

Sorption irreversibility and coagulation behavior of ^{234}Th with marine organic matter

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Abstract

The partitioning of ^{234}Th to natural organic matter (NOM) in the colloidal size range (1 kDa–0.1 μm) was evaluated in order to examine the sorption and coagulation behavior of marine colloidal organic matter. Colloids were isolated using large volume cross-flow ultrafiltration and the partitioning of ^{234}Th was quantified using stirred cell ultrafiltration and radioactive assay. The uptake of ^{234}Th by NOM is irreversible over a period of 5 days, implying that over the mean life of ^{234}Th , very little release of ^{234}Th would occur after binding to NOM. Furthermore, the Th–NOM complex is stronger than the Th–EDTA complex, as EDTA was unable to displace the ^{234}Th from its association with NOM. The extent of the initial partitioning of ^{234}Th to suspended matter and colloids is similar and independent of pH in the range from 3 to 9. Coagulation experiments show that ^{234}Th complexed with low molecular weight (1–10 kDa) colloids is transferred to larger (> 0.1 μm) filter retained fractions. However, ^{234}Th is transferred to a greater extent than is organic matter and this results in greater partitioning coefficients for ^{234}Th onto particle phases with time. The final equilibrium between 0.1 μm filter-retained and filter-passing ^{234}Th activity is the same regardless of whether the Th was tagged initially to colloidal or suspended matter fractions. The coagulation of colloidal organic matter, COM, consists of both fast and slow steps, with kinetic rate constants on the order of 0.02–0.03 and 0.003–0.007 h^{-1} , respectively. The stickiness (or collision efficiency) factor, α , for COM was experimentally determined to be 0.7(–) for seawater conditions. Using the colloidal pumping model of Honeyman and Santschi [J. Mar. Res. 47 (1989): 951], the ‘predicted’ ‘fast-phase’ coagulation rate coefficient is 0.03 h^{-1} in our coagulation experiments when the measured α value and the experimental conditions are used for model inputs. These experiments demonstrate that coagulation is the dominant step in the transport of ^{234}Th to the particulate phase. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Sorption irreversibility; Coagulation behavior; ^{234}Th ; dissolved organic material; colloids; particles; seawater

1. Introduction

Thorium isotopes of different half-lives (e.g. ^{234}Th , ^{228}Th , ^{230}Th , ^{232}Th) have been applied for three decades as particle cycling tracers on different

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time and space scales. U–Th series disequilibrium approaches with radioactive mother–daughter pairs have been frequently used to estimate scavenging and removal rates of particle reactive substances (e.g. Bhat et al., 1969; Broecker et al., 1973; Li et al., 1979; Santschi et al., 1979, 1980, 1983, 1987; Kaufman et al., 1981; Bacon and Anderson, 1982; Baskaran et al., 1992, 1996), and to estimate particle fluxes (or new production rates) in the open ocean (e.g. Buesseler, 1991; Buesseler et al., 1994; Murray et al., 1996; Moran et al., 1997; Santschi et al., 1999). But there is some ambiguity as to exactly what processes (i.e. physical particle movement or chemical exchanges between aqueous and solid phases) that Th isotopes are tracing. In addition, researchers utilizing Th isotopes to calculate particle fluxes through the water may be relying on assumptions, which have not been rigorously tested, and thus, may or may not be accurate (e.g. Kim et al., 1999; Buesseler, 1991; Buesseler et al., 1994; Murray et al., 1996). A better understanding of particle types and modes of Th(IV) transport from the dissolved to the sinking particle state is needed to better interpret marine U–Th disequilibrium data (e.g. Buesseler et al., 2000).

It is important to note that ‘sorption’ is used generically to describe the interaction of Th with non-aqueous-phase materials. While it is reasonable to assume that Th sorbs to colloidal organic matter, COM, through the formation of Th/ligand complexes, the mechanism of the process is as of yet not explicitly known. In this paper, sorption and complexation are used interchangeably.

Over the years, thorium-particle interaction models have evolved from simple three box models incorporating reversible thorium sorption kinetics (e.g. Bacon and Anderson, 1982; Clegg and Whitfield, 1991) to more complex four box models, which include interactions with colloidal sized particles and utilize either irreversible sorption kinetics (e.g. Honeyman and Santschi, 1989; Honeyman and Santschi, 1991; Quigley et al., 1996) or reversible sorption kinetics (e.g. Clegg and Whitfield, 1993). However, both of these model types incorporate a progression for the transport of sorbed metal from dissolved to sinking particles. That is, metals are first scavenged by the smallest size fractions and then transported, via coagulation and aggregation, into larger sinking

particles (Honeyman and Santschi, 1989). Honeyman and Santschi (1989) conceptualized the “colloidal pumping model” (CPM) to include not only this serial progression of ^{234}Th from small to large particles in a reversible process, but also envisioned parallel reactions in which dissolved species are available for complexation by all available surfaces. However, with the data available, the mathematical representation of the CPM model was only able to incorporate the serial reaction pathways of metal sorption and transfer to particles large enough to sink out of the water column. In other words, the mathematical model assumes that parallel adsorption of ^{234}Th onto or release from existing particles could be ignored. A recent scavenging model developed by Burd et al. (2000) incorporates the parallel adsorption of dissolved Th onto a particle size spectrum, which is assumed to be in steady state. However, the model is assuming anomalously low colloidal abundance, and as such, translation to field data is difficult (Burd et al., 2000). In order to completely describe the actual kinetic processes occurring in the water column, it is critical that models are based on experimental data, which will establish if parallel sorption of dissolved metals to all particle sizes is an important step in the kinetics of trace metal scavenging. Due to its high abundance and its relatively large surface area and site concentration, it is likely that colloidal matter is the dominant sorbent in marine surface water environments. Serial reactions are defined as reactions initially taking place between the metal ion and the colloidal size fraction of NOM, which is subsequently transferred, via coagulation, to larger size fractions. In contrast, in a parallel reaction, the metal ion interacts with all available size fractions simultaneously and then follows any movement of the bulk or carrier material from one size fraction to another, i.e. through aggregation or disaggregation.

While it is customary in chemical oceanography to assume that Th(IV) sorption to marine particles is reversible (e.g. Bacon and Anderson, 1982), there is strong evidence that the sorption of Th(IV) to at least some micro-particles (e.g. hematite, $\alpha\text{-Fe}_2\text{O}_3$; Quigley et al., 1996) can be irreversible. The apparent reversibility which has been either seen experimentally (Moore and Hunter, 1985; Moore and Millward, 1988) or postulated by other investigators (e.g.

Bacon and Anderson, 1982; Clegg and Whitfield, 1991; Murnane et al., 1990) can also be ascribed to the colloidal nature of the carrier phase (Quigley et al., 1996), that is, colloid disaggregation. If Th(IV) is desorbing very slowly or not at all, it could be due to the surface-active nature of the main colloidal carrier phase, which might sterically mask complexed ions and hinder the release of ^{234}Th . “Colloidal pumping” would then be able to transport ^{234}Th across the particle size spectrum during the coagulation of its surface-active carrier phase.

The objectives of this study, carried out on NOM collected from coastal and oceanic waters of the Gulf of Mexico, are: (1) to test our hypothesis that matter and ^{234}Th transport in the marine particle-size spectrum is mainly a serial process, rather than parallel, which is the basic foundation of the colloidal pumping model; (2) to evaluate the reversibility of the sorption reaction; and (3) to determine the ability of Th(IV) to serve as a proxy for marine organic carbon movement between different size fractions.

2. Materials and methods

2.1. Sample collection

Natural organic matter was collected from the upper 1 m of surface water in Galveston Bay and the Gulf of Mexico. A sample description is given in Table 1.

Water samples were pumped peristaltically through a prefilter (mostly 0.2 μm) and polypropylene tubing into polyethylene containers (for Galve-

ston Bay samples) or directly into the ultrafiltration reservoir on board ship (for Gulf of Mexico samples). Prefiltered water samples were then ultrafiltered in the laboratory using an Amicon DC-10 ultrafiltration system with a 1000-nominal molecular weight cut-off, NMWCO, ultrafilter (Amicon S10N1) to collect the ≥ 1 kDa (~ 1 nm) fraction of colloidal organic matter, COM (Guo et al., 1995; Guo and Santschi, 1996, 1997). The ultrafiltration of coastal and estuarine waters began within 2 h of sample collection. Initial sample volumes were in the range of 200–1000 l, with a final colloid concentrate volume of about 2 l. An aliquot of colloid concentrate was dialyzed using a ≥ 1 -kDa ultrafilter and high purity (18 M Ω cm) filtered H₂O to remove the salt, and then freeze-dried. Detailed procedures were described in Quigley (2000).

2.2. ^{234}Th separation from ^{238}U and preparation of colloid-free ^{234}Th stock solution

All Th(IV) spike experiments were carried out using ^{234}Th , which had been separated from its parent ^{238}U (in the form of uranium nitrate) by anion exchange resin columns using Teflon ware and clean exchange resin columns using Teflon ware and clean reagents and laboratory procedures (Quigley, 2000). Without clean procedures, variable ^{234}Th losses to filters and walls are observed (e.g. McCubbin and Leonard, 1995), which can be ascribed to colloidal impurities in the stock solutions. Clean standard and experimental solutions can be obtained by the prior destruction by concentrated HNO₃/HCl of organic impurities co-eluted from ion exchange columns under conditions that minimized particle deposition

Table 1
Sample locations and characteristics

Sampling date	Sample number	Location	S (‰)	Nature of COM	Remarks
3/7/1996	FA96	Galveston Bay	9	Fresh	Upper Trinity Bay
8/16/1995	EP95	Galveston Bay	15	Fresh	Eagle Pt.
6/26/1998	GB9802	Galveston Bay	16	Fresh	Eagle Pt.
1/30/1996	TC96	Galveston Bay	25	Fresh	Texas City Dyke
6/12/1998	GB01	Galveston Bay	25	Fresh	Texas City Dyke
6/12/1996	PI96	Galveston Bay	27	Fresh	Pelican Island Ship Channel
7/16/1999	GOM99	Gulf of Mexico	26	Fresh or freeze-dried	Off Galveston Island
1992	92G09	Gulf of Mexico	35	Freeze-dried	R/V Gyre
1997	97P01	Gulf of Mexico	35	Fresh	R/V Pelican
1998	98PE28	Gulf of Mexico	35	Fresh	R/V Pelican

from laboratory air (Quigley, 2000). In each separation experiment, 10 g of the uranium salt (equivalent to 5.8×10^4 Bq) were used to obtain final ^{234}Th activities of typically 3.3×10^4 Bq or greater, which yielded a 10^{-11} M ^{234}Th stock solution.

2.3. ^{234}Th sorption experiments and evaluation of wall sorption losses

Some experiments were run using reconstituted COM (e.g. 92G09; Table 1), i.e. a dilute amount of the concentrated, freeze-dried, solid COM redissolved in 1-kDa permeate water from where the sample was taken in a sodium perchlorate solution or in an artificial seawater solution (Appendix of Riley and Chester, 1970–1990). Most other experiments (see Table 1) were run using a liquid colloid concentrate, i.e. 1-kDa ultrafilter retentate, diluted using 1-kDa permeate, a solution of the inert electrolyte sodium perchlorate, or an artificial seawater solution of the same salinity. Typical concentrations of NOM used in these experiments were in the 5–10 ppm range. Experimental Th(IV) concentrations were about 1 fM. This low concentration ensured ambient conditions, whereby, the complexation of Th(IV) by organic functional groups does not alter the bulk surface characteristics of the NOM or induce bridging reactions as a major cation. The addition of the ^{234}Th spike was followed by an adjustment of the pH to the experimental value using reagent grade NaOH. The Th–COM or Th–sorbent mixture was stirred in a Teflon beaker with a Teflon-coated magnetic stir bar at 60 rpm for a minimum of 30 min but for no more than an hour before separation by filtration. Exceptions to this were time series experiments where aliquots were taken from the batch reactor at specific time intervals for filtration. The initial equilibration time was established in an attempt to reach a balance between the times for uptake of ionic ^{234}Th , which are of the order of minutes, vs. those for the coagulation of Th–COM complexes, which are of the order of hours. The relatively short-time scales for the time series coagulation experiments, 3–5 days maximum, were chosen in order to capture coagulation events before major alterations by bacterial activity could take effect. Studies of bacterial growth in ≤ 0.2 μm colloid samples (which are ultraclean and initially devoid of bacteria, but not sterile) have shown that

within 48 h, the count of viable bacteria can increase by an order of magnitude and by two orders of magnitude within 96 h (Chen and Buffle, 1996). Since bacteria are eliminated by 0.2- μm filters, solutions are initially “bacteria-free”, but will have bacteria present since clean but not sterile procedures were applied.

Particulates were filtered using a 0.1- μm polycarbonate disk membrane (Poretics). Separate experiments with two filter membranes demonstrated that adsorption of “dissolved” Th onto 0.1- μm polycarbonate filters is negligible (i.e. $\leq 5\%$). The ultrafiltered samples were run in parallel to the 0.1 μm filtration and were separated using Amicon’s stirred cell ultrafiltration (model 8200) with either a YM-1 (1 kDa, ~ 1 nm) or YM-10 (10 kDa, ~ 3 nm) membrane filter. The concentration factor of the retentate was typically four to five. For experiments where YM-10 and YM-1 ultrafiltrations were run on the same sample, separate aliquots were taken and the ultrafiltrations were carried out in parallel. Aliquots of all fractions were taken for TOC analysis on a Shimadzu TOC 5000 (Guo et al., 1994) and for ^{234}Th activity determination by liquid scintillation counting (LSC) or gamma counting (see Section 2.4). POC values were calculated by difference using the TOC concentration (Guo et al., 1994, 1995) in the total sample and in the 0.1- μm filter permeate.

While the batch experiments were carried out in Teflon containers, which had minimal wall sorption losses of ^{234}Th , the stirred ultrafiltration cell, because it is constructed from polysulfone with regenerated cellulose as membrane material, showed measurable wall losses. Therefore, the time course of the sorptive wall losses of ^{234}Th –COM was evaluated for the stirred ultrafiltration cell as a mass balance. ^{234}Th was reacted with COM in a Teflon container for 30 min before an aliquot was transferred to a stirred ultrafiltration cell. As a test, the Th–COM solution was stirred for 2 h, while aliquots were taken. The Th–COM solution was then discarded and the stirred cell was quickly rinsed with dH_2O followed by the addition of Th-free COM solution, which had been treated in an identical manner to the ^{234}Th –COM solution. The Th-free solution was stirred in the cell for approximately 2 h and the ^{234}Th activity in solution was again monitored. The results indicate that between 10% and 25% of the

initial Th–COM activity can be lost to the walls over 2 h and that between 3% and 10% of the initial total Th (or 30–33% of the sorbed Th activity) can be reversibly desorbed from the stirred cell walls (Fig. 1). Since containers were acid washed before use, this Th release from the walls was therefore not a problem. None of the stirred ultrafiltration cell exper-

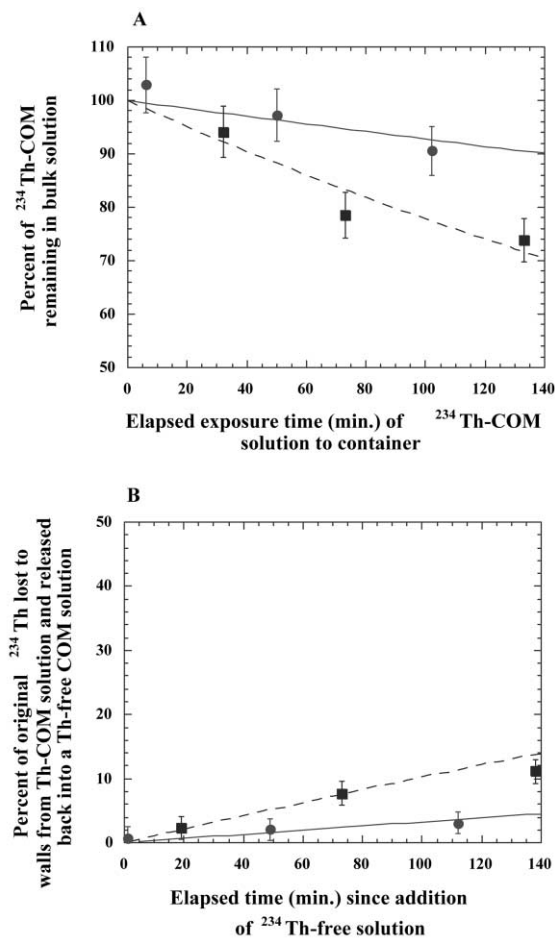


Fig. 1. Replicate runs where ²³⁴Th was reacted with 150 ml PI96 COM ($S = 26$) and added to an Amicon 8200 stirred cell ultrafiltration apparatus. The loss of activity in the water due to wall adsorption was monitored over time (A). The model lines were calculated as an exponential loss from solution with time with rate constants of 0.045 (●) and 0.15 h^{-1} (■). The Th–COM mixture was discarded and a Th-free PI96 COM ($S = 26$) solution was added to the stirred cell and the activity released back into solution was monitored over time (B). The model lines were calculated as an exponential release into solution with rate constants of 0.02 (●) and 0.065 h^{-1} (■).

iments took more than an hour for a typical 50–80-ml filtration. The maximum of 1-h time frame for ultrafiltration translates into a loss to the ultrafiltration container walls ranging from 6% to 16% of the total Th(IV) in solution. While no attempt was made to correct the experimental data for the loss of ²³⁴Th–COM to the walls of the stirred cell apparatus, this fraction of ²³⁴Th–COM would have sorbed to particles had they been present, as suspended particles have comparable surface areas and sorption capacities. Therefore, this fraction constitutes a surface reactive fraction, which more likely would have appeared in to the filter-retained fraction and not the filter-passing fraction. As will be seen in Section 3, the filter-retained ²³⁴Th activity accounted for most of the total ²³⁴Th activity in solution, on the order of 80%, whereas, the filter-passing ²³⁴Th activity accounted for a minor fraction of the total. If the fraction of total ²³⁴Th that was lost to the walls would have been a subfraction of the filter-retained activity, the inclusion or exclusion of this fraction would only make, at maximum, of a 1.2% difference in the calculated $\log K_c$ values for these experiments (e.g. $K_c = \text{colloid-water partition coefficient} = (1.0 \pm 0.2) \times 10^7$). However, it was decided not to correct the experimental data for the wall loss fraction of ²³⁴Th.

2.4. ¹⁴C radiolabeling

A fraction of the freeze-dried 92G09 COM and GOM99 COM was taken and radiolabeled with ¹⁴C using the method of Wolfenbarger and Crosby (1983). In short, the procedure involved reacting the COM solid with ¹⁴C dimethyl sulfate (Sigma) in 0.1 M NaOH for 45 min followed by dialysis in 1-kDa cut-off dialysis bags until permeate ¹⁴C activity dropped below detection limits (5–7 days). The labeling reaction is a methylation reaction and the reagent should react mainly with the hydroxyl groups of both neutral and amino sugars (Wolfenbarger and Crosby, 1983). The ¹⁴C radiolabeled COM was stored in dH₂O in a sterilized amber bottle at 4 °C. Generally, a small aliquot of the ¹⁴C–COM was used in a batch reactor also containing unlabeled colloids and particles. Often, ²³⁴Th was added to these reactions and the activity of both isotopes was measured in the different size fractions using a liquid scintillation counter (LSC).

2.5. Determination of the α -factor

Using the methodology of Litton and Olson (1993), column experiments were run to determine α , the stickiness factor, of NOM. The stickiness of a microparticle or macromolecule is generally defined as the ratio of the number of successful attachments per number of collisions between macromolecules or microparticles. Glass beads with a mean diameter of 2 mm were cleaned with concentrated HCl, followed by concentrated $\text{H}_2\text{Cr}_2\text{O}_7$, and then, as a final cleaning step, in concentrated HCl. A 12-cm column, 0.9-cm diameter, was then packed and conditioned for 24 h in a pH 3 solution of HCl. After conditioning, the column was then preconditioned with the background electrolyte at the experimental pH for 24 h. The experimental material, GOM99 COM and GOM99 polysaccharide-enriched COM, was diluted in either a 0.01 M NaClO_4 (pH of 4) solution or in 1-kDa permeate seawater at a pH of 8.0, to a final concentration of 10-ppm NOM. The experimental COM was radiolabeled with either ^{14}C (see Section 2.4) or ^{234}Th , and the effluent activity was measured in discrete 1-ml samples. The effluent was collected until 10-pore volumes had passed through the column. The stickiness factor, α , was determined from the break through curve using Eq. (1) (Litton and Olson, 1993).

$$\alpha_{\text{exp}} = -\ln(C/C_0) [4a_c/3(1-f)LN_0] \quad (1)$$

where C/C_0 is the activity in the effluent relative to the input activity, a_c is the average collector diameter ($a_c = 2$ mm), f is the porosity ($f = 0.13$), L is the column length ($L = 12$ cm) and N_0 is the theoretical collector efficiency for transport by diffusion ($N_0 = 0.013$ – 0.018 , dependent primarily on flow velocity, which varied between 0.0004 and 0.0002 m s^{-1}). Eq. (1) is valid for colloidal sized particles (Yao et al., 1971). The value of N_0 was determined by the equation

$$N_0 = 0.9(kT/\mu d_p dV_0)^{2/3} \quad (2)$$

where k is the Boltzman's constant (1.3807×10^{-23} $\text{kg m}^2 \text{s}^{-2} \text{K}^{-1}$), T is the temperature in K, μ is the viscosity ($\mu = 0.0009$ $\text{kg m}^{-1} \text{s}^{-1}$), d_p is the average particle (colloid) diameter (3 nm), d is the collector diameter (2 mm), and V_0 is the flow velocity

in meters per second. The value of 3 nm for the colloidal diameter was chosen based on the 2D electrophoresis results of the GOM99 COM (Quigley et al., 2001), which showed the ^{234}Th -labeled colloids were mostly of a size equivalent to about 12 kDa in molecular weight. The calculated α values can then be incorporated into coagulation models and the fitting parameters adjusted to get a best fit to the experimental data.

2.6. Radioisotope detection

The two isotopes used in this study, ^{234}Th and ^{14}C , are both measurable on a LSC. Counting was carried out on a Beckman LSC 8100 with Ecolume liquid scintillation cocktail (ICN), at a cocktail to sample ratio of 3:1. ^{234}Th activity and ^{14}C activity could be measured in the same sample after 100 min by counting the protactinium-234 ($t_{1/2} = 19.7$ min, 0.512 MeV) window, assuming secular equilibrium with its parent ^{234}Th ($t_{1/2} = 24.1$ days, 0.199 MeV), and correcting the counts in the lower energy window, where both ^{234}Th and ^{14}C were counted. Samples were monitored for quenching and the counter was calibrated for both ^{234}Th and ^{14}C activity (separately and in combination). Counting times of 20 min were used in all cases. A separate background sample, which consisted of the experimental solution without any radioisotopes, was used in each experimental data set. The minimal detectable activity for the defined ^{234}Th window on the Beckman LSC 8100 was 6.8 dpm while the minimal detectable activity (MDA) for the ^{14}C window was 6.36 dpm.

^{234}Th activity was also measured using a Canberra Ge well Gamma detector, calibrated using an acidified U standard solution which had ^{234}Th in secular equilibrium (Santschi et al., 1999).

2.7. Partitioning experiments

The ^{234}Th spike and the sample COM were allowed to equilibrate at the experimental pH for 30 min prior to the first stirred cell ultrafiltration unless otherwise noted. This equilibration time was used in order to find a compromise between the rapid complexation phase, on the order of minutes, and the slower coagulation phases that occur on orders of hours to days.

The irreversible complexation experiments were carried out in artificial seawater in order to approximate the ionic strength of open ocean seawater and to ensure that there were no solution sources of ^{234}Th . The EDTA competition studies used freeze-dried COM and monosodium EDTA in a simple background electrolyte solution reacted with ^{234}Th to evaluate the relative strength of the Th–COM complex since a Th–EDTA complex will pass a 1-kDa ultrafilter.

The partitioning and coagulation experiments followed the same basic protocol where an isolated fraction of COM or a bulk NOM sample was reacted with ^{234}Th and then ultrafiltered. The coagulation experiments were allowed to sit over time and aliquots were taken for filtration. The partitioning experiments were carried out in a simple electrolyte solution so that the only organic matter present was the sample COM. Coagulation reactions were carried out in a background electrolyte solution (0.01 M NaClO_4) or the 1-kDa permeate seawater from which the colloidal material had been extracted in order to better approximate the true coagulation rate in natural waters.

3. Results and discussion

3.1. ^{234}Th irreversible sorption

Experiments were conducted to evaluate the reversibility of ^{234}Th sorption onto marine colloidal matter. The results from sorption and desorption experiments show that ^{234}Th , once bound to COM, does not significantly desorb in order to reestablish equilibrium conditions (Fig. 2). The apparent partitioning coefficient of Th onto colloidal matter ($[\text{Th-colloids}]/[\text{Th-solution}]$) was higher for desorption by at least an order of magnitude than for the adsorption case (e.g. $\log K_c$ of > 7.3 for desorption, 6.3 for adsorption). Thorium's irreversible surface complexation held up over time periods of up to 72 h and was independent of initial equilibration time between Th and COM (Fig. 2). Time zero in Fig. 2 marks the addition of the ^{234}Th -free artificial seawater to the ^{234}Th -COM 1-kDa retentate, i.e. the beginning of the desorption event.

As a comparison of our data to anticipated reversibility, a simple reversible kinetic model (e.g.

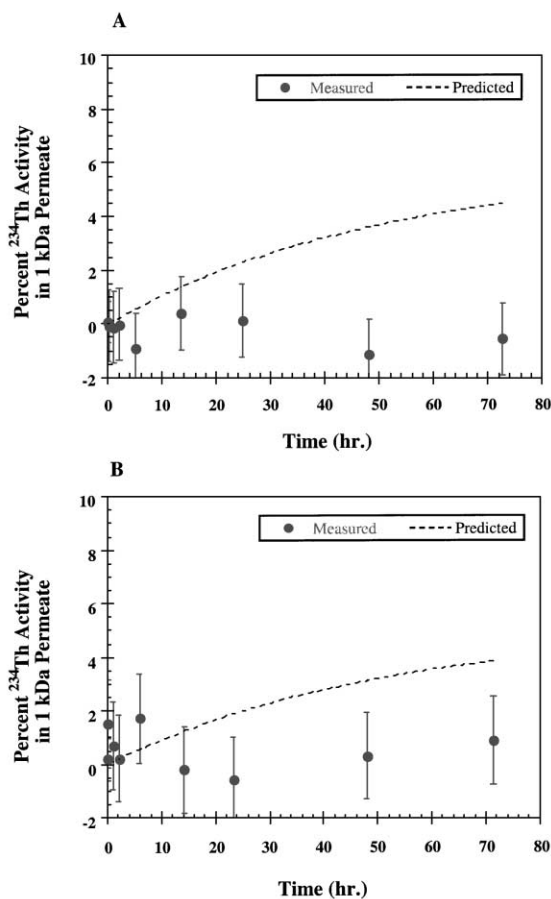


Fig. 2. Long-term ^{234}Th desorption from 92G09 COM in an artificial seawater solution containing no dissolved ^{234}Th . The COM had been equilibrated for (A) 1 and (B) 24 h prior to pre-ultrafiltration with a 1-kDa ultrafilter. Circles are the measured 1-kDa ultrafilter permeate activities after resuspension and the squares represent model predictions of permeate concentration based on a $k = 0.02 \text{ h}^{-1}$ rate constant.

Farrington and Westall, 1986; Carvalho et al., 1999) can be invoked

$$C_w = C_s \frac{k_1}{k_2} \quad (3)$$

where C_w is the isotope concentration in solution and C_s is the isotope concentration in the solid phase. Note that the equations used are for the case when the concentration in the water is not constant, but varies in proportion to the uptake by the

particle(s). The release of ^{234}Th from the initial concentration (C_{S0}) in the particulate or colloidal phase into ^{234}Th -free solution is given by

$$C_s = C_{S0} e^{-(k_1+k_2)t} \quad (4)$$

with C_s = concentration of tracer associated with the solid phase (Bq/l) at time = t , C_{S0} = initial concentration at time = 0, k_1 = uptake rate constant (time^{-1}), and k_2 = release rate constant (time^{-1}). The release rate constant that was used here was the experimentally determined value for the uptake phase. Only the sum of the two rate constants ($k_1 + k_2$) is relevant for predicting the Th(IV) release from COM. k_2 values for suspended particles in the literature are on the order of 1 year^{-1} (Bacon and Anderson, 1982; Murnane et al., 1990). Thus, $k_1 \gg k_2$ is likely, and the exact value for k_2 becomes unimportant here. For the ^{234}Th concentration in solution, C_w , the expected increase in solution due to tracer release from colloids is

$$C_w = (1 - e^{-(k_1+k_2)t}) C_s / K_p C_p \quad (5)$$

where C_p is the particle concentration (g/ml) and K_p is the isotope-partitioning coefficient between the solid and solution phases (ml/g). If we define C_{tot} as the total ^{234}Th activity (solid plus solution), then the fraction of ^{234}Th in the solution phase is $f_w = C_w / C_{\text{tot}}$ and the fraction of ^{234}Th in the solid phase is $f_p = C_s / C_{\text{tot}}$. Rewriting Eq. (5) in terms of f_w gives

$$f_w = (1 - e^{-(k_1+k_2)t}) f_p / K_p C_p \quad (6)$$

Applying Eq. (6) to the experimental conditions in Fig. 2, and using a kinetic rate constant ($k_1 + k_2$) of 0.02 h^{-1} from the uptake phase of the experiment (see Fig. 11 and Section 3.6) gives the 'predicted' percent of ^{234}Th released into 1-kDa permeate over time (Fig. 2). While a ($k_1 + k_2$) rate constant of 0.02 h^{-1} is a larger rate constant than that proposed by Bacon and Anderson (1982) and Murnane et al. (1990) for marine suspended particulate matter, it is smaller in value than that for laboratory microparticles determined by Moore and Millward (1988) ($k'_1 = 4.24 \text{ h}^{-1}$, $k_{-1} = 0.231 \text{ h}^{-1}$). The 'predicted' release (Fig. 2) would reach a solution phase value of 4–5% after 72 h, while the experimentally deter-

mined value remained at $0 \pm 1\%$. Complexation of $^{234}\text{Th(IV)}$ to COM was thus shown to be irreversible within the errors of the measurements on the time scale of 3 days. At most, 1–2% of ^{234}Th could have been released within 72 h, resulting in a maximum release rate constant of about 1 year^{-1} . For all practical purposes, ^{234}Th thus appears to sorb irreversibly to COM. Also, the irreversible nature of Th(IV) sorption is independent of initial equilibration time. It is, however, important to point out that Th(IV) sorption onto silica particles with larger pores was shown to be reversible using the same methodology. Experiments with these model silica particles demonstrated that there was no significant difference between values of particle-water partition coefficients, K_d , determined from adsorption or desorption experiments (Quigley, 2000). Therefore, given that ^{234}Th is only tracing reactions with time scales of days to a few months, if Th(IV) is sorbing to sheltered sites within the interior of the macromolecule (e.g. "egg box" chelation with acid polysaccharides; Grant et al., 1973), very little Th(IV) will be released back into the aqueous phase. Once complexed by NOM, therefore, the Th(IV) will trace the movement of a labeled subfraction of NOM on time scales of hours to days to weeks.

3.2. EDTA competition with COM for the complexation of ^{234}Th

In order to get a relative sense for the strength of the ^{234}Th -COM complex, a competition experiment with EDTA was carried out. Several batch reactors containing 5 ppm of freeze-dried 92G09 COM and varying amounts of EDTA in 0.1 M NaClO_4 were reacted with ^{234}Th . The procedure for a standard stirred cell ultrafiltration separation was followed. The ability of EDTA to complex with ^{234}Th and pass a 1-kDa ultrafilter was established by spiking an EDTA solution, without COM present, with ^{234}Th , and then ultrafiltering the solution through a 1-kDa ultrafilter. Greater than 95% of the ^{234}Th was recovered from the permeate in the presence of EDTA without natural COM.

While there was some variability in the calculated $\log K_c$ values (e.g. 6.4–6.7, not shown), no significant trend was evident from the data. Within the

error of the measurements, the log K_c values did not change with EDTA concentration over the measured range (0.0–10 ppm EDTA).

EDTA was thus not able to displace ^{234}Th from natural marine COM. The equilibrium constant for Th(IV) complexed with EDTA (1:1 complex) under standard conditions is $K = 10^{23.2}$ (Martell and Smith, 1992). Since no significant change is exhibited in the partitioning of ^{234}Th between a system with no EDTA and a system where EDTA had a 30 times higher equivalent acid-COOH concentration than COM, i.e. 120 vs. 4 μM C, respectively, the equilibrium constant for the ^{234}Th complex with COM has to be considerably higher than that of the Th(IV)–EDTA complex.

3.3. ^{234}Th distribution between different COM fractions

The nature of colloids samples (e.g. reconstitution of freeze-dried material vs. fresh liquid colloid concentrates) is provided in Table 1. Freeze-dried colloids readily dissolved in permeate water and resulted in the same K_c values as fresh colloidal material, within the errors of the measurements, when considering the different concentrations of chelating low molecular weight DOC in the two different solutions (Quigley, 2000).

While our partitioning experiments were carried out at elevated ^{234}Th concentrations, they are many orders of magnitude below the range where they might be expected to affect the partitioning results. Assuming 1.3 meq/g of strong acid sites (Quigley et al., 2001; Santschi et al., 1995), this would result in a ratio of bound Th(IV) to acid sorption sites of $10^{-14} \text{ M} / 1.5 \times 10^{-5} \text{ M} = 7 \times 10^{-10}$. Given that the –COOH (or organic sulfate or phosphate ester) sites concentration in seawater is of the order of μM (Quigley et al., 2001), and the ambient [Th] is 10^{-18} M , the ambient [Th]/[–COOH] ratio in seawater would be of the order of 10^{-12} , assuming full coverage. According to Buffle (1990), problems (i.e. dependency of equilibrium constants on surface coverage) have not been observed to arise at ratios below 10^{-3} . The conditional constants Th determined by Hirose and Tanoue (2001) were determined at ratios of about 5×10^{-4} , orders of magnitude above our

experimental conditions. Thus, under our experimental conditions, we would not expect any Th(IV) concentration effect on partition coefficients.

When ^{234}Th was added to a solution containing a bulk mixture of prefiltered COM, the Th initially sorbed onto all NOM size fractions. The initial partitioning of the ^{234}Th activity among the different size fractions varied only slightly when normalized to the mass of organic carbon in each filter fraction. For example, in one experiment, Th was reacted with ^{14}C -labeled NOM over a range of pH values (Fig. 3). Each pH point in Fig. 3 is a discrete experiment, whereby, all points were run under the same conditions (i.e. $2 \times 10^{-14} \text{ M}$ ^{234}Th , 12 ppm COM) with identical equilibration times of 30 min.

The reason for carrying out the experiments in batch mode rather than as a titration was to eliminate any alterations which may have been caused by coagulation of the NOM and to provide an unbiased comparison of the effects of pH on Th–NOM sorption reactions. As can be seen in Fig. 3, at a pH of 8.1, there is no statistical difference between the amounts of Th sorbed to suspended particles ($> 0.1 \mu\text{m}$) and HMW colloids, when normalized to NOM mass. Using a $0.1\text{-}\mu\text{m}$ filter, the 10- and 1-kDa ultrafilter, the log Γ (moles of retained Th/gram retained NOM) values for each filter fraction were -12.04 , -12.02 and -11.86 , respectively. Similar

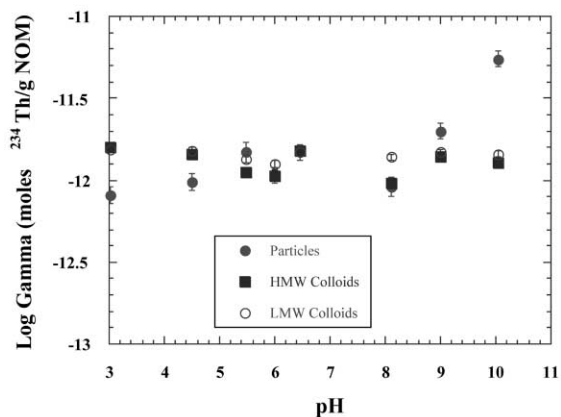


Fig. 3. Adsorption edge of ^{234}Th onto 92G09 COM in dH_2O ($I \leq 0.001$). Each pH point is a discrete batch experiment with an equilibration time of 30 min before filtration through a $0.1\text{-}\mu\text{m}$ filter (particles), a 10-kDa ultrafilter (HMW colloids) and a 1-kDa ultrafilter (LMW colloids).

values were obtained over a very large pH range (Fig. 3). Even at very low pH values, Th was binding similarly to the different NOM fractions, except at the extreme pH values of 10 and 3, where the particle-bound ^{234}Th deviated more significantly from the colloid-bound ^{234}Th . This suggests a strong Th(IV)-binding ligand that is also a relatively strong acid, as was previously proposed by Hirose and Tanoue (1994,1998).

The initial partitioning of Th(IV) into a system with a mixed NOM size spectrum is thus onto all the filter fractions equally when based on the amount of sorbed Th(IV) per mass of NOM (Fig. 3). Even at very low pH values, ^{234}Th sorbed to these NOM fractions to nearly the same extent (Fig. 3) as at higher pHs, suggesting that the responsible ligands are strong acids with $\text{p}K_a$ values of three or lower (Quigley et al., 2001).

Equilibrium K_d and K_c values determined in the lab for COM are remarkably similar to those determined in the field, given differences in sample sizes and collection times (Table 2), thus, justifying the validity of laboratory results. Laboratory experiments, however, give insights into the details of mechanisms and kinetics.

3.4. COM coagulation

After the initial complexation phase, there was a movement of bound ^{234}Th into larger filter-retained sizes. Fig. 4 shows the change with time in the filter-retained activity of ^{234}Th for particulate ($\geq 0.1 \mu\text{m}$ filter), HMW colloid (10 kDa– $0.1 \mu\text{m}$), LMW colloid (1–10 kDa), and dissolved ($< 1 \text{ kDa}$) phases.

Table 2

Values of ^{234}Th partition coefficients (K_d , particulate activity, in Bq/g solids divided by dissolved activity in Bq/ml) from controlled laboratory experiments as compared with those of field measurements in the Gulf of Mexico (Guo and Santschi, unpublished results)

Sample name	$\log K_d(\pm 0.1)$		$\log K_c(\pm 0.1)$	
	Field	Laboratory	Field	Laboratory
97PE-Sta-2	5.2	5.4	5.4	5.4
97PE-Sta-3	5.1	5.9	5.2	5.7
97PE-Sta-5	5.9	n/a	6.2	5.7
98PE-Sta-1	5.8	5.5	n/a	n/a
98PE-Sta-4	5.1	5.0	n/a	n/a

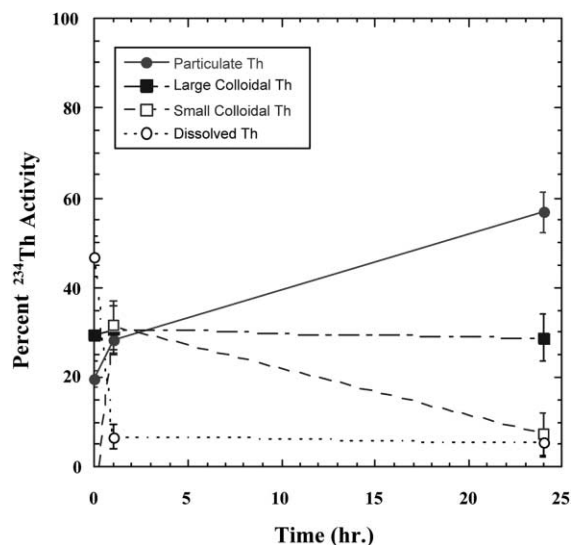


Fig. 4. ^{234}Th coagulation experiment with freshly collected FA96 COM at a pH of 7.6 and salinity of nine in ambient 1 kDa permeate water. Particulate (closed circles) = $0.1 \mu\text{m}$ filter-retained, Large Colloidal (closed squares) = $0.1 \mu\text{m}$ filter-passing but 10 kDa ultrafilter-retained, Small Colloidal (open squares) = 10 kDa ultrafilter-passing but 1 kDa ultrafilter-retained, and Dissolved (open circles) = 1 kDa ultrafilter-passing.

Interestingly, the LMW colloidal fraction decreased between 1 and 24 h by the same amount as the particulate amount increased while the HMW colloidal ^{234}Th fraction remained constant. This trend continued even over longer time periods. This makes it likely that the LMW colloidal Th is surface-active and was scavenged by suspended particles. This finding is in agreement with the fact that an acid polysaccharide-rich compound of 12-kDa molecular weight was identified by Quigley et al. (2001), which is mostly responsible for binding of ^{234}Th . Approximately, 50% of such a compound would initially pass an ultrafiltration membrane of 10-kDa nominal molecular weight (Guo and Santschi, 1996; Guo et al., 2000).

Although both of the experiments shown in Figs. 4 and 5 were carried out using $0.4\text{-}\mu\text{m}$ prefiltered COM, the observations held true in solutions with preformed, natural particulate matter $> 0.4 \mu\text{m}$, where the full size range of natural particles was available for Th complexation and where the initial ^{234}Th was primarily in the fraction passing a $0.1\text{-}\mu\text{m}$ filter, but with the filter retained fraction accounting

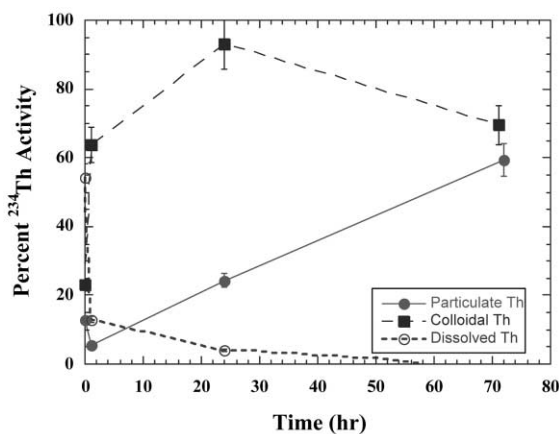


Fig. 5. ^{234}Th coagulation experiment where TC96 COM was reacted with ^{234}Th in 1 kDa dialysis bags for 48 h and then combined with unlabeled NOM $< 0.4 \mu\text{m}$ at a salinity of 25. Particulate (closed circles) = $0.1 \mu\text{m}$ filter-retained activity, Colloidal (closed squares) = $0.1 \mu\text{m}$ filter-passing activity retained by a 1-kDa ultrafilter, Dissolved (open circles) = activity passing a 1-kDa ultrafilter. Dissolved ^{234}Th activities below a 5% value are not significantly different from 0 within the errors of the measurements.

for $\sim 10\%$ of the total activity (data not shown), similar to the range seen in Figs. 4 and 5. Therefore, a comparison of systems where preformed particulates have been removed and a system where preformed particulates were present shows that results are not significantly different.

In order to identify the size fraction of marine NOM that is important for ^{234}Th coagulation, another experiment was carried out. In this experiment, NOM was first prefiltered with a $0.4\text{-}\mu\text{m}$ filter and then three size fractions—"particulate" ($\geq 0.1 \mu\text{m}$), HMW colloids ($10 \text{ kDa} - 0.1 \mu\text{m}$) and LMW colloids ($1 - 10 \text{ kDa}$)—were collected by ultrafiltration. A subsample of each size fraction was taken and radiolabeled with ^{234}Th and dialyzed in 1-kDa dialysis bags in the $< 1\text{-kDa}$ permeate sample seawater for 48 h. Following dialysis, each of the Th–COM solutions was added to a separate batch reactor, which contained the other resuspended, unlabeled NOM fractions at a concentration roughly 10 times ambient (Fig. 6). The time when the ^{234}Th radiolabeled NOM was introduced to the batch reactor was taken as time zero. Aliquots were taken at time intervals and filtered through $0.1\text{-}\mu\text{m}$ polycarbonate

filters with "particulate" Th defined as the filter-retained ^{234}Th activity and "dissolved" Th defined as the filter-passing ^{234}Th activity. Values in Fig. 6 are

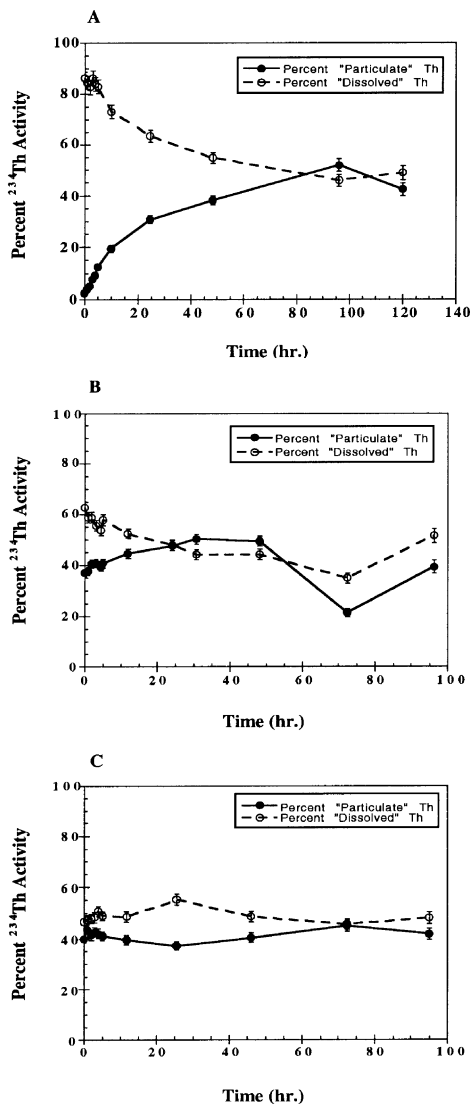


Fig. 6. Three separate coagulation experiments carried out with EP95 NOM. ^{234}Th -tagged concentrated size fractions, (A) LMW COM $< 10 \text{ kDa}$, $\geq 1 \text{ kDa}$, (B) HMW COM $< 0.1 \mu\text{m}$, $\geq 10 \text{ kDa}$ and (C) "particles" $< 0.4 \mu\text{m}$, $\geq 0.1 \mu\text{m}$, were added to batch reactors containing unlabeled NOM fractions at roughly 10 times ambient concentration (TOC = 15 ppm) in ambient ($S = 15$) 1-kDa permeate. "Particulate" is the ^{234}Th activity retained on a $0.1\text{-}\mu\text{m}$ filter, and "dissolved" is the ^{234}Th activity in the $0.1\text{-}\mu\text{m}$ filter-passing permeate.

reported as the activity relative to the total activity in the sample at that time.

The coagulation of ^{234}Th labeled LMW COM is shown in Fig. 6A. In this case there was a rapid transfer of ^{234}Th activity to the 0.1- μm filter-retained fraction within the first 5 h, followed by a slower but ever increasing transfer up to 100 h, until a value close to 50% was reached.

In the case of the ^{234}Th -labeled HMW COM experiment (Fig. 6B), there was a slight increase in filter-retained activity with time, with a final fraction value nearly identical to the initial ($t = 0$) value. This was also the case with ^{234}Th -labeled “particles” where little change with time was observed (Fig. 6C). In all three experiments, the filter-retained ^{234}Th activity reached a constant value near 50%. However, the changes in ^{234}Th activity were not necessarily mirrored by changes in the colloidal bulk OC (Fig. 7). While most (80–90%) of the OC was found in the colloidal fraction, colloidal ^{234}Th increased to a maximum of 60% and then decreased to less than 40%.

Note that the experimental results given in Figs. 4, 5 and 6A,B,C were carried out differently and with different materials (see figure captions), under slightly different conditions (e.g. salinity). While the experiment shown in Fig. 6A started with Th-labeled low molecular weight colloids < 10 kDa, those in Fig 6B were carried out with > 10 kDa colloids, and those in Fig 6C with labeled > 0.1- μm particles. Experiments shown in Fig. 4 used radiolabeled col-

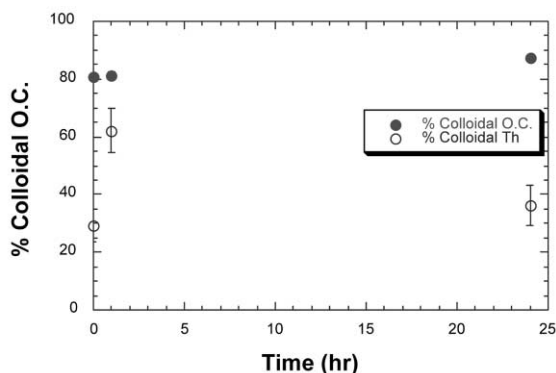


Fig. 7. The same data as plotted in Fig. 4 except the 10-kDa retained fractions have been combined with the 1-kDa fractions to get a total colloidal activity for ^{234}Th and total COC mass.

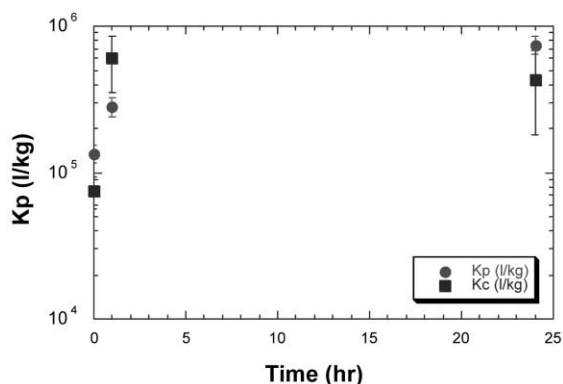


Fig. 8. Partitioning coefficients for ^{234}Th onto estuarine COM retained by a 0.1- μm filter (K_p) and a 1-kDa ultrafilter (K_c) during a time series coagulation experiment. Data from the same experiment presented in Figs. 4 and 7.

loids > 1 kDa, which were added to 1-kDa permeate water, and those shown in Fig. 5, Th-labeled colloids > 1 kDa were added to unlabeled COM (1 kDa–0.4 μm).

Results shown in Fig. 7 indicate that colloidal ^{234}Th in these laboratory experiments did not exactly track the % COC over 24 h. Since the results of Guo et al. (1997) indicated that the colloidal Th(IV) is close to the colloidal organic carbon partitioning in field situations at near-steady state, this discrepancy is at first surprising. The difference is likely due to the fact that: (1) only short-term kinetics of colloidal partitioning of OC and ^{234}Th can be observed in our experimental system, and (2) our experimental system was enriched in COC and devoid in living and non-living particles.

As shown in Fig. 8, the colloid partitioning coefficient (K_c) initially increased by nearly an order of magnitude and then remained constant with time (within statistical error). The partitioning coefficient for the ^{234}Th interacting with the particulate phase, while initially of smaller value than for the colloidal phase, became statistically indistinguishable from the partitioning coefficient for the colloidal phase. Therefore, while the colloidal phase was initially enriched in ^{234}Th relative to the colloidal organic matter, this fraction perhaps became slightly depleted in ^{234}Th as the ^{234}Th was transferred, or pumped, out of the colloidal pool and into larger filter-retained

fractions. The net result is that the particulate ^{234}Th phase is continually enriched in ^{234}Th with time relative to the particulate organic matter mass. This behavior of the colloidal fraction supports the model wherein colloidal ^{234}Th is an intermediary in the particle uptake process (e.g. Honeyman and Santschi, 1989, 1991; Quigley et al., 1996), by which ^{234}Th is adsorbing to, and following the coagulation of, a subfraction of bulk NOM, which contains ligands with pK_a values of about three or below.

3.5. ^{234}Th – ^{14}C labeled NOM system

In order to verify whether or not Th is indeed following the movement of organic matter, a series of experiments was carried out utilizing ^{14}C - and ^{234}Th -tagged COM. Partitioning experiments showed that both ^{234}Th and ^{14}C activities were predominately, 90% and 80%, respectively, present in the 1-kDa ultrafilter-retained fractions. Additionally, and most significantly, fractionation experiments as a function of pH demonstrate that ^{234}Th - and ^{14}C -labeled COM partition the same way into colloidal and particulate fractions (Fig. 9). In other words, the

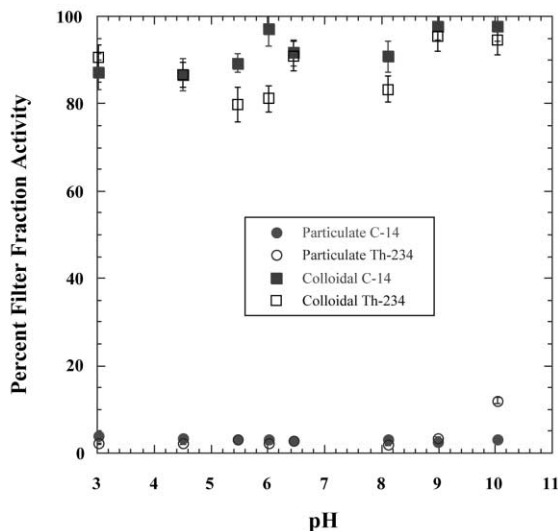


Fig. 9. Adsorption edge of ^{234}Th onto 92G09 ^{14}C radiolabeled COM. Each pH point is a discrete batch experiment with a 30-min equilibration time between the ^{234}Th and the ^{14}C -COM. Particulate activity was measured on 0.1- μm polycarbonate filters and colloidal activity was measured in 1-kDa ultrafiltration retentate fractions.

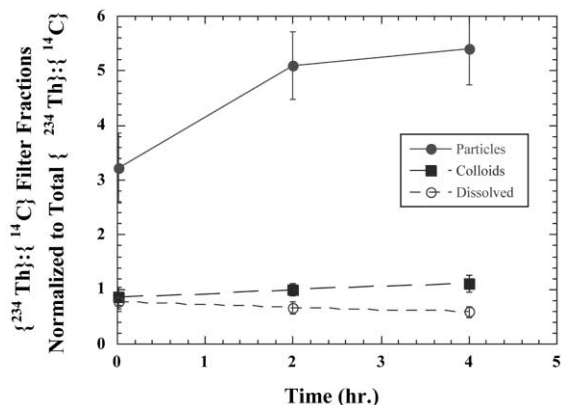


Fig. 10. Short term coagulation experiment with ^{14}C radiolabeled 92G09 COM spiked with ^{234}Th . Activity ratio of $^{234}\text{Th}/^{14}\text{C}$ is normalized to the total solution activity ratio.

portion of ^{234}Th and ^{14}C activity found in the 0.1- μm filter retained and 1-kDa filter retained fractions relative to the total solution activity for each isotope is nearly identical. This relationship holds true even at very low pH values (Fig. 9).

Time series experiments (Fig. 10) demonstrate that, for the colloidal fraction, a plot of the activity ratio of ^{234}Th to ^{14}C , normalized to the total activity ratio, is close to unity. Indeed, this relationship holds true over a wide range of ^{234}Th to ^{14}C -NOM ratios. As was previously shown in Fig. 8, the greater than 0.1- μm filter-retained fractions became enriched in ^{234}Th relative to the carbon fraction, represented by ^{14}C activity (Fig. 10) or organic carbon mass (Fig. 8). This means that more ^{234}Th moved into the particulate fraction than expected from OC or ^{14}C data. Despite the strong correlation seen in Fig. 9 between ^{234}Th activity and ^{14}C -NOM activity, however, there is also evidence from these short-term tracer experiments, which contained enriched or depleted colloids and/or particulate fractions, that ^{234}Th is not always tracing bulk NOM (Figs. 7 and 10) but rather, is following a subfraction of NOM that is actively undergoing coagulation and aggregation (Figs. 4–6A).

3.6. ^{234}Th coagulation model

Using the first-order kinetic model described in Stordal et al. (1996) and Wen et al. (1997), for simulating the movement of colloiddally bound trace

metals into the particulate pool, the transfer of ^{234}Th out of the colloidal phase can be described by

$$M_c/(M_c + M_p) = e^{(-k_1 t)} \quad (7)$$

where M_c is the concentration of ^{234}Th in the colloidal phase, M_p is the concentration associated with the particulate phase and k_1 is the removal rate constant (h^{-1}). Eq. (7) was developed with the assumption that all of the ^{234}Th is either bound by particles or bound by colloids and that no ‘dissolved’ ^{234}Th exists. This assumption is supported by the data presented in Fig. 6 where the entire 0.1- μm filter passing ^{234}Th is complexed by COM.

A plot of $\ln(M_c/(M_c + M_p))$ vs. time (h) yields a series of lines whose slopes are equal to the kinetic rate constant, k_1 . Fig. 11 is a plot of the data previously shown in Fig. 6A. Fig. 6A data transformed in Fig. 11 yield two apparent reactions: a fast initial coagulation phase (0–5 h) and a slower (5–120 h) coagulation phase. Stordal et al. (1996) and Wen et al. (1997) observed similar behavior in their studies of Galveston Bay colloids. The resulting rate constants are 0.021 and 0.0035 (h^{-1}), respectively, for the fast and slow reactions (Fig. 11). The first kinetic rate constant, k_1 is smaller than that observed by Stordal et al. (1996) and Wen et al. (1997)

(0.13–6.2 h^{-1}), i.e. the transfer is slower, but the second rate constant, k_2 , is of the same order of magnitude as what has been observed before for other trace metals (0.0004–0.0011 h^{-1}). The difference is likely due to the difference in experimental protocols.

A similar analysis can be performed on the data originally presented in Fig. 5. This data set is for 1-kDa ultrafilter passing ^{234}Th activity.

$$(M_c + M_d)/(M_d + M_c + M_p) = e^{(-k_1 t)} \quad (8)$$

where M_c , M_p and k_1 are as defined above and M_d is the concentration of ^{234}Th in the ultrafilter (< 1 kDa) passing, dissolved phase. The transformed Fig. 5 data are shown in Fig. 12. In this case, the transformed data yield a single reaction. Once again, this value is smaller than that seen for the fast, initial kinetic rate constant, k_1 , calculated by Stordal et al. (1996) and Wen et al. (1997), but is of similar magnitude to the slower rate constant, k_2 , they derived and to the second rate constant, k_2 , developed in Fig. 11.

The data in Figs. 11 and 12 result from experiments where the colloidal fraction (1–10 kDa) was first tagged with ^{234}Th before being added to a batch reactor containing unlabeled NOM fractions < 0.4

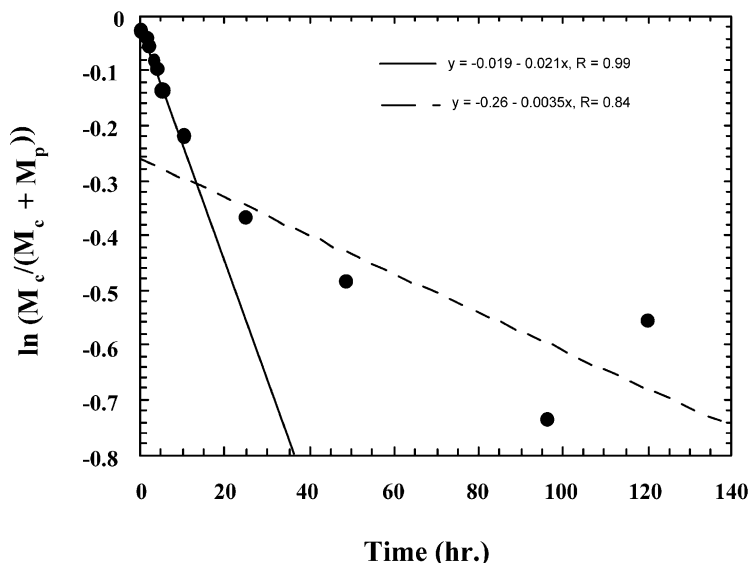


Fig. 11. Fraction of ^{234}Th lost from the colloidal phase due to coagulation over time plotted as $\ln(M_c/(M_c + M_p))$ vs. time and divided into a fast (0–5 h) phase and a slow phase (5–120 h). Data from Fig. 6A.

μm . These results demonstrate that this subfraction of NOM is highly active in terms of Th coagulation into larger filter retained sizes. Similarly, when ^{234}Th is reacted with $0.4\text{-}\mu\text{m}$ prefiltered PI96 ($S = 27$) COM, and the distribution of ^{234}Th activity among the “particulate” ($\geq 0.1 \mu\text{m}$), colloidal ($1 \text{ kDa} - 0.1 \mu\text{m}$) and the “dissolved” ($< 1 \text{ kDa}$) phases is monitored over time, the resulting data transformation is shown in Fig. 13. Once again, the data transformation yields a kinetic rate constant ($k_1 = 0.033 \text{ h}^{-1}$) of the same magnitude as in previous results (Fig. 11, $k_1 = 0.02 \text{ h}^{-1}$) and intermediate between the fast and slow rate constants reported by Stordal et al. (1996) and Wen et al. (1997) for other metals in controlled laboratory experiments using Galveston Bay water.

The transfer of initially dissolved ^{234}Th up the particle size spectrum through coagulation and flocculation processes can also be described by a three-phase model:



where D = dissolved, C = colloidal, and P = particulate fraction of ^{234}Th , with rate constants λ_1 and λ_2 for the transfer from D to C and C to P, respectively. λ_2 , the coagulation rate constant, is equivalent to k_1 of the previous models.

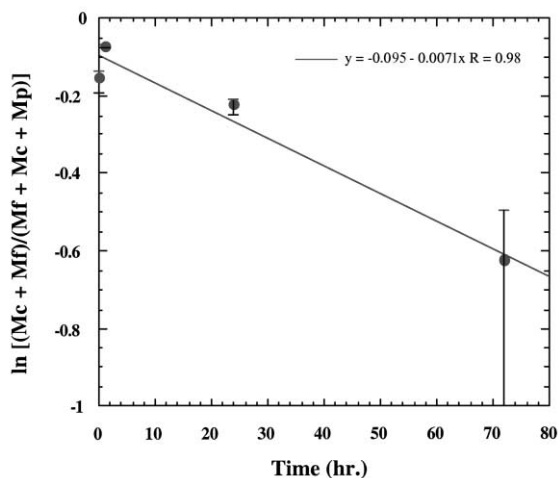


Fig. 12. Fractional loss of ^{234}Th from the colloidal phase (M_c) and the filter-passing phase (M_f) to the particulate phase (M_p) over time plotted as $\ln (M_c + M_f)/(M_f + M_c + M_p)$ vs. time (h). Data is the same as in Fig. 5. Error bars for the hour 72 sample are excessively large because the filter passing activity, M_f , was at background with a large relative counting error.

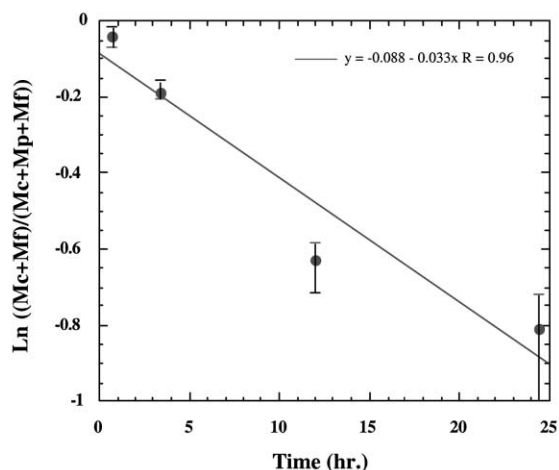


Fig. 13. Fractional loss over time of ^{234}Th from solution ($M_f + M_c + M_p$) to the $0.1\text{-}\mu\text{m}$ filter-retained, particulate (M_p), phase versus time (h). The slope of the line gives the kinetic time rate constant for the coagulation of ^{234}Th complexed by COM. The sample was prefiltered ($0.4 \mu\text{m}$) PI96 COM ($S = 27$), which had been reacted with ^{234}Th for ~ 30 min before the first filtration was begun ($0.1 \mu\text{m} > M_c \geq 1 \text{ kDa}$; $M_f < 1 \text{ kDa}$).

The differential equations are similar to parent–daughter radioactive decay and growth equations (e.g. Choppin et al., 1996). Modeling the data (not shown) from Fig. 5 results in a λ_2 value, which is indeed identical to the k_1 value, i.e. 0.03 h^{-1} . λ_1 is of the order of 1 h^{-1} . Since the test solutions were pre-equilibrated for 30 min before the start of the experiment, the data are not quite adequate, as this initial phase transfer from the dissolved to the colloidal fraction is not adequately observed. However, the coagulation experiments of Wen et al. (1997) and Stordal et al. (1996), using methodology designed to capture this very fast process, observed initial rate constants of about 1 h^{-1} ($0.1\text{--}6 \text{ h}^{-1}$).

3.7. Stickiness factor (α) of COM

An important property of COM needed for predicting coagulation rates of COM using coagulation theory is its collision efficiency, or ‘stickiness’ factor (α), i.e. its α value. Results for Gulf of Mexico coastal surface water COM and polysaccharide-enriched COM (GOM99), radiolabeled with ^{14}C , passed through SiO_2 columns, in the presence of 1-kDa ultrafiltered seawater ($S = 35$) of $\text{pH} = 8$, as

well as for 0.01 M NaClO₄ at pH = 4.4 (the same conditions of Litton and Olson, 1993) are shown in Fig. 14. The α value of COM in ambient seawater (pH of 8) of 0.71 was twice as high as that for the 0.01 M NaClO₄ solution of lower ionic strength and pH (i.e. 0.36). The difference is mainly due to the difference in ionic strength and Ca concentrations, as we have shown here that the extent of Th-complexation to COM is independent of pH in that range. The highest α value of 0.88 was that of polysaccharide-enriched, ethanol-precipitated COM, clearly demonstrating the sticky properties of acid polysaccharides.

3.8. Coagulation rates predicted by the colloidal pumping model (Honeyman and Santschi, 1989)

The derived value for the stickiness factor (–), α , can now be applied to the colloidal pumping model of Honeyman and Santschi (1989) to calculate a pseudo-first-order rate coefficient as described by Eq. (9).

$$B_t = B_b C_p^{0.3} + B_{sh} C_p^{0.9} \quad (9)$$

where B_b and B_{sh} are Brownian and shear coagulation coefficients, respectively. The coagulation ex-

periments were not stirred and as such the shear coefficient was minimized at 0.01 s⁻¹. 0.01 s⁻¹ for the shear coefficient is a typical value under unstirred conditions. Its exact value is irrelevant, since it was set to a value low enough so that the shear term would become negligible in the resulting removal rate constant. Thus, the Brownian coefficient remained the dominant term in Eq. (9). The difference in the density of the particle floc and the fluid is uncertain, and was estimated at 0.1 g cm⁻³ using previous work (Komar et al., 1981; Alldredge and Gotschalk, 1988; Stordal et al., 1996). The measured value for α , 0.7(–), in seawater conditions was used (Table 2). Since the final estimate of the removal rate constant depends not only on the exact value of alpha (is only to the 0.4th power), but also on the assumed density contrast between aggregates and solution (to the 0.3th power), the final result has uncertainties, which are mostly due to error in the density contrast rather than due to the alpha factor (which is 5% or less, see Fig. 14).

Eq. (9) was applied to the experiment which produced the data given in Fig. 15, i.e. where ²³⁴Th was reacted with the entire NOM spectrum < 0.4 μ m. The measured particle concentration, C_p , is 0.5

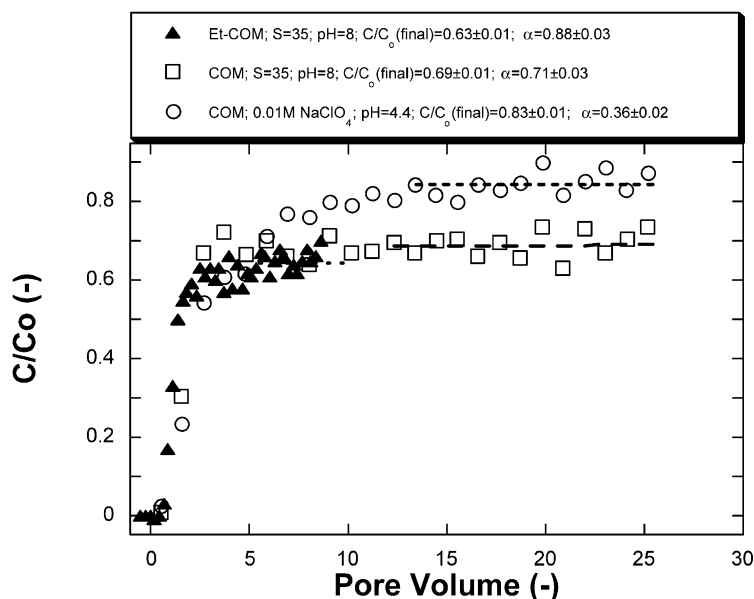


Fig. 14. Glass bead column breakthrough curves measured as the ¹⁴C activity of the effluent (C) relative to the input ¹⁴C activity (C_0) for ¹⁴C labeled bulk and polysaccharide-enriched GOM99 COM under different solution conditions.

(mg l^{-1}) and the batch reactor has a height of 12 cm. An application of Eq. (9) results in a coagulation rate coefficient, B_1 , of 0.035 h^{-1} . This value agrees very well with the kinetic coagulation rate constant calculated from the slope of the line in Fig. 13 using Eq. (8) (0.033 h^{-1}). This good agreement between the two approaches to calculating the kinetic removal rate constant is very encouraging. Final proof of the validity of the colloidal pumping model will require the measurement of the in situ density of the colloids, a measurement, which is not available from the literature.

4. Summary and conclusions

Many oceanic particle scavenging models view the removal process of Th(IV) from seawater as a serial process, while one would expect that simultaneous complexation by solution particle ligand groups would be a parallel process. Our experimental work indicates that the initial complexation step of Th(IV) reacting with all particle and colloid surfaces is indeed a parallel reaction. The results of this study show that ^{234}Th is distributed evenly across the size spectrum on a per organic carbon mass basis. But the fraction that was initially in the particulate, 0.1- μm filter-retained fraction was small, between 10% and 15%, and the majority of the ^{234}Th activity was associated with the colloidal fraction. However, the sorbed Th was then transferred, in a serial reaction pathway, i.e. coagulation, to larger filter fractions. This is seen by the transfer with time of ^{234}Th out of the colloidal fraction and into the 0.1- μm filter-retained fraction. While dissolved ^{234}Th will adsorb onto organic matter of any size, the fraction on the larger sizes is initially minimal and the main transport reaction resulting in the transfer of ^{234}Th to larger filter-retained fractions is the coagulation of colloidally bound ^{234}Th , which is a serial reaction. The observed experimental coagulation rate coefficient can be well predicted by the colloidal pumping model, when the measured stickiness factor, $\alpha(0.7)$ and a colloid density contrast between particles and seawater of 0.1 g cm^{-3} is assumed.

Our experimental evidence furthermore demonstrates that ^{234}Th can indeed be used as a proxy for the removal of a surface reactive subfraction of

colloidal organic matter from the water. The surface reactive fraction moves rapidly into the larger size fractions, taking with it complexed Th and other metals and reactive chemicals on time scales of hours to days. This subfraction, which is both surface-active and has a strong Th complexation capacity, contains ligands with low $\text{p}K_a$ values, thus rendering the Th association with COM insensitive to pH in the range from pH 3 to 10. Although the initial uptake of ^{234}Th from the dissolved state, a parallel reaction, occurs evenly to all colloidal and particulate size classes, the transfer of complexed ^{234}Th , which is predominately in the colloidal size range, a serial reaction, becomes the most important reaction during the “colloidal pumping” phase. During that phase, most ($\geq 90\%$) of the particle uptake of colloidally bound Th takes place.

Also, complexation of $^{234}\text{Th(IV)}$ to COM was shown to be irreversible, within the errors of the measurements, on the time scale of 3 days. No significant Th desorption from colloids was observed over this time, despite the fact that desorption of Th would have been expected, based on predictions from Th uptake kinetics. Since Th desorption is clearly hindered, and Th cannot, once complexed by colloids, be exchanged by another strong ligand such as EDTA, ^{234}Th can therefore be viewed as an excellent tracer for this “colloidal pumping” process.

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