

Short residence time of colloids in the upper ocean estimated from ^{238}U - ^{234}Th disequilibria

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RECENT observations of abundant, nonliving, submicrometre particles in the upper ocean¹⁻³ and new measurements of 'dissolved' organic carbon⁴⁻⁷ have fuelled speculation concerning the role of colloidal matter in ocean chemistry and biology. Colloids may act as reactive intermediates in the marine geochemistry of trace metals⁸⁻¹², and a biologically labile pool of colloidal matter would affect models of ocean carbon cycling¹³⁻¹⁶. Here we report the use of naturally occurring ^{234}Th as an *in situ* tracer to estimate the residence time of colloidal matter in the surface waters near Bermuda. The ^{234}Th activity of colloidal matter (size range 10,000 nominal molecular weight to 0.2 μm) is similar to that of small particles (0.2-53 μm). Modelling of our results indicates a mean residence time of colloidal ^{234}Th with respect to aggregation into small particles of 10 days, which is roughly the same as for small-particle ^{234}Th , yet a factor of ~ 6 less than for the dissolved pool. These results suggest that, more generally, macromolecular colloidal matter has a short residence time and hence a rapid turnover rate in the upper open ocean.

The boundary between the dissolved and particulate phase in the oceans has traditionally been defined operationally using filters of 0.2-1 μm pore size. Owing to their small size, of order 1 nm to 1 μm (ref. 17), and flexible nature¹, colloids can pass through such filters and thereby be included in the 'dissolved' (<0.2-1 μm) phase. Quantifying the role of colloids in oceanic biogeochemical processes is particularly important if we are to understand the dynamics of the marine carbon cycle. Here we used cross-flow filtration¹⁸ to sample the colloidal size class directly. Furthermore, measurements of the ^{234}Th isotopic signature in dissolved, colloidal, and particulate phases reported here allow estimates of the timescales over which these size classes are cycled in the surface open ocean. Thorium-234 has a strong chemical reactivity for marine particle surfaces¹⁹⁻²¹ and a well constrained radiogenic source function²². In addition, with a half-life of 24.1 days, ^{234}Th is an excellent tracer for quantifying rates of particle cycling on timescales of ~ 1 -100 days¹⁹⁻²¹, which correspond to rates of biogenic processes occurring within the surface euphotic zone.

We collected seawater samples from the upper ocean at the United States Joint Global Ocean Flux Study (JGOFS) Bermuda

Atlantic time-series (BATS) station located in the western North Atlantic (31° 50' N, 64° 10' W) during May 1991. Sea water was pumped from discrete depths onboard through 53- μm Nitex screen (1,300-3,100 l) to collect large particles, sequentially through 1- μm Nuclepore and 0.2- μm Gelman filters (240-290 l) to collect small particles, and a subsample of the filtrate (80-100 l) collected in acid-cleaned polyethylene containers. Filtration through 0.2- μm filters removes bacteria (evident from bacterial counts) and all larger microorganisms. Pre-filtered (<0.2 μm) sea water was ultrafiltered using a Millipore cross-flow filtration system modified for oceanic trace-metal sampling¹⁸ with a filter of 10,000 nominal molecular weight (NMW), equivalent to a pore size of ~ 1 -10 nm (ref. 18). The high flow rate (~ 25 l h^{-1}) of the cross-flow system facilitated the collection of large-volume (80-100 l) samples required for radiochemical determination of ^{234}Th in the colloidal and dissolved (<10,000 NMW) phase. Cross-flow filtration of each sample was completed in 4-5 hours and all samples were processed within 48 hours of collection.

Sorptive loss of ^{234}Th to the container walls and cross-flow system was <2% of the total ^{234}Th activity (determined by leaching with 1 M HCl). This is consistent with mass-balance results that indicated that total ^{234}Th activities (sum of all size classes) were within 10% of activities determined independently using large-volume sampling and γ -ray counting techniques²⁰. By comparison, a study of colloidal thorium isotopes in the shelf and slope waters in the Gulf of Mexico¹¹ reported sorptive losses of 10-40% of total ^{234}Th . Several factors may account for our relatively low sorptive losses. First, our cross-flow filter is made of regenerated cellulose which has lower sorption characteristics¹⁸ than the polysulphone filter used in the Gulf of Mexico study¹¹. Furthermore, the surface area of our Millipore filter (0.46 m^2) and system walls¹⁸ is roughly half that of the Amicon system (0.88 m^2 filter)¹¹. In addition, loss of colloids and associated ^{234}Th due to fouling of the cross-flow filter is expected to be less problematic in open ocean waters than in particle-rich shelf and slope waters.

Vertical profiles of ^{234}Th activity (Fig. 1a) are characterized by low dissolved values and elevated colloidal plus particulate levels in the upper 100 m relative to the deeper water. The deficiency of total ^{234}Th relative to ^{238}U (Fig. 1a) in the more biologically productive upper 100 m (Fig. 1c) is consistent with scavenging and export of ^{234}Th by biologically produced colloidal and particulate matter. Colloidal ^{234}Th activities range from 0.15-0.20 d.p.m. l^{-1} and show no systematic variation over the depth range sampled (Fig. 1b). ^{234}Th activities in the 0.2-1 μm particulate fraction are high in the near-surface waters and decrease toward the base of the euphotic zone. A broad maximum in ^{234}Th activity is evident in the 1-53 μm size class, slightly below the chlorophyll *a* maximum. Large-particle

FIG. 1 Vertical profiles of a, ^{234}Th activity on the sum of the colloidal and particulate phases (●, >10,000 NMW), the dissolved phase (○, <10,000 NMW) and the total (■, sum of all size classes) and dissolved ^{238}U activity²² (dotted line); b, ^{234}Th activity on colloidal (●, 10,000 NMW to 0.2 μm), small particle (○, 0.2-1 μm); Δ , 1-53 μm), large particle (\blacktriangle , >53 μm), and the sum of the >10,000 NMW (■, colloidal plus small and large particle) size classes; c, chlorophyll *a* (●) and particulate organic carbon (○) in the upper ocean at the BATS station (31° 50' N, 64° 10' W), 14 May 1991. Colloidal and particulate ^{234}Th activities were determined by ion-exchange and beta-counting procedures³³; dissolved ^{234}Th was collected on MnO_2 impregnated cartridges and quantified using γ -ray counting techniques²⁰. Error bars (sometimes smaller than the data symbol) were determined from counting statistics. Particulate organic carbon and chlorophyll *a* concentrations were determined using standard methods³⁴.

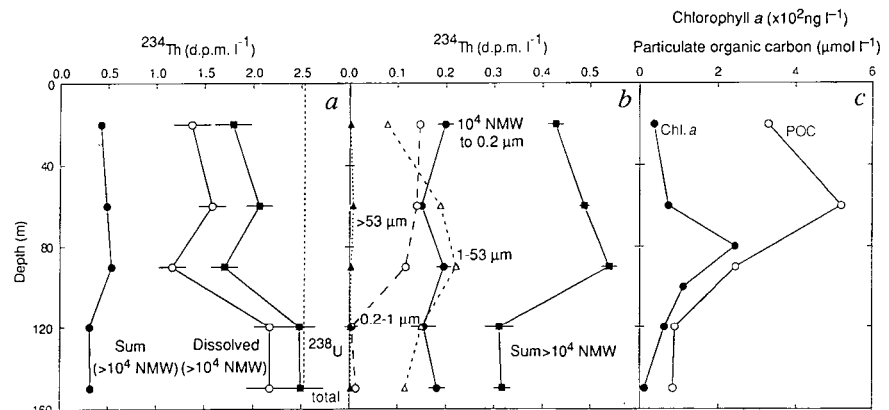


TABLE 1 Average of size-fractionated ^{234}Th results from 0–150 m off Bermuda

Quantity	Dissolved	Colloidal	Small particle	Large particle
^{234}Th (d.p.m. l^{-1})	1.62 ± 0.10	0.18 ± 0.01	0.25 ± 0.01	0.0040 ± 0.0002
τ (days)	61.3 ± 7.4	9.6 ± 1.4	18.3 ± 3.8	0.3 ± 0.1
Percentage of particulate	—	41.5 ± 2.7	57.6 ± 3.0	0.9 ± 0.1
Percentage of total	78.8 ± 6.2	8.8 ± 0.7	12.2 ± 0.8	0.2 ± 0.1

Size classes defined as: dissolved, <10,000 NMW; colloidal, 10,000 NMW to 0.2 μm ; small particle, 0.2–53 μm ; large particle, >53 μm . Errors were propagated from counting statistics and average ^{234}Th inventories (0–150 m) using trapezoidal integration. Results from 14 May 1991.

(>53 μm) ^{234}Th activities are extremely low (0.002–0.008 d.p.m. l^{-1}) and correlate to some extent with particulate organic carbon ($r^2 = 0.67$, $n = 5$).

A striking aspect of the size-fractionated data is that, on average, ^{234}Th activities in the colloidal size range and on small particles are similar in magnitude (Table 1). As a percentage of the total ^{234}Th activity, colloids and small particles each constitute ~10%, with the balance primarily in the dissolved (<10,000 NMW) phase. The implication of these results is that oceanic colloidal matter may be as important as traditionally defined suspended particulate matter (0.2–53 μm) in the cycling of Th^{19–24}, and possibly other reactive elements^{9,12,25–27}, between dissolved and particulate forms.

We calculated mean residence times of ^{234}Th in the dissolved, colloidal and particulate phases using an existing scavenging model^{19,20} that includes colloidal and large particle size classes (Fig. 2). The principal model assumptions are that the ^{234}Th activity is at steady state, scavenging of ^{234}Th is essentially irreversible, and advection and diffusion terms are negligible relative to net removal fluxes^{19,20}. The activity of dissolved ^{234}Th is controlled by a balance between production from its soluble parent, ^{238}U (half-life 4.5×10^9 years), loss by radioactive decay, and removal on colloids and larger particles. Colloid–particle interactions are simplified as a sequential process such that the ^{234}Th activity in each pool is maintained by production from a smaller size class, loss by radioactive decay and a net transfer to the next larger size class. Rapid export of ^{234}Th from the surface waters occurs only on large, fast-sinking aggregates. With these assumptions, the differential equations describing scavenging of ^{234}Th in the upper ocean are

$$\partial A_{\text{Th}}^{\text{d}} / \partial t = 0 = A_{\text{U}} \lambda - A_{\text{Th}}^{\text{d}} \lambda - J_{\text{Th}}$$

$$\partial A_{\text{Th}}^{\text{c}} / \partial t = 0 = J_{\text{Th}} - A_{\text{Th}}^{\text{c}} \lambda - C_{\text{Th}}$$

$$\partial A_{\text{Th}}^{\text{p}} / \partial t = 0 = C_{\text{Th}} - A_{\text{Th}}^{\text{p}} \lambda - P_{\text{Th}}$$

$$\partial A_{\text{Th}}^{\text{l}} / \partial t = 0 = P_{\text{Th}} - A_{\text{Th}}^{\text{l}} \lambda - L_{\text{Th}}$$

where A_{U} is the activity of ^{238}U ($0.069 \times \text{salinity}^{22}$), λ is the decay constant for ^{234}Th (0.0288 day^{-1}) and A_{Th} is the activity (d.p.m. l^{-1}) of ^{234}Th in dissolved (d), colloidal (c), small-particle (p), and large-particle (l) size classes. The terms J_{Th} , C_{Th} , P_{Th}

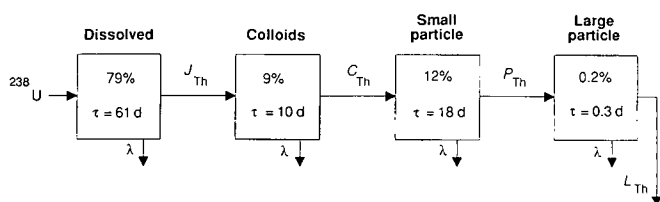


FIG. 2 Particle cycling model used to calculate mean residence times of ^{234}Th in dissolved, colloidal, small particle, and large particle size classes in the upper ocean. J_{Th} , C_{Th} , P_{Th} and L_{Th} represent net removal fluxes of ^{234}Th from the various pools and λ represents the radioactive decay constant for ^{234}Th . Also shown is the percentage of the total ^{234}Th activity associated with each size class and the corresponding residence time.

and L_{Th} represent net removal fluxes (d.p.m. $\text{l}^{-1} \text{ day}^{-1}$) of dissolved, colloidal, small- and large-particle ^{234}Th , respectively.

Clearly, interactions between colloids, small particles, and large particles are complex²⁸ and presumably mediated by a combination of biotic (bacterial and other microorganism activity, zooplankton grazing) and abiotic (adsorption, aggregation, disaggregation) processes. The critical aspect of our model that determines colloidal ^{234}Th residence times is the coagulation of colloids with small particles. It is conceivable that additional interactions, for example scavenging of dissolved ^{234}Th directly onto the surfaces of picoplankton and fine detritus, may operate to bypass the colloidal pool; such interactive effects could be investigated using additional Th isotopic information^{23,24}. Recent theoretical⁸ and laboratory¹⁰ studies, however, support our model assumptions that coagulation is the rate-limiting step for the transfer of reactive metals from the dissolved to the particulate phase. Moreover, the simplified scavenging model used here allows the calculation of residence times using a single Th isotope^{19–21}.

The mean residence time (τ) of ^{234}Th in the i th size class is calculated using $\tau_i = A_{\text{Th}}^i / R_i$, where A_{Th}^i is the ^{234}Th activity and R_i is the net removal flux. We calculated residence times for each size class using average ^{234}Th values for the upper 150 m (summarized in Table 1). The mean residence time of ~10 days calculated for ^{234}Th in the colloidal fraction is within a factor of 2 of the residence time of ^{234}Th on small particles and 6 times less than for the dissolved pool. The extremely short residence time of ^{234}Th on large particles (<1 day) is consistent with their rapid export from the surface waters.

One of the intriguing aspects of the recent 'dissolved' organic carbon (DOC) data is the large vertical and horizontal gradients in the surface oceans^{4,5}. Although the amount of DOC in the oceans is at present controversial^{4–7}, such spatial variability is unlikely to be eliminated because of DOC blank corrections²⁹. The observed gradients imply that DOC is produced and remineralized more rapidly than previous estimates suggested^{13–16}. Our size-fractionated ^{234}Th results allow for an estimate of the time-scale over which high-molecular-weight colloidal matter is cycled in the upper ocean. In relating the residence time of colloidal ^{234}Th to colloids in general, we must assume that ^{234}Th adsorbs on all colloids. Given the high reactivity of ^{234}Th for oceanic particle surfaces^{19–21}, this is a reasonable approximation. The implication of our results is that, on average, the high-molecular-weight component of 'dissolved' organic carbon is cycled on the order of ~1–2 weeks in the surface open ocean. Moreover, such high colloidal turnover rates have recently been reported in the Gulf of Mexico¹¹.

The mean residence time of the colloidal size class reported here is comparable to DOC residence times of 30–40 days estimated from incubation experiments and of 10–160 days determined *in situ* during a spring phytoplankton bloom³⁰. Such rapid turnover times are considerably shorter than the previous estimate for the mean apparent ^{14}C age of DOC in the upper ocean of >1,000 years³¹, further suggesting that some fraction of DOC is actively involved in carbon cycling in ocean surface waters³¹. Indeed, Benner *et al.*⁶ report that high-molecular-weight components of dissolved organic matter are reactive and support much of the heterotrophic activity in the surface ocean.

Thus, the size-fractionated^{23,24} Th results reported here provide new evidence for a more dynamic role of 'dissolved' organic carbon in the ocean carbon cycle than previously believed³². □

Received 30 March; accepted 31 July 1992.

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ACKNOWLEDGEMENTS. We thank A. F. Michaels and the Bermuda Biological Station for Research, Inc. for providing the sampling opportunity and ancillary data, E. R. M. Druffel, M. P. Bacon, P. H. Santschi, M. Baskaran and B. D. Honeyman for comments, and R. M. Moore, J. E. A. Andrews and M. C. Hartman for technical assistance. Financial support was provided by NSERC of Canada, WHOI, the NOAA Sea Grant Program and the NSF.