MedFlux: Particulate Organic Carbon-^{234}Th Relationships in Particles Separated by Settling Velocity in the Northwest Mediterranean

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.: Abstract :.

Calculation of ^{234}Th-derived POC flux estimates require knowledge of a POC/^{234}Th ratio representative of material exported from the photic zone. Causes of the variability in the POC/^{234}Th ratio and their implications for ^{234}Th as a POC flux proxy have received increased attention (Moran et al., 2003, Buesseler et al., 2006 *in press*). As part of the MedFlux program, we measured the POC/^{234}Th ratio of sinking material at the DYFAMED site in the northwest Mediterranean. During early March to early May in 2003 (61 d deployment) and early March to late April in 2005 (55 d deployment), material was collected from depths of 200-1800 m and separated by settling velocity using indented rotating sphere (IRS) sediment traps operated in a settling velocity mode. The POC/^{234}Th ratio of exported material was determined for 10 settling velocity classes ranging from <1 to >490 m/d. Compositional data for settling velocity classes may lead to a mechanistic explanation for POC/^{234}Th variability. In future POC flux studies, this understanding will help assess the applicability of POC/^{234}Th ratios measured for samples acquired by traditional methods (in situ pump and time series sediment traps) for use in POC flux estimates. The comparatively higher POC/^{234}Th ratios in 2003 are consistent with algal material, while the lower values in 2005 are consistent with expectations for fecal pellet material, enriched in ^{234}Th relative to POC. It is likely that the decrease in POC/^{234}Th through the twilight zone is driven by both POC degradation with depth and depletion of ^{234}Th in the upper water column relative to deep water. Overall, it is clear that particle size alone does not predict the relationships between POC/^{234}Th and settling velocity, but rather that additional factors such as particle composition and remineralization are responsible for the observed patterns.

.: Methods :.

IRS traps were originally designed as swimmer-exclusion traps. Particles settled onto a sphere that routinely swept them into a lower settling column to be collected in discrete cups. In the settling velocity mode, the sphere rotates once every 24 hours, dumping captured material into the lower settling column of the IRS trap (Fig. 1c). The carousel containing 11 cups (Fig. 1d) rotates such that each successive cup is open to receive falling particles for progressively longer periods of time. The material in each cup is interpreted as belonging to a class of particles with a minimum settling velocity calculated as the distance between the ball and cup mouth divided by the amount of time evolved from the ball rotation to the cup's rotation out of position.

Mathematical description of the pattern observed for the mass flux of all IRS SV trap deployments (mass flux initially high for lowest settling velocity class and peaks at ~500 m/d), show the IRS SV trap distinguishes between faster and slower settling velocity particles. (For further explanation see *Xue et al.* presentation, Session OS24H-02). The question of particle alteration (such as collapse on the ball) within the IRS SV trap is an area of active research within the MedFlux group.

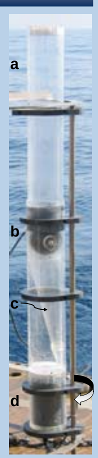


Figure 1. IRS SV Sediment Trap depicting the (a) particle interceptor, (b) indented rotating sphere, (c) funnel that feeds into sample collection cups, and (d) carousel housing the sample collection cups.

.: Variation of POC/^{234}Th with Settling Velocity :.

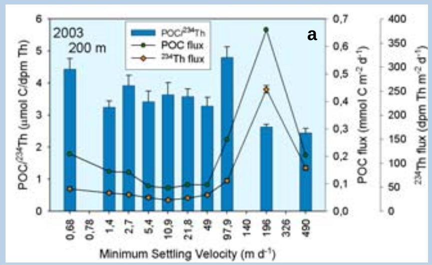


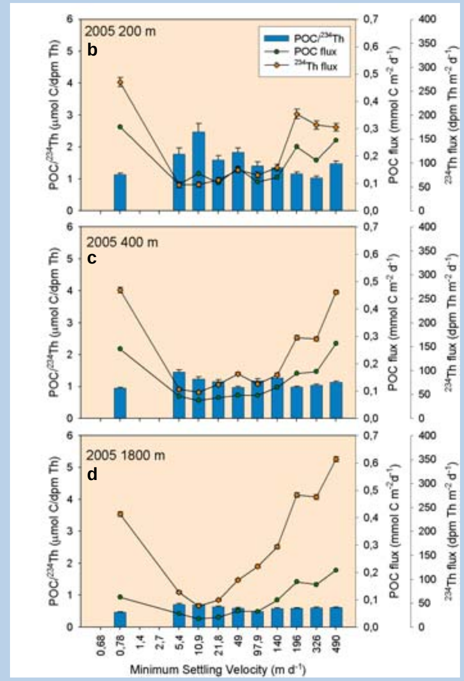
Figure 2. POC/^{234}Th ratios (µmol C/dpm Th) and fluxes of POC (mmol C m^{-2} d^{-1}) and ^{234}Th (dpm m^{-2} d^{-1}) for 10 settling velocity classes plotted for the following sampling years and depths: (a) mass-weighted average of 2 replicate SV traps at 200 m in 2003, (b) SV trap at 200 m in 2005, (c) and (d) mass-weighted average of 2 replicate SV traps at 400 m and 1800 m, respectively, in 2005. Analytical errors on POC/Th ratios and Th flux are plotted for (b) and errors for (a), (c), and (d) are mass-weighted averages of 2 trap replicate analytical errors.

2003 Results

POC/^{234}Th ratio of the settling velocity classes at 200 m ranged from 2.4 ± 0.3 to 4.4 ± 0.3 µmol C/dpm Th. There is little variation with settling velocity. However, disregarding the high POC/^{234}Th of 4.8 ± 0.3 µmol C/dpm Th for the 97.9 – 195 m d^{-1} fraction (driven by a high value of 7.2 ± 0.6 µmol C/dpm Th in one trap replicate), a slight decrease in the ratios with increasing settling is discernable. This is the reverse of the trend expected if particle size (or surface area: volume ratio) were the dominant control on particulate ^{234}Th.

2005 Results

POC/^{234}Th ratios for the settling velocity classes (<1 to >490 m/d) ranged from 1.0 ± 0.1 to 2.5 ± 0.3 µmol C/dpm Th at 200 m, 0.9 ± 0.03 to 1.4 ± 0.1 µmol C/dpm Th at 400 m, and 0.5 ± 0.02 to 0.7 ± 0.04 µmol C/dpm Th at 1800 m. In contrast with 2003, in all 2005 IRS SV traps the POC/^{234}Th is initially low peaking between ~5 and 11 m/d with little variation with settling velocity.



At 200 m 2005 POC/^{234}Th ratios are on average ~60% less than those in 2003. The difference in the POC/^{234}Th for 2003 and 2005 may be due to differences in spring bloom intensity and phytoplankton and zooplankton community structure.

.: Changes in POC/^{234}Th through the Twilight Zone :.

In 2005, the overall POC/^{234}Th ratio dropped from 200 m to 1800 m (see Figs. 2b-d). The decrease in POC flux with depth, possibly due to degradation of sinking material, does not alone explain this drop; an additional factor is the increase in ^{234}Th flux with depth. Chemical makeup within each sample cup represents an average signal for that SV class over the whole time period the trap was deployed. This is because material is allowed to fall into each cup every 24 hours. The shallower traps located near the site of particle creation may feel the "memory" effect of ^{234}Th, i.e., ^{234}Th depleted waters resulting from loss of ^{234}Th carried with sinking particles with a concomitant time lag before ^{234}Th reaches equilibrium with its parent ^{238}U. Conversely, the deeper trap may see more ^{234}Th over the duration of trap deployment due to additional scavenging of ^{234}Th on settling particles. Note the smaller offset in the POC/^{234}Th ratio at the faster settling velocities for the upper two traps.

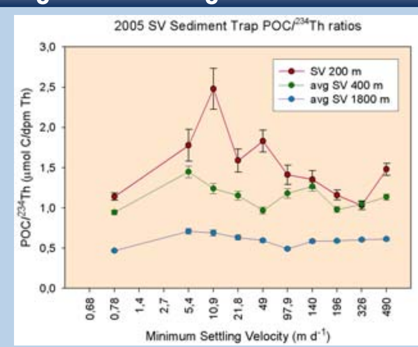


Figure 3. 2005 POC/^{234}Th versus settling velocity plotted for each deployment depth including 200 m IRS SV trap, mass-weighted average of two replicate deployments at 400 m and 1800 m. Errors for 400 and 1800 m depths are based on mass-weighted averages of analytical error; errors for 200 m are analytical.

.: Composition and POC/^{234}Th :.

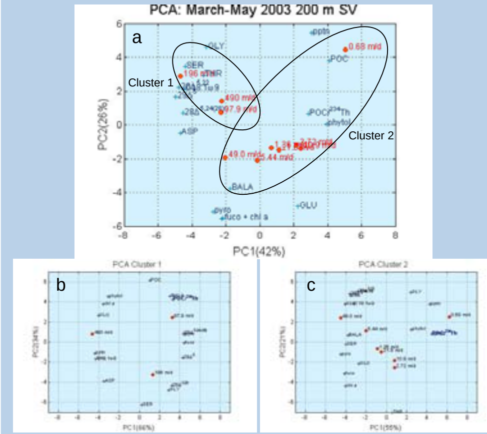


Figure 4. Correlation analyses of 2003 IRS SV trap organic composition data (amino acids, neutral lipids, fatty acids, pigments, %POC) and POC/^{234}Th including (a) PCA of mass-weighted averaged data for all SV classes at 200 m in 2003, (b) and (c) PCA results for the two clusters of SV classes shown in 4a. These are 196 to 490 m d^{-1} and 0.68 to 97.9 m d^{-1}, respectively.

Compositional analyses for the 2003 samples have been completed and provide insights into the causes of variation in POC/^{234}Th. Principle component analysis (PCA) of the 200 m IRS SV trap results shows settling velocity classes split into 2 clusters; cluster 1 typified by phytoplankton-derived organic material and fecal pellets and cluster 2 consisting of bacterially reworked marine aggregates. PCA results imply that POC/^{234}Th ratios have two modes for the 2003 settling velocity samples; this may help explain the slight decrease in POC/^{234}Th with increasing settling velocity.

PCA Results

PC1 of cluster 1 explains 66% of the variability indicating differences in material source of the three settling velocity classes along its axis, e.g. diatom-rich fecal pellets versus fresh and bacterially reworked phytoplankton-enriched particles. POC/^{234}Th is most closely associated with fecal pellet-derived material (see Fig. 4b).

In cluster 2, POC/^{234}Th overlaps %POC indicating they are highly correlated within this grouping of slower settling particles. The composition of the material collected in the last cup (settling velocity class 0.68-1.36 m d^{-1}) is an end-member of first principal component (explains 55% of variation in samples) and is associated with indicators of bacterially reworked particles (see Fig. 4c).

Observations and thoughts on 2005 sample composition and POC/^{234}Th…

- Little diatom presence (microscopic observations).
- More crustacean zooplankton and little gelatinous zooplankton in comparison to 2003 (visual observation).

The preferential uptake of carbon by zooplankton may have led to ^{234}Th enrichment in fecal pellets and lower POC/^{234}Th ratios in 2005. See *A. Rodriguez y Baena et al.* talk , Session OS32H-05 for more information on POC/^{234}Th in 2005 MedFlux fecal pellet samples.

.: Acknowledgements & References :.

Funding for the MedFlux project came from the NSF Chemical Oceanography Program. We thank S.Wakeham and C.Lee for use of organic compound class data.

1. Buesseler et al. 2006. Marine Chemistry, *in press*.
2. Moran et al., 2003. Limnol. and Oceanogr., 48: 1018-1029.

For more information on MedFlux please visit http://www.msrc.sunysb.edu/MedFlux