on the deck of the R/V *Oceanographer* (now retired). Rama had joined the ship in Massawa, Eritrea (then

Ethiopia), and was collecting atmospheric radon samples in the Arabian Sea to determine the trajectory of air masses responsible for the onset of the Indian SW monsoon. When I told him I was measuring ^{228}Ra and ^{228}Th in sea water, he asked if I had a thorium-230 spike. When I replied that yes, I did, he suggested we use it to measure the depth distribution of ^{234}Th in sea water, a project he had wanted to do for some time. I knew ^{228}Th was depleted relative to ^{228}Ra , but had not considered that ^{234}Th might be depleted as well. We arranged to collect a depth profile in the central Arabian Sea a few days before we reached Bombay (now Mumbai). There must have been a recent bloom, because I remember the water was literally sparkling with plankton. Using a single Niskin bottle, we collected the samples, spiked them with ^{230}Th to measure our recovery and scavenged the Th using simple iron hydroxide precipitations. The precipitates were taken to the Tata Institute of Fundamental Research in Bombay where two young students, Suman Bhat and S. Krishnaswami, snatched the samples and began chemical purification for beta counting. The first samples were in the counters within a few hours. The rest is history (Bhat et al., 1969).

While ^{234}Th continued to be used as a tracer of particle dynamics (e.g. sediment resuspension and bioturbation, particle coagulation, etc.), it was not until almost twenty years later that the link between $^{234}\text{Th}:$ ^{238}U disequilibria and biological activity in the upper ocean was made (Coale and Bruland, 1985; 1987). This finding initiated the use of ^{234}Th as a direct particle flux proxy, whereby other elemental fluxes could be determined by multiplying the measured ^{234}Th flux (derived from $^{234}\text{Th}:$ ^{238}U disequilibria) by the ratio of other elements to ^{234}Th on sinking particles. For example, carbon (C) fluxes can be determined by multiplying the ^{234}Th flux by the $\text{C}/^{234}\text{Th}$ measured on sinking particles

at the specific flux horizon of interest. This empirical method was first applied and published by Buesseler et al. (1992) to determine organic C export associated with the onset of the spring bloom in the North Atlantic. Since then, the Th-approach has been expanded and applied to determine not only C, but other elemental fluxes as well, ranging from particulate inorganic C (Bacon et al., 1996) to polycyclic aromatic hydrocarbons and polychlorinated biphenyls (Gustafsson et al., 1997a, b) to trace metals (Gustafsson et al., 2000a; Weinstein and Moran, 2005).

Like any method, the use of ^{234}Th as a flux tracer has strengths and weaknesses. As a radioactive tracer, ^{234}Th provides a more integrative view of particle export and is more forgiving in terms of the spatial patchiness and time dependence (e.g. blooms) often associated with biological activity. Recent advances in methodology have enabled ^{234}Th sample collection over a range of depths throughout the water column. Thus, fine scale examination of particle fluxes and remineralization with depth are now possible. However, a number of questions still remain regarding methodology, Th speciation, reactivity, and modeling strategies. These questions affect our ability to interpret ^{234}Th disequilibrium and its application to sinking particle export of other elements. Given the increasing use and reliance on ^{234}Th as a tracer of particle export in aquatic systems, it is essential to explore these questions in more detail.

In the following papers, internationally renowned experts in the field of radiochemistry, and ^{234}Th in particular, discuss and define the current state of knowledge with regard to the use and application of ^{234}Th in aquatic systems. The first five papers derive from discussions that occurred during the Future Applications of ^{234}Th in Aquatic Ecosystems (FATE) workshop that was held in August 2004 (Benitez-Nelson and Th-

Group, 2004). These papers provide an overview and compilation of current knowledge on key issues necessary to understand and use ^{234}Th as a flux tracer of other elements. Waples et al. introduce the historic applications of ^{234}Th and discuss how it may be applied in the future to issues beyond mass flux. Rutgers van der Loeff et al. focus on the wide range of techniques currently used to collect and measure ^{234}Th and detail the inherent strengths and weaknesses of each. Buesseler et al. examine trends in particulate $\text{C}/^{234}\text{Th}$ ratios with depth, region, and sample collection method; while Savoye et al. review Th sorption and export models and discuss the assumptions underlying each. Santschi et al. tackle the difficult question of inorganic and organic Th speciation.

The remaining papers detail specific aspects of ^{234}Th geochemistry, such as improvements on methodology (Cai et al., Rodriguez y Baena et al., Gustafsson et al.), particle dynamics and the power of combining ^{234}Th with other Th isotopes (Sabine, Coppola et al.), how blooms and flocculation affect elemental/Th ratios (Passow et al., Waite and Hill) and Th speciation and possible bioaccumulation (Quiroz et al., Rodriguez y Baena et al.).

It is interesting to note that many of the issues discussed by Rama, Krishnaswami (Swami) and Moore back in the late 1960's are still of interest today. Below are two excerpts from letters exchanged during the initial analysis and writing of the first ^{234}Th paper.

“We have added Th-234 spike to millipore filtered seawater and refiltered the water through a 0.45 micron millipore. The retention of Th-234 was less than 5 % of that added on the filter... We also tried to see if live plankton cells pick up Thorium from seawater...initial numbers show the retention (if any) may be very less.”

Letter from Swami to Moore, August 6, 1968.

“One of the things we must remember in reference to plankton vs. particle uptake of Th-234 is that there are many types of plankton with a wide spectrum of sizes...”

Letter from Moore to Swami, Sept 6, 1968.

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