

Control of acid polysaccharide production and ^{234}Th and POC export fluxes by marine organisms

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[1] Ratios of particulate organic carbon (POC) to particulate ^{234}Th activities ($\text{POC}/^{234}\text{Th}$) in the ocean are used to determine the POC export flux, and thus, the power of the biological pump. In order to understand the main reasons why this ratio frequently varies as a function of depth, size, and kind (suspended vs. sinking particles), we measured vertical profiles in a cold core ring and warm core ring in the Gulf of Mexico in May 2001. Here we show that particulate $^{234}\text{Th}/\text{POC}$ ratios in the Gulf of Mexico are positively correlated to the content of different Th(IV)-binding polysaccharide fractions (uronic acids, total acid polysaccharides, total polysaccharides) in both suspended and sinking particles as well as to prymnesiophyte abundance, but negatively correlated to bacterial production. Variations in acid polysaccharide compounds, produced by both algae and bacteria, but degraded only by bacteria, can account for observed variations in $\text{POC}/^{234}\text{Th}$ ratios seen in the ocean. **INDEX TERMS:** 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4860 Oceanography: Biological and Chemical: Radioactivity and radioisotopes; 4807 Oceanography: Biological and Chemical: Chemical speciation and complexation. **Citation:** Santschi, P. H., C.-C. Hung, G. Schultz, N. Alvarado-Quiroz, L. Guo, J. Pinckney, and I. Walsh, Control of acid polysaccharide production and ^{234}Th and POC export fluxes by marine organisms, *Geophys. Res. Lett.*, 30(2), 1044, doi:10.1029/2002GL016046, 2003.

1. Introduction

[2] Improved predictions of the global carbon cycle require a better understanding of particulate organic carbon (POC) export flux, aggregation mechanisms and ocean carbon sequestration. The biotic uptake of ^{234}Th , produced by ^{238}U decay in the ocean, has been widely used to estimate the POC flux out of the euphotic zone based on $\text{POC}/^{234}\text{Th}$ ratio and ^{234}Th flux. However, $\text{POC}/^{234}\text{Th}$ ratios generally decrease with increasing depth and particle size [Buesseler *et al.*, 1995; Murray *et al.*, 1996; Bacon *et al.*,

1996], but can also show the opposite trend [Buesseler *et al.*, 1998; Charette *et al.*, 1999], often giving rise to disagreement between POC fluxes estimated from sinking and suspended ($>53\ \mu\text{m}$) particles.

[3] The decrease of $\text{POC}/^{234}\text{Th}$ ratios with increasing particle size suggests that aggregation by coagulation is responsible for ^{234}Th uptake [Burd *et al.*, 2000; Quigley *et al.*, 2001, 2002]. However, while coagulation would suggest organic carbon transfer up the particle size spectrum, the gain in POC from coagulation of surface-active colloidal organic matter appears to be small [i.e., 10 % or less; Quigley *et al.*, 2001]. Even though the major carbon flow appears to be from large to small particles and molecules to dissolved CO_2 through the degradation of labile marine organic matter [Amon and Benner, 1994; Santschi *et al.*, 1995], there are, however, other accounts that put this emerging carbon flow theory into question by proposing that significant amounts of organic matter are transferred up the size spectrum through bacteria grazing by protists and liposome and “picopellet” excretion [e.g., Nagata and Kirchman, 1999].

[4] Recent laboratory [Quigley *et al.*, 2002] and field [Guo *et al.*, 2002] evidence strongly suggests that surface-active acid polysaccharides (APS) are the compounds responsible for ^{234}Th binding and removal by coagulation in seawater.

[5] APS-rich fibrils have been identified as important biopolymers in different aquatic systems [Allredge *et al.*, 1993; Leppard, 1997; Santschi *et al.*, 1998]. Exopolymeric compounds are part of the marine DOC pool and have a modern radiocarbon age [Santschi *et al.*, 1998], compared to the bulk of DOC.

[6] We report here new results from vertical profiles taken during a May 2001 expedition to the Gulf of Mexico across a Cold Core Ring (CCR) and a Warm Core Ring (WCR), in order to assess the relationship between $\text{POC}/^{234}\text{Th}$ ratios and particle composition, such as polysaccharide and APS contents, and biological parameters, such as species composition and bacterial production, as well as the relative importance of APS compounds. Detailed polysaccharide data, as well as detailed size-fractionated ^{234}Th data from this data set, will be published elsewhere

[Hung et al., Distributions of carbohydrate species in the Gulf of Mexico, submitted to Mar. Chem., 2002a; Hung et al., Production and fluxes of carbohydrate species in the Gulf of Mexico, submitted to Global Biogeochemical Cycles, 2002b; Hung et al., in preparation, 2002c]. Since ^{234}Th and its interactions with biomolecules are the main focus of the paper, and since ratios involving POC are mainly used in oceanographic applications of ^{234}Th , the discussions in the paper center on $^{234}\text{Th}/\text{POC}$ ratios, rather than their inverse.

2. Methods

[7] Seawater was size fractionated into the $<0.5\ \mu\text{m}$, $0.5\text{--}1\ \mu\text{m}$, $1\text{--}10\ \mu\text{m}$, $10\text{--}53\ \mu\text{m}$, and $>53\ \mu\text{m}$ fractions, with the $>53\ \mu\text{m}$ fraction most often used to calculate $\text{POC}/^{234}\text{Th}$ ratios. Sinking particles were collected by sediment traps (cylindrical plastic core tubes of 6.8 cm diameter and 1:10 aspect ratio), exposed for 24 hours, at depths of 65, 90 and 120 m, at sta-4 at 27.65 latitude and 95.07 longitude, and sta-6 at 26.35 latitude and 95.00 longitude in May 2001. Particles were processed for ^{234}Th and carbohydrate analysis according to Guo et al. [2002].

[8] Concentrations of dissolved and size-fractionated particulate ^{234}Th (dpm/L) were determined according to Guo et al. [2002], total carbohydrate ($\mu\text{g-C/L}$) and uronic acids (URA, $\mu\text{g-C/L}$, an APS with carboxylic acid groups) according to Myklestad et al. [1997] and Hung and Santschi [2000], POC ($\mu\text{g-C/L}$) and APS ($\mu\text{g-C}$ alginic acid equivalents), according to Guo et al. [2002] and Hung et al. [2002a].

[9] Briefly, the concentrations of APS in the particulate phase were measured by an alcian blue stain method [Passow and Alldredge, 1995], using extensive re-calibrations and other improvements, including corrections for the amount of carbohydrates (CHO) of standard compounds that was retained by the filter (rather than artifact-prone filter net weight increase). The concentration of APS was expressed as $\mu\text{M-C}$ alginic acid equivalents, as alginic acids are major classes of APS compounds.

[10] Both POC and particulate polysaccharides were corrected for the amounts lost into the filtrate, by adding the extra DOC in the water after filtration to the POC fraction. The abundance of algal groups, reported as $\mu\text{g-Chl.a}$ equivalents/L, was determined using CHEMTAX (CHEMical TAXonomy), a matrix factorization routine for calculating algal class abundances based on the concentrations of diagnostic chlorophyll and carotenoid photopigments measured by HPLC [Mackey et al., 1996]. Bacterial production was determined using standard methods [Fuhrman and Azam, 1982; Kirchman et al., 1985].

3. Results and Discussion

[11] Results from vertical profiles taken during a May 2001 expedition to the Gulf of Mexico revealed that only a small fraction of the CHO consists of surface-active APS compounds: URA make up $6.7 \pm 0.45\%$ of CHO ($r = 0.9$, $p < 0.001$, $n = 16$), and total APS make up $10.9 \pm 1.5\%$ of CHO ($r = 0.42$, $p < 0.1$, $n = 16$). This finding, even though much lower than previously reported [i.e., APS of 50–100% of POC, or higher; Passow and Alldredge, 1995; Engel and Passow, 2001], is likely more reliable due to our improved

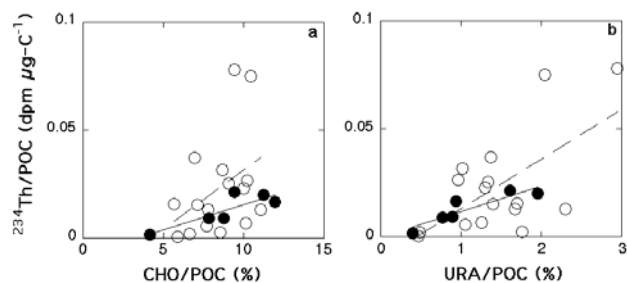


Figure 1. Correlation between $^{234}\text{Th}/\text{POC}$ and a) CHO/POC ($p < 0.02$), and b) URA/POC ($p < 0.01$) for sinking matter (filled circles) collected at 65, 90 and 120 m, and suspended ($753\ \mu\text{m}$) matter (open circles) samples from all stations and water depths in May 2001.

procedures. Low abundance but high surface activity of these metal binding biopolymers reconcile the decade-old enigma of contradictory findings [Alldredge et al., 1993; Amon and Benner, 1994; Santschi et al., 1995] by allowing for a major fraction of ^{234}Th to bind to the minority APS compounds and be transferred by coagulation up the particle size spectrum into large particles, without having a large effect on the main carbon flow, which is from the breakdown of large to small molecules. Interestingly, this coagulation process is further modified by the enzymatic release of smaller fragments of fibrillar APS [Santschi et al., 1998] into the “dissolved” phase, where they are still able to complex with freshly produced ^{234}Th and coagulate back into the particulate size fraction [Quigley et al., 2001]. The relatively low and constant percentage of particulate polysaccharides as APS compounds also explains the tight correlation that was reported by Quigley et al. [2002] between the log of the conditional binding constant of ^{234}Th and the total polysaccharide content of the macromolecular organic matter, making the total polysaccharide content of suspended matter a good predictor of both APS and ^{234}Th content.

[12] While a close relationship between polysaccharide [Quigley et al., 2002] or APS [Guo et al., 2002] content of suspended matter and $^{234}\text{Th}/\text{POC}$ ratios had previously been demonstrated, these results are the first ones to assess relationships between the two main phases that are being used for ^{234}Th -based new production assessments, i.e., suspended matter $> 53\ \mu\text{m}$ and sinking matter, in their extent of natural ^{234}Th binding, relative to their URA and APS contents. All correlations between POC normalized polysaccharide fractions (CHO, URA and APS) and $^{234}\text{Th}/\text{POC}$ in the Gulf of Mexico were significant at the 90–99 percent confidence level, but correlation coefficients were highest ($p \leq 0.02$) for sinking particles (Figure 1), suggesting that they provide a more “sorted”, and less variable, assembly of particles for calculating POC and APS fluxes. The fact that average URA/POC and APS/POC ratios in sinking particles were similar to those in large ($>53\ \mu\text{m}$) suspended particles, but that $^{234}\text{Th}/\text{POC}$ ratios were, on the average, higher in $>53\ \mu\text{m}$ particles, agrees with the notion that ^{234}Th is transported by coagulation up the size spectrum, while the bound ^{234}Th content in sinking particles can get diminished by enzymatic degradation of Th(IV)-binding APS compounds. It is important to note that the range we observed for $^{234}\text{Th}/\text{POC}$ ratios in the $>53\ \mu\text{m}$ particles is

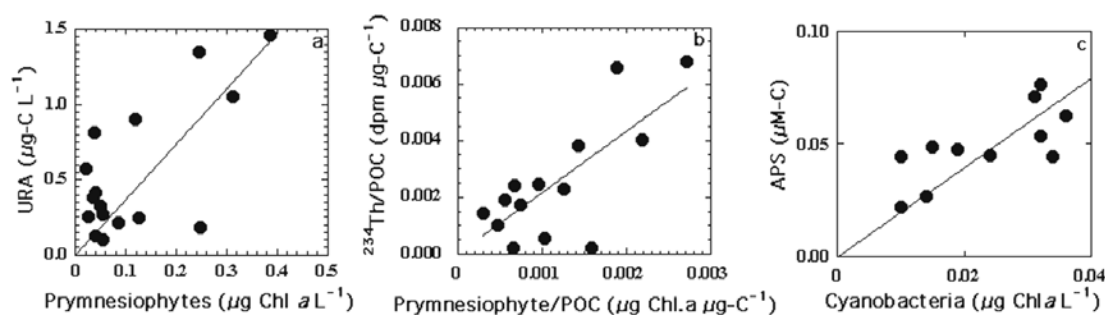


Figure 2. Correlation between prymnesiophytes abundance ($\mu\text{g Chl.a equivalents/L}$) and (a) URA ($\mu\text{g-C/L}$) ($p < 0.005$) and (b) $^{234}\text{Th/POC}$ ($p < 0.001$), measured during May 2001, and c) between cyanobacteria abundance and APS concentration (July 2000) ($p < 0.05$).

similar to that in the Pacific Ocean [Benitez-Nelson *et al.*, 2001] and Arabian Sea [Buesseler *et al.*, 1998]. However, differences between $^{234}\text{Th/POC}$ ratios in suspended particles vs. sinking particles from depths near the bottom of the euphotic zone (120 m) in profiles taken at the same station within 24 h in the 2001 Gulf of Mexico cruise can be substantial (i.e., up to a factor of 4 different). Even larger differences were observed at shallower depths. This demonstrates that discrepancies between $^{234}\text{Th/POC}$ ratios in sinking or large suspended matter can still exist in different oceanic environments, strongly suggesting that a better understanding of Th(IV) binding to polysaccharide-rich biopolymers is of crucial importance.

[13] A number of photosynthetic organisms are known to produce APS compounds. In May 2001, the abundance of prymnesiophytes, known producers of mucilaginous APS compounds of which coccolithophorids are a major group, and the main phytoplankton species at that time, along with dinoflagellates and prasinophytes (not shown) correlated significantly with APS (not shown) and URA abundance (Figure 2a) and $^{234}\text{Th/POC}$ ratios (Figure 2b). Cyanobacteria abundance was extremely low at that time. Prasinophytes often co-occur with prymnesiophytes. Large blooms of these phytoplankton species are often problematic in coastal regions because of the mucilage surrounding the algal cells. In July 2000, it was the cyanobacteria, known APS producers [Shah *et al.*, 2000] that showed significant correlations to APS abundance (Figure 2c). Even though cyanobacteria were only the third most abundant phytoplankton in the Gulf of Mexico during the time of sampling in 2000 [Hung *et al.*, 2002a], they can still be, at times, the major APS producers

[De Philippis and Vincenzini, 1998]. As unicellular organisms, they can form colonies held together by APS mucilage.

[14] These correlations do not imply that these are the only phytoplankton species that are secreting APS compounds, as diatoms [Ducklow *et al.*, 2001] and others are known to produce APS compounds as well. However, these data make it very likely that different microorganisms can be responsible for the presence of Th(IV)-binding APS-rich mucilage at different times, thus facilitating the removal of ^{234}Th from the water column, albeit at different efficiencies.

[15] Phytoplankton, such as prymnesiophytes in May 2001 (Figures 2a and 2b), and cyanobacteria in July 2000 (Figure 2c) showed significant correlations between their biomass and total APS (not shown) and URA concentrations (Figure 2a) or $^{234}\text{Th/POC}$ ratios (Figure 2b). However, attached bacteria also produce abundant APS compounds [Leppard, 1997]. Thus, significant relationships between APS concentrations and heterotrophic bacterial production (BP) (Figure 3a), and $^{234}\text{Th/POC}$ ratios and BP (Figure 3b) were observed, which strongly suggest microbial involvement through their APS production and enzymatic activities. Since the positive correlation between BP and APS concentration had a non-zero APS intercept (Figure 3a), this suggests that bacteria might be co-responsible for APS production. There was, however, a negative correlation between BP and $^{234}\text{Th/POC}$ ratios (Figure 3b), demonstrating that bacteria are also involved in the enzymatic hydrolysis and release of Th(IV)-binding APS biopolymers. It

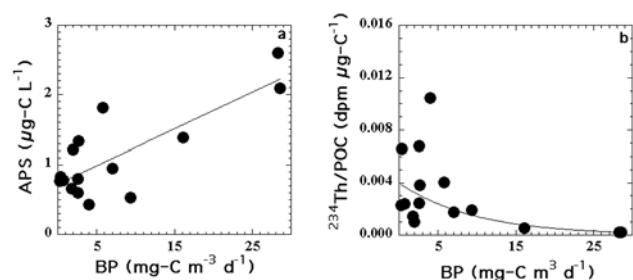


Figure 3. Correlation between bacterial production (BP) and (a) total APS concentration ($\mu\text{g-C/L}$) ($p < 0.001$), and (b) $^{234}\text{Th/POC}$ ratios (May 2001, Gulf of Mexico) ($p < 0.01$).

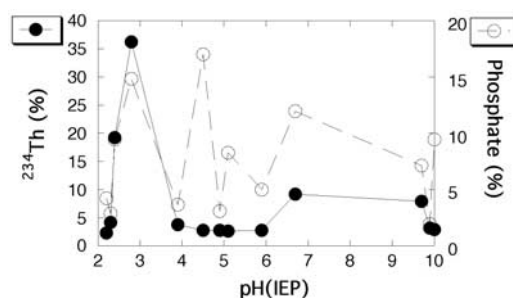


Figure 4. Results of isoelectric focusing experiments of colloidal organic matter, collected in 2001. Note that Th(IV) is expected to track P only in the low pH regions, as P occurs in other biomolecules, such as non-Th(IV) binding DNA and RNA with higher pH_{IEP} values.

appears that the role of photosynthesizing microorganisms is mainly to produce metal- (e.g., Th(IV)-) binding APS, while that of attached heterotrophic bacteria is also to reduce the algae-produced APS content by releasing enzymatically degraded smaller fragments from the filterable aggregates into the surrounding solution [Bacon, 1979].

[16] Th(IV) binding to a phosphate-containing APS with low isoelectric points (pH_{IEP}) of 3 or less (Figure 4) and molecular weight of about 10 kDa (not shown) is further suggested by the isoelectric focusing experiments with colloidal organic matter from the May 2001 cruise. The fact that phosphate is present in biomolecules of low IEP, likely in the form of phospholipids or phosphated polysaccharides occurring in bacterial cell walls, might suggest that the Th(IV)-binding ligand originates from bacteria, in agreement with the suggestions by Hirose and Tanoue [2001]. However, since both phytoplankton and bacteria activities are closely coupled, further studies are needed that consider both groups of microorganisms, as well as, possibly, zooplankton and protists, when evaluating their contributions to the standing crop of ^{234}Th -binding APS compounds.

[17] Our studies thus not only show that different members of the microbial community can be responsible for controlling $^{234}\text{Th}/\text{POC}$ ratios by excretion of metal binding APS compounds, but they also demonstrate the effects of the close coupling of total APS production and consumption on $^{234}\text{Th}/\text{POC}$ ratios. The results further show that particulate $^{234}\text{Th}/\text{POC}$ ratios are positively correlated to the content of different Th(IV)-binding polysaccharide fractions in both suspended and sinking particles. Sinking particles appear, however, to provide a more consistent $^{234}\text{Th}/\text{POC}$ ratio.

[18] **Acknowledgments.** We would like to acknowledge the crew of R/V Gyre, Elizabeth Fejes and Beth Lumsden for some of the pigment analyses, Kim Roberts, Jennifer Haye, Kathy Schwehr for help in sampling on the cruise, Scott Bean for help in the laboratory, and the NSF and the Texas Institute of Oceanography for financial support.

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