

Role of colloids in upper ocean biogeochemistry in the northeast Pacific Ocean elucidated from ^{238}U – ^{234}Th disequilibria

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Abstract

Detailed upper ocean profiles of ^{234}Th in dissolved ($<10,000$ Daltons), colloidal (10,000 Da– $0.45\ \mu\text{m}$), and particulate ($>0.45\ \mu\text{m}$) forms were measured at a station ($46^{\circ}45'\text{N}$, 126°W) in the northeast Pacific Ocean. On average, dissolved, colloidal, and particulate ^{234}Th accounted for ~ 78 , 12, and 10% of the total ^{234}Th in the euphotic zone (0–100 m). A highly positive correlation exists between colloidal ^{234}Th and chlorophyll *a*; both are characterized by higher concentrations in surface waters, a subsurface maximum at 55 m in the seasonal thermocline, and undetectable levels below the euphotic zone. POC:Chl *a* ratios in the water column suggest phytoplankton as primary producers of the colloidal material. Scavenging residence times of dissolved, colloidal, and particulate ^{234}Th with respect to their removal processes in the euphotic zone are ~ 50 , 6, and 8 d. The scavenging rate constant of Th apparently increases with the concentration of colloids.

Within the past few years, the role of colloids in oceanic biogeochemical processes has been increasingly recognized from laboratory experiments (Niven and Moore 1988; Honeyman and Santschi 1991) and field observations (Moran and Moore 1989; Baskaran et al. 1992; Moran and Buesseler 1992, 1993). Although the term “colloids” is still subject to an operational definition, there is a general consensus that colloids fall largely in the nanometer to submicrometer size range (Hurd and Spencer 1991). The conventional procedure of using membrane filters with pore sizes in the range of 0.2– $1\ \mu\text{m}$ does not isolate colloidal material, but includes it in the “dissolved” (<0.2 – $1\ \mu\text{m}$) fraction. As a consequence, what is elucidated from the sampling scheme about the kinetic and equilibrium behavior of chemicals may be misleading or even at odds with theory. A case in point is the so-called particle concentration effect on the distribution coefficient of Th, which, after taking into account the role of colloids, can be dismissed for most oceanic conditions (Honeyman and Santschi 1991; Moran and Buesseler 1993).

Chemical scavenging and particle dynamics in the upper ocean are controlled to a large extent by biological processes, which typically operate on time scales of days to months. With a half-life of 24.1 d and a strong affinity for particles, ^{234}Th is an excellent tracer to study such processes. To add to the emerging data and further elucidate the role of colloids, we report detailed profiles showing the partitioning of ^{234}Th between dissolved ($<10,000$ Daltons), colloidal (10,000 Da– $0.45\ \mu\text{m}$), and particulate ($>0.45\ \mu\text{m}$) phases in the upper water column (0–250 m) at a site ~ 140 km off the Washington coast in the northeast Pacific Ocean.

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Methods

Seawater samples of 20-liters were collected on 7 August 1993 onboard the RV *Wecoma* with Niskin bottles mounted on a CTD rosette. The samples were drained from the bottles into 20-liter polyethylene carboys and immediately stored in the dark at ~ 2 – 3°C before filtration. The samples were prefiltered to isolate particulates and then ultrafiltered to isolate colloids from the bulk solution. Prefiltration was performed within 1 h of sample collection. Samples were retrieved from the walk-in freezer one at a time for filtration with a Millipore Pellicon Cassette system (Millipore XX42 P2K 60). We used cross-flow filtration with a $0.45\text{-}\mu\text{m}$ Durapore filter cassette (Millipore HVMP000C5) to concentrate $>0.45\text{-}\mu\text{m}$ particles in the retentate. The filter cassette has a membrane surface of $0.46\ \text{m}^2$ embedded in polypropylene screens. By using cross-flow prefiltration, we realized at least two benefits. First, it is time-efficient, taking only ~ 10 min to process a 20-liter sample and achieve a concentration factor of 30–50 for $>0.45\text{-}\mu\text{m}$ particles in the final retentate. Second, and more importantly, the use of a high tangential flow to sweep across the membrane surface minimizes the artifacts of solute polarization, particle breaking, and coalescing of colloids onto particulates commonly associated with dead-ended membrane filtration.

Following prefiltration, the retentate was immediately spiked with ^{230}Th and acidified with double-distilled HCl to pH ~ 2 and the filtrate returned to the freezer until ultrafiltration. At the conclusion of prefiltration (of all samples), the prefilter was switched to an ultrafilter cassette (Millipore PTGC0005) with a nominal molecular weight cutoff of 10,000 Da. The ultrafilter membrane was constructed of polyethersulfone with a surface area of $0.46\ \text{m}^2$ and a nominal pore size of 1–2 nm, which approximates the lower size limit of colloids (Whitehouse et al. 1990). It typically takes ~ 1 h to process a 20-liter sample with a concentration factor of 20–40 for colloids. The filtrate and retentate from ultrafiltration were immediately acidified and spiked in the same way as the prefil-

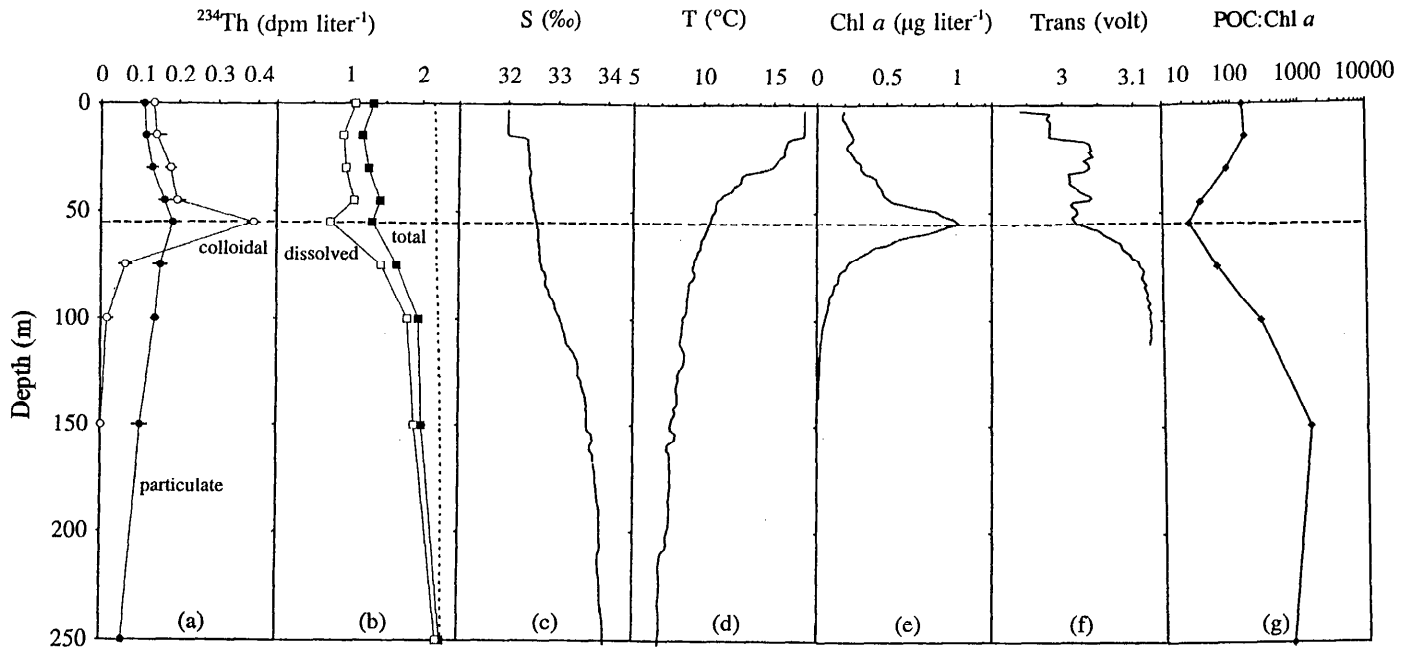


Fig. 1. Profiles of (a) ^{234}Th in colloidal and particulate phases, (b) ^{234}Th in dissolved phase, total ^{234}Th , and ^{238}U (dotted line; calculated from salinity), (c) salinity, (d) temperature, (e) chlorophyll *a*, (f) light transmission, and (g) POC:Chl *a* in the upper water column of the study site ($46^{\circ}45'\text{N}$, 126°W , water depth = 2,590 m), 7 August 1993. Error bars for the ^{234}Th data based on counting statistics (not shown if smaller than the data symbol).

tration retentate. Thus, every sample was size fractionated into three fractions. In this work, ultrafiltration of all samples was completed within 24 h of sample collection.

Th was separated and purified with the following standard methods. Briefly, Th isotopes were coprecipitated with $\text{Fe}(\text{OH})_3$, dissolved in 8 N HCl, and separated from U by anion exchange resin (AG1x8, 100–200 mesh). This was done within 3 d of sample collection. After further purification in the laboratory, the Th source was mounted onto a stainless steel planchet. Chemical yield of Th (generally 60–90%) was determined by counting ^{230}Th in an α -spectrometer with calibrated silicon surface-barrier detectors. Counting efficiency and α/β cross-talk of the β counter was calibrated with a set of ^{230}Th and ^{234}Th standards. Background of the β counter stayed at 0.40 ± 0.03 cpm during this work. Corrections were made for ^{234}Th decay between sample collection and counting and for the ingrowth of ^{234}Th from ^{238}U decay between sample collection and U/Th separation with the equation

$$^{234}\text{Th} \text{ (dpm liter}^{-1}\text{)} = \frac{\text{cpm}}{REV} \exp[\lambda(t_3 - t_1)] - ^{238}\text{U} \{ \exp[\lambda(t_2 - t_1)] - 1 \}.$$

cpm is the count rate of ^{234}Th in the β counter (corrected for background and cross-talk), *R* is chemical recovery, *E* is counting efficiency, *V* (in liters) is sample volume, λ ($= 2.0 \times 10^{-5} \text{ min}^{-1}$) is the decay constant of ^{234}Th , ^{238}U is the activity of ^{238}U (in dpm liter $^{-1}$), and t_1 , t_2 , and t_3 are the time (to the minute) of sample collection, U/Th separation, and beginning of β counting.

Concentrations of colloidal and particulate ^{234}Th were calculated by subtracting the concentration of ^{234}Th in the filtrate from that in the retentate and dividing the difference by the concentration factor. The adsorptive loss of ^{234}Th in the sampling process was evaluated by cleaning the filtration system and sample containers with 0.5 N HNO_3 and 4 N HCl, respectively; ^{234}Th was not detectable in the lechates. This finding, along with the data for the 250-m sample, which shows radioactive equilibrium between ^{238}U and total ^{234}Th (see Fig. 1b), demonstrates that mass balance of ^{234}Th can be attained with the protocol described.

We collected the following ancillary data to interpret the ^{234}Th data in the context of hydrodynamic and biogeochemical processes. Salinity, temperature, and light transmission were obtained directly from the CTD in tandem with the collection of water samples. Particulate organic C (POC) and N (PON) collected on precombusted GF/F filters were measured by standard elemental analysis (Hedges and Stern 1984). Chl *a* was measured on-board with the standard fluorometric method (Strickland and Parsons 1972) used to establish a calibration ($\text{Fluo} = 1.10 \times \text{Chl } a + 0.085$, $r^2 = 0.993$) to convert the output (in V) of the CTD-mounted fluorometer to Chl *a* concentration (in $\mu\text{g liter}^{-1}$).

Results

Figure 1 illustrates profiles of dissolved, colloidal, and particulate ^{234}Th , along with ancillary data for the sampling site. A 15-m mixed layer with an underlying sea-

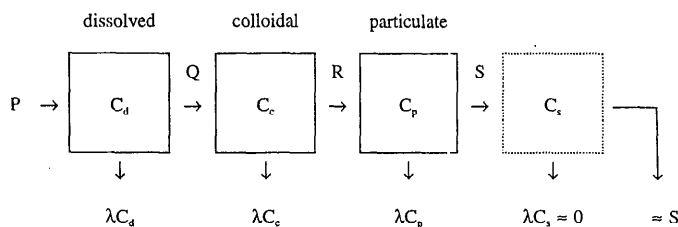


Fig. 2 Scavenging model used to calculate residence times of dissolved, colloidal, and particulate ^{234}Th in the upper ocean. The dotted box indicates a large-particle pool not considered in the calculation because its state cannot be represented by 20-liter samples due to very rapid removal and, hence, low abundance of such particles in the water column.

sonal thermocline characterizes the water column. The fluorescence profile revealed a pronounced subsurface chlorophyll maximum at 55-m depth—the depth of the 1–10% light level and a sharp decrease beneath the euphotic zone. Such profiles typify chlorophyll distributions in stable oceanographic regimes throughout the North Pacific (Longhurst and Harrison 1989). Elevated concentrations of suspended particulate materials were evident throughout the upper water column (0–60 m) as indicated by reduced light transmission. POC and PON concentrations were also highest in the upper water column and poorly correlated with chlorophyll concentration ($r = 0.26$ and 0.59 , respectively). Atomic ratios for POC to PON were lowest (6.8) in the chlorophyll maximum, closely matching Redfield stoichiometry for phytoplankton, and increased to ≤ 11 above and below this depth. If we assume a range of POC:Chl ratios for field samples of phytoplankton (30–100 wt/wt; Weischmeyer and Lorenzen 1984), the phytoplankton contribution to POC can be calculated from Chl *a* estimates. The calculation suggests that phytoplankton dominated POC in the seasonal thermocline (POC:Chl = 25 at 55-m depth). In comparison, phytoplankton biomass comprised a much lower fraction of POC in the overlying mixed layer (POC:Chl = 150–160) and a negligible fraction below the euphotic zone (POC:Chl > 700). At these other depths, a large fraction of POC was probably heterotrophic organisms or nonliving organic detritus.

As in most previous observations, dissolved ^{234}Th constituted the largest pool of ^{234}Th , whereas colloidal and particulate ^{234}Th were smaller pools of comparable magnitude in the surface water. On average, dissolved, colloidal, and particulate ^{234}Th accounted for ~ 78 , 12, and 10% of the total ^{234}Th in the euphotic zone (0– ~ 100 m). Total ^{234}Th exhibited a typical disequilibrium relationship with ^{238}U in the ocean surface: a large ^{234}Th deficiency in the upper euphotic zone followed by a downward increase of ^{234}Th toward equilibrium with ^{238}U at depth. A striking feature is the subsurface colloidal ^{234}Th maximum and highly positive correlation between colloidal ^{234}Th and Chl *a* calibrated from fluorescence ($r = 0.99$, $n = 9$). Another noteworthy aspect of the data is that colloidal ^{234}Th is consistently higher than particulate ^{234}Th in and above the seasonal thermocline, whereas the

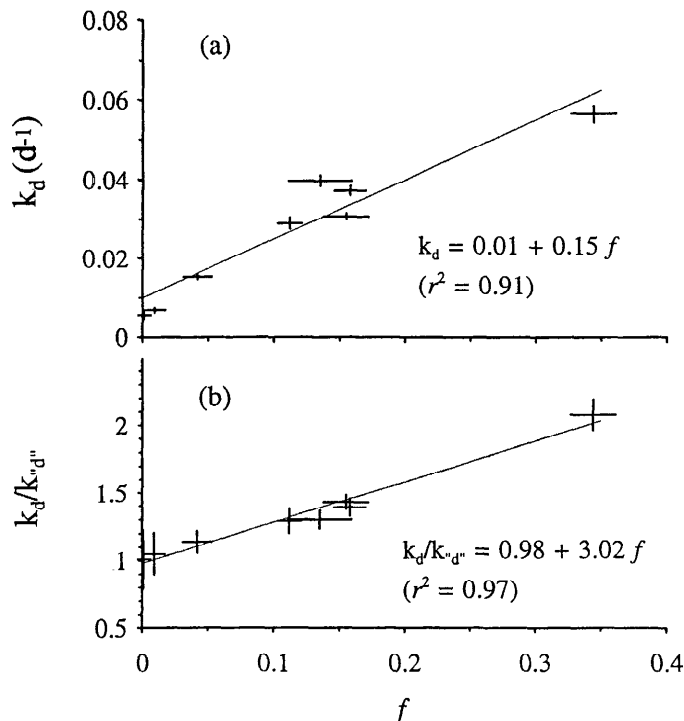


Fig. 3. (a) Scavenging rate constant (k_d) vs. f (a) and k_d/k_d^0 vs. f (b). See text for explanation.

opposite is true below the seasonal thermocline. Furthermore, note a greater inverse correlation between dissolved ^{234}Th and colloidal ^{234}Th ($r = -0.88$, $n = 9$) than between dissolved ^{234}Th and particulate ^{234}Th ($r = -0.67$, $n = 9$). These observations are in line with the perception that colloids are mainly organic-rich matter produced in the upper water column by biological activities, especially from exudates of phytoplankton (Niven and Moore 1988; Wells and Goldberg 1993) and that they are key to removing dissolved ^{234}Th from solution. The disappearance of colloidal ^{234}Th , but not particulate ^{234}Th below the euphotic zone, is consistent with removal of colloids and associated chemicals by aggregation and sedimentation processes.

As with previous studies (Moran and Buesseler 1992, 1993), we used a three-box scavenging model (Fig. 2) to quantify fluxes and residence times of ^{234}Th in the three size classes. The model assumes steady state distribution of ^{234}Th and that advection and diffusion terms are negligible in the equation of conservation. With only one tracer, it is also necessary to consider the scavenging processes to be irreversible, which is more valid in surface waters than in the deep ocean (Huh and Beasley 1987). With these assumptions, the mass balance between dissolved, colloidal, and particulate ^{234}Th can be written as

$$\frac{\partial C_d}{\partial t} = P - \lambda C_d - Q = 0,$$

$$\frac{\partial C_c}{\partial t} = Q - \lambda C_c - R = 0,$$

Table 1. Scavenging residence times (τ) of size-fractionated ^{234}Th . As in the text, size classes are indicated by subscript: d —dissolved, c —colloidal, p —particulate, and “ d ”—“dissolved.” All errors ($\pm 1\sigma$) were propagated from counting statistics.

Depth (m)	τ_d	τ_c	τ_p	$\tau_{\text{“}d\text{”}}$	$\tau_{\text{“}d\text{”}}/\tau_d^*$	f^\dagger
	(d)					
0	35±2	4.9±0.4	4.6±0.5	44±2	1.29±0.09	0.11±0.01
15	25±1	4.4±0.8	4.0±0.4	33±1	1.30±0.07	0.14±0.02
30	27±1	5.9±0.5	4.9±0.6	37±1	1.39±0.07	0.16±0.01
45	33±1	7.2±0.8	7.3±0.7	47±1	1.43±0.05	0.16±0.02
55	18±1	13±1	7.3±0.9	37±1	2.08±0.11	0.34±0.02
75	65±3	3.1±0.9	9.6±1.3	73±4	1.14±0.08	0.042±0.011
100	146±15	1.4±1.3	18±3	153±16	1.05±0.16	0.009±0.008
150	179±27	0.2±0.9	13±4	170±26	1.01±0.22	0.001±0.005

* First-order scavenging rate constant is defined as the reciprocal of residence time ($k = \tau^{-1}$); therefore, $\tau_{\text{“}d\text{”}}/\tau_d = k_d/k_{\text{“}d\text{”}}$.

† f is the fraction of “dissolved” ^{234}Th in colloidal form.

$$\frac{\partial C_p}{\partial t} = R - \lambda C_p - S = 0.$$

C_d , C_c , and C_p are the concentrations of ^{234}Th (dpm kg^{-1}) in dissolved, colloidal, and particulate forms; λ ($= 0.0288 \text{ d}^{-1}$) is the decay constant of ^{234}Th ; P is the production rate of dissolved ^{234}Th from ^{238}U decay (calculated by $P = \lambda \times \text{concn of } ^{238}\text{U}$); and Q , R , and S are the flux of ^{234}Th from solution to colloids, from colloids to small (i.e. suspended) particles, and from small particles to large (i.e. settling) particles. The scavenging residence time of ^{234}Th in the three pools can then be calculated as

$$\tau_d = \frac{C_d}{Q}, \quad \tau_c = \frac{C_c}{R}, \quad \tau_p = \frac{C_p}{S}.$$

In light of the large variation in size-fractionated distribution of ^{234}Th with depth, scavenging residence times were calculated at each depth. The results, given in Table 1 not only confirm the brief residence times of colloidal matter in the upper ocean (Baskaran et al. 1992; Moran and Buesseler 1992, 1993) but also suggest a direct impact of colloids on chemical scavenging.

One way to assess the role of colloids in chemical scavenging is by comparing the scavenging residence time (τ_d) and first-order scavenging rate constant (k_d ; $= \tau_d^{-1}$) of truly dissolved ^{234}Th with those of “dissolved” ^{234}Th ($\tau_{\text{“}d\text{”}}$ and $k_{\text{“}d\text{”}}$). The latter can be calculated with a simplified two-box model by pooling the colloidal phase and the truly dissolved phase to yield the operationally defined “dissolved” ($< 0.45 \mu\text{m}$) phase. $\tau_{\text{“}d\text{”}}$ values thus calculated are also listed in Table 1 for comparison with τ_d . The effect of colloids (expressed in terms of f : fraction of “dissolved” ^{234}Th on colloids) on k_d is illustrated in Fig. 3a. The quasi-linear relationship between k_d and f suggests a lower limit of $\sim 0.005 \text{ d}^{-1}$ (at $f = 0$; implying direct adsorption onto $> 0.45\text{-}\mu\text{m}$ particles) and an upper limit as high as 0.16 d^{-1} (by extrapolation of $f = 1$) for k_d in the upper water column. Figure 3b shows that Th scavenging by colloids will lead to lower apparent scavenging rates (i.e. $k_{\text{“}d\text{”}}$, with respect to corresponding true scavenging rates, k_d) by a factor up to ~ 4 (at $f = 1$).

Discussion

Although ^{234}Th has been proposed to be a potential tracer for quantifying new production in the upper ocean (Coale and Bruland 1987; Murray et al. 1989), the theoretical basis is unclear but may lie in the role of colloids. Although the high correlation between colloidal ^{234}Th and fluorescence is reported here for the first time, it has been observed in the southern California Bight (Huh unpubl. data) and could be a common phenomenon. As a fundamental biological quantity commonly measured in oceanographic cruises, Chl a data can be acquired relatively readily. If its linkage with colloidal ^{234}Th (and by extension, with other radionuclides and trace metals) is substantiated by further observation, Chl a may be a viable parameter for modeling chemical scavenging.

Previous studies indicated that scavenging of reactive metals from seawater takes place by the formation of organo-metal complexes on suspended particles coated with an organic film resembling humic acids (Balistrieri et al. 1981). Assuming that metal binding sites were provided by organic ligands, Hirose and Tanoue (1994) constructed a vertical profile of Th complexing capacity in the western North Pacific that showed a subsurface maximum below the mixed layer followed by rapid decrease with depth. Now, because we recognize the abundance of colloids in surface waters, especially near the seasonal thermocline (Wells and Goldberg 1993), it becomes more intuitive to think of colloids instead of suspended particles as the major provider of organic ligands as metal binding sites. Note that although the activity of ^{234}Th in suspended particles is comparable to that in colloids, much of the particulate ^{234}Th originates from colloidal ^{234}Th , as depicted by the model. Our results now provide a plausible interpretation to the subsurface maximum of “dissolved” ^{234}Th often found in more stratified water columns (Huh and Bacon 1985).

In addition to chemical scavenging of particle-reactive species, colloids may also play an important role in carbon cycling in the upper ocean. Time-series data reported recently for both coastal waters and open-ocean sites have demonstrated that the consumption of dissolved inor-

ganic C in surface waters greatly exceeds that predicted from nitrate consumption and the Redfield C:N ratio, suggesting that the growth of plankton as a sink for atmospheric CO₂ may have been underestimated (Sambrotto et al. 1993). One plausible explanation to reconcile the carbon overconsumption is the presence of a large pool of carbon-rich material that cycles through the upper ocean rapidly in a yet unknown way (Toggweiler 1993). The brief residence time of colloids in the upper ocean and increasing evidence that colloidal organic C may account for a significant fraction of submicron filterable organic C (Benner et al. 1992; Kepkay and Johnson 1992) suggest that colloids may indeed play an all-important role in biogeochemical processes.

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