

$^{234}\text{Th}:$ ^{238}U disequilibria within the California Current¹

Kenneth H. Coale and Kenneth W. Bruland

Center for Marine Studies, University of California, Santa Cruz 95064

Abstract

Profiles of dissolved and particulate ^{234}Th were determined at several stations within the California Current. Modeling of the disequilibria between the ^{234}Th and ^{238}U within the surface waters provides for estimates of the residence time of dissolved thorium with respect to particle scavenging (τ_d varies from 6 to 50 days), the particle residence time (τ_p varies from 2 to 20 days), and the particulate ^{234}Th flux exiting the surface layer. The model-derived, first-order scavenging rate constant for dissolved thorium is observed to be proportional to the rate of primary production. Particle residence times seem to be governed by the rate of zooplankton grazing and the types of zooplankton present. Model-derived particulate ^{234}Th fluxes are in good agreement with direct measurements by sediment traps.

^{234}Th ($t_{1/2} = 24.1$ d) is continuously produced from the alpha decay of ^{238}U ($t_{1/2} = 4.5 \times 10^9$ yr) in seawater. Uranium in seawater exists principally as the dissolved $\text{UO}_2(\text{CO}_3)_3^{4-}$ species and is relatively unreactive to particulate absorption ($\leq 0.1\%$ of uranium in seawater is particulate; Hodge et al. 1979). As a result uranium exhibits a conservative distribution in the open ocean [^{238}U (dpm liter⁻¹) = $0.07081 \times$ salinity; Ku et al. 1977]. In contrast, dissolved thorium exists as the hydrolysis product $\text{Th}(\text{OH})_n^{(4-n)+}$ (Turner et al. 1981)—particle reactive species that can be removed from the dissolved state by adsorption onto particles. The extent of radioactive disequilibrium occurring in the water column between the particle reactive daughter, ^{234}Th , and its soluble parent, ^{238}U , can be used to quantify removal rates for thorium.

The use of $^{234}\text{Th}:$ ^{238}U disequilibria to study the scavenging of thorium from oceanic surface waters began with the work of Bhat et al. (1969) and was expanded on by Matsumoto (1975), Knauss et al. (1978), and Kaufman et al. (1981). In these studies, low $^{234}\text{Th}:$ ^{238}U activity ratios (~ 0.2) were observed in near-coastal shelf waters, implying intensified scavenging with a mean residence time of thorium, with respect to nonradioactive removal, of the order of 10

days. In open ocean surface waters, activity ratios were closer to equilibrium (~ 0.75 – 1.0) with mean residence times for thorium of the order of hundreds of days. Comparable studies on the isotope pair ^{228}Th ($t_{1/2} = 1.91$ yr); ^{228}Ra ($t_{1/2} = 5.7$ yr) have yielded similar results (e.g. Broecker et al. 1973; Li et al. 1979, 1980; Feely et al. 1980). An important aspect of these studies is that only total thorium isotopes in seawater are reported; i.e. the thorium isotope content of unfiltered samples. Hence, these residence times represent a combination of the time required for the uptake of dissolved thorium by the particulate matter with that for the removal of the particulate thorium. Bhat et al. (1969) assumed that essentially all ^{234}Th in seawater was in particulate form, whereas Matsumoto (1975) assumed particulate ^{234}Th to be an insignificant part of the total ^{234}Th .

In this paper, we present several profiles of ^{234}Th in both dissolved and particulate form. This allows a more informative scavenging model to be applied to the surface euphotic layer. Since the decay of ^{238}U (which exists almost entirely in the dissolved form) produces dissolved ^{234}Th at a constant rate, the observed dissolved and particulate disequilibria can yield both the rate of removal from dissolved to particulate form and the rate of removal of particulate ^{234}Th . The rate of dissolved thorium removal onto particles appears to be a function of primary productivity or particle production, whereas the mean life of the par-

¹ This research was supported by National Science Foundation grants OCE 77-2366684, OCD 79-19928, and OCE 79-23322.

Table 1. Cruise designations and station locations.

Cruise designation	RV	Date	Location
MLML Pit cruise-1	<i>Acania</i>	31 Mar 77	36°42'N, 122°13'W
CC III cruise-1	<i>Acania</i>	31 Mar 77	36°47'N, 122°10'W
CC III cruise-2	<i>Scammon</i>	8 May 77	36°47'N, 122°10'W
CEROP I	<i>Wecoma</i>	11-17 Nov 78	37°00'N, 124°12'W
CEROP II	<i>Wecoma</i>	9-16 Jul 78	36°52'N, 122°53'W
MLML Pit cruise-2	<i>Wecoma</i>	9-17 Dec 78	36°50'N, 123°00'W
CEROP III	<i>Wecoma</i>	2-20 Mar 79	35°59'N, 125°58'W
VERTEX I	<i>Wecoma</i>	24 Aug-9 Sep 80	36°36'N, 123°48'W

ticles carrying ^{234}Th in the surface layer is a function of particle removal processes such as zooplankton grazing activity and the resultant production of fecal pellets. The half-life of ^{234}Th is optimal to elucidate such processes occurring in the euphotic zone on time scales of one to hundreds of days and the ^{234}Th : ^{238}U disequilibrium can rapidly respond to seasonal changes in the oceanographic regime.

We thank the crew and officers of the RV *Scammon*, *Acania*, and *Wecoma*, and S. Johnson and R. Franks for their assistance with the shipboard collection and radiochemical processing of these samples; we

also thank D. DeMaster for reviewing the manuscript.

Sampling and analysis

Samples were collected within the California Current off central California during several different cruises. Cruise designations, dates, and locations are presented in Table 1, and cruise locations are shown in Fig. 1.

Seawater samples were collected with Teflon-coated, 30-liter, General Oceanics Top Drop or Go-Flo samplers. Upon surfacing, the sampler was pressurized with filtered nitrogen and seawater passed via Teflon

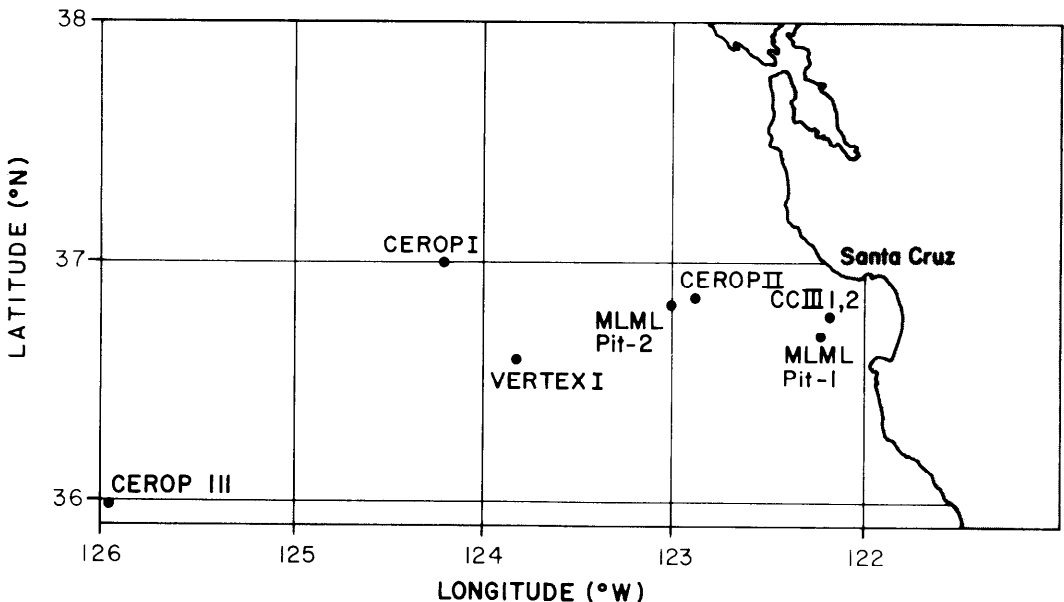


Fig. 1. Station locations.

tubing to a Teflon filter sandwich supporting a preweighed 142-mm Nuclepore membrane filter (0.3- μm pore size). Filtrates were collected in 20-liter Cubitainers and acidified with 50 ml of concentrated HCl. Filters (from 55 to 110 liters of seawater) were folded and stored frozen until analysis. This processing typically was completed within 30 min from the time the sampler reached the surface.

Due to the short half-life of ^{234}Th , rapid separation from its ^{238}U parent is necessary to avoid significant "ingrowth" corrections. After acidification, 20 dpm of ^{230}Th yield tracer and 100 mg of Fe (as FeCl_3) were added to the dissolved samples. The samples were thoroughly mixed by bubbling with filtered nitrogen for 60 min for spike equilibration. Such vigorous mixing of filtered seawater samples acidified to $\text{pH} = 1.5$ allows spike equilibration to occur within 60 min. The pH was then adjusted to 8 by adding NaOH, and the $\text{Fe}(\text{OH})_3$ precipitate formed was further mixed for 60 min to ensure efficient scavenging. The Cubitainers were inverted and the precipitate allowed to settle. The precipitate was drained and collected on 47-mm glass-fiber filters. The $\text{Fe}(\text{OH})_3$ was dissolved in 40 ml of 8 N HCl and passed through an anion exchange column (AG 1 \times 8, 100–200 mesh, 7.5 ml of resin volume). The column effluent and rinses (four successive 5-ml portions of 8 N HCl) containing the Th fraction were collected in polybottles for return to UCSC; the U and Fe remained on the column.

At UCSC, the 8 N HCl fraction was taken to dryness. The residue was taken up in ~ 10 ml of 1.5 N HCl and passed through an anion exchange column (AG 1 \times 8, 100–200 mesh, 5-ml resin volume) to separate lead for subsequent ^{210}Pb analysis. The column effluent and rinses containing the Th fraction were taken to dryness, the residue was taken up in ~ 10 ml 7.5 N HNO_3 and passed through yet another anion exchange column (AG 1 \times 8, 100–200 mesh, 3-ml resin volume). Under these conditions Th adsorbs and the remaining salts are rinsed from the column. Th is eluted with 25 ml of 8 N HCl, taken to dryness, taken up in 2 N, $\text{pH} 2.2$ NH_4Cl solution, and electro-

deposited on Pt planchets (Goldberg and Koide 1962).

The particulate samples were dried at 55°C for 48 h, weighed, and transferred to 40-ml Teflon bombs for spiking and digestion (Egimann and Betzer 1976). The particulate samples were taken to dryness, then processed like the dissolved samples, except that no 8 N HCl anion exchange column separation was performed.

The samples were alpha-counted with silicon surface barrier detectors to determine the yield by the ^{230}Th activity. The planchets were then mounted in a (Delrin) planchet holder, covered with Mylar (6.6 mg cm^{-2}), and beta-counted using low background (0.1–0.2 cpm) anticoincidence, gas flow beta detectors to determine their ^{234}Th activity. The alpha detectors were calibrated with a set of plated ^{230}Th standards. The plated ^{230}Th standards yielded alpha detector efficiencies within 0.5% of those obtained with NBS certified, plated ^{238}Pu and ^{241}Am standards (corrected for the difference in source diameter, Wang et al. 1975). The beta detectors were calibrated with plated ^{238}U standards with ^{234}Th , $^{234\text{m}}\text{Pa}$ in secular equilibrium. A small correction was applied for alpha particles penetrating the Mylar and contributing to the apparent beta activity (~ 0.002 cpm per alpha dpm). For the dissolved and particulate samples, the ^{230}Th spike added 0.03 cpm per sample. The seawater samples analyzed required no significant correction for any contribution to the beta count rate from natural alpha-emitting Th isotopes (i.e. ^{228}Th). The resultant ^{234}Th activity was yield-corrected and then decay-corrected to the time of separation and collection.

As a check on the accuracy and precision of the determination of ^{234}Th , we analyzed four equilibrated deep water samples from the central North Pacific by the techniques described above (these samples had been filtered and stored acidified for 1 year). Both Turekian and Chan (1971) and Ku et al. (1977) have shown uranium to have a conservative distribution in oceanic waters with the uranium activity, ^{238}U (dpm liter^{-1}) = $0.07081 \times S\text{‰}$. Thus, the ^{234}Th activity determined in the equilibrated samples should

Table 2. Accuracy and precision verification of the ²³⁴Th determination. "Old" equilibrated Hawaii-77 (sta. 17) filtered and acidified deep seawater samples.

Depth (m)	²³⁴ Th*	²³⁸ U†	Activity ratio <i>A^d_{Th}:A_U</i>
	(dpm liter ⁻¹)		
1,000	2.383±0.006	2.348	1.015 ^o
4,000	2.418±0.079	2.364	1.022 ⁶
5,000 (A)	2.350±0.087	2.363	0.994 ³
5,000 (B)	2.364±0.046	2.363	1.000 ³
			$\bar{x} = 1.008 \pm 0.013$
mean precision of individual counts = 2.3% (RSD)			

* Each sample counted three times.
† Based on U:salinity ratio of Ku et al. 1977.

equal the ²³⁸U activity calculated by the salinity relationship. The results of this exercise are presented in Table 2. On the basis of a single count, analogous to most sample determinations, the precision is estimated to be 2.3% (RSD). The four calibration samples were each counted three times and averaged to obtain a relative precision of 1.3%. The mean ²³⁴Th:²³⁸U activity ratio of the four samples was 1.008 ± 0.013, in excellent agreement with the expected equilibrium value.

A surface water scavenging model

Historically, studies of ²³⁴Th in surface seawater have involved the determination of total ²³⁴Th:²³⁸U (or ²²⁸Th:²²⁸Ra) activity ratios. Neglecting advection and diffusion terms, the following equation has been used to describe the change in total ²³⁴Th activity in surface waters with respect to time:

$$\frac{\partial A^{\Sigma}_{Th}}{\partial t} = A_U \lambda_{Th} - A^{\Sigma}_{Th} \lambda_{Th} - A^{\Sigma}_{Th} \lambda_c \quad (1)$$

where *A_U* is the activity of ²³⁸U, *λ_{Th}* is the decay constant of ²³⁴Th, *A^Σ_{Th}* is the activity of total ²³⁴Th, and *λ_c* is a first-order scavenging rate constant for ²³⁴Th. The product *A_Uλ_{Th}* is equal to the rate of production of ²³⁴Th, the product *A^Σ_{Th}λ_{Th}* is the rate of radioactive decay of ²³⁴Th, and the product *A^Σ_{Th}λ_c* is the rate of ²³⁴Th removal by processes other than radioactive decay. At steady state

$$\frac{\partial A_{Th}}{\partial t} = 0$$

and the mean life of the total ²³⁴Th, *τ_Σ*, in the surface waters is

$$\tau_{\Sigma} = \frac{1}{\lambda_c} = \frac{1/\lambda_{Th}}{(A_U/A^{\Sigma}_{Th}) - 1} \quad (2)$$

However, if we determine both the dissolved and particulate fractions of ²³⁴Th, we can apply a more informative scavenging model to the surface waters. Assuming advection and diffusion terms to be negligible, we can express the rate of change in dissolved ²³⁴Th activity by the equation

$$\frac{\partial A^d_{Th}}{\partial t} = A_U \lambda_{Th} - A^d_{Th} \lambda_{Th} - J_{Th} \quad (3)$$

where *A^d_{Th}* is the dissolved ²³⁴Th activity. Since ²³⁸U exists as a dissolved species, its decay will produce dissolved ²³⁴Th at the rate of *A_Uλ_{Th}*. *A^d_{Th}λ_{Th}* is the loss by radioactive decay of dissolved ²³⁴Th, whereas *J_{Th}* is the rate of removal of ²³⁴Th from the dissolved to particulate form. Similarly for the particulate ²³⁴Th:

$$\frac{\partial A^p_{Th}}{\partial t} = J_{Th} - A^p_{Th} \lambda_{Th} - P_{Th} \quad (4)$$

where *A^p_{Th}* is the activity of particulate ²³⁴Th. *J_{Th}* is now a source term, *A^p_{Th}λ_{Th}* is the radioactive decay rate of particulate ²³⁴Th, and *P_{Th}* is the rate at which ²³⁴Th is transported out of the surface layer by the particle flux.

Under steady state conditions the mean residence time of dissolved ²³⁴Th in the surface layer with respect to removal onto particles is

$$\tau_d = \frac{A^d_{Th}}{J_{Th}} \quad (5)$$

whereas the mean residence time of particulate ²³⁴Th with respect to removal from the surface layer is

$$\tau_p = \frac{A^p_{Th}}{P_{Th}} \quad (6)$$

When both dissolved and particulate forms of ²³⁴Th are present, the loss of ²³⁴Th due to radioactive decay on suspended particles within the surface zone leads to *τ_d* + *τ_p* being

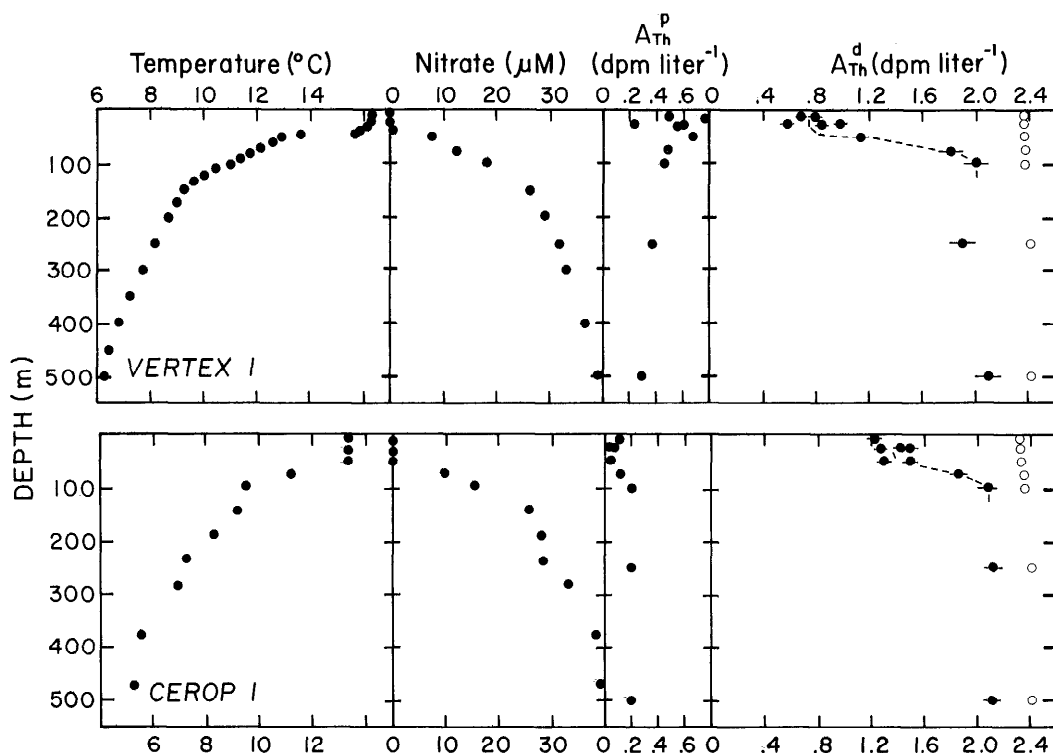


Fig. 2. Vertical profiles of temperature, nitrate, particulate and dissolved ^{234}Th activity (A_{Th}^p and A_{Th}^d) for VERTEX I and CEROP I, II, and III. ^{238}U activity—O.

less than τ_{Σ} . For example, if $A_{\text{Th}}^{\Sigma}:A_{\text{U}} = 0.5$, with $A_{\text{Th}}^d:A_{\text{U}} = 0.3$ and $A_{\text{Th}}^p:A_{\text{U}} = 0.2$, then $\tau_{\Sigma} = 35$ days, whereas $\tau_d = 15$ days and $\tau_p = 14$ days (i.e. $\tau_d + \tau_p = 29$ days).

Results

Vertical profiles of dissolved and particulate ^{234}Th , nitrate (plus nitrite), and temperature in the upper 500 m of the California Current during VERTEX I, CEROP I, II, and III are presented in Fig. 2. The temperature and nitrate profiles delineate the surface mixed layer and the location of the major thermocline and nutricline. The nitrate profiles also indicate the extent of upwelling; for example, the CEROP II station has elevated nitrate levels in the surface mixed layer. Within the eutrophic and mesotrophic California Current the depth of the photic zone (1% light level) is generally within this surface layer.

At depths below 100 m, the total ^{234}Th was always near equilibrium with its parent, ^{238}U , and continued to be throughout the rest of the deep water column. For depths between 1,000 and 4,000 m, the mean $^{234}\text{Th}:$ ^{238}U activity ratios for dissolved, particulate, and total thorium are 0.925 ± 0.062 , 0.065 ± 0.016 , and 0.990 ± 0.064 , with the average total ^{234}Th within 1% of equilibrium with its parent ^{238}U . This was expected because Th is not removed from the deep sea on time scales of less than a year. A detailed discussion of deep water thorium isotopes in both dissolved and particulate forms has been presented elsewhere (Bacon and Anderson 1982).

In contrast, marked deficiencies of both dissolved and total ^{234}Th exist in the surface layer. On MLML Pit cruises 1 and 2, as well as CC III cruises 1 and 2 only near-surface and mixed layer samples were taken. These samples also show marked ^{234}Th deficiencies within the surface mixed layer.

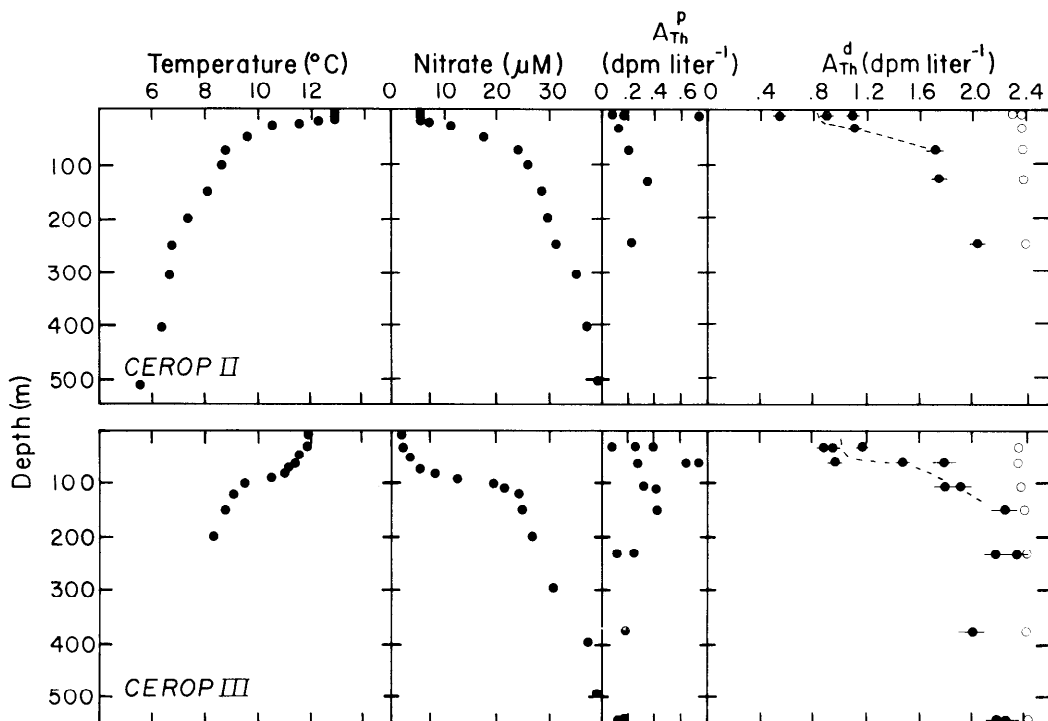


Fig. 2. Continued.

VERTEX I—During the 18 days of *VERTEX I*, there was a well mixed surface layer down to 25 m, a slight decrease in temperature to 45 m, and then a sharp thermocline below 50 m (Fig. 2). The surface nitrate concentration averaged $0.3 \mu\text{M}$. On the basis of detailed primary productivity measurements (Martin et al. 1984), the depth of the photic zone is estimated to be 50 m with an average integrated primary productivity of $47 \pm 7 \text{ mmol C m}^{-2} \text{ d}^{-1}$. This zone of intense biogenic particle production in the surface 50 m corresponds to the zone of marked dissolved ^{234}Th deficiency (Fig. 2). The activity ratio, $A_{\text{Th}}^{\text{d}}:A_{\text{U}}$, within this surface layer for three separate sampling periods during the 18 days, was relatively uniform at 0.33 ± 0.06 , implying steady state conditions. Given this activity ratio, our model implies a mean Th residence time in the dissolved state with respect to removal to particulate form of 17 days.

During *VERTEX I* there was a relatively high concentration of suspended particles, averaging $250 \mu\text{g liter}^{-1}$ in the surface layer.

This decreased rapidly through the thermocline to values near $40 \mu\text{g liter}^{-1}$ at 75 and 100 m. The net zooplankton abundances were relatively low for the California Current (Tuel and Knauer pers. comm.). These observations imply a relatively low zooplankton grazing activity. This is substantiated by the large amount of ^{234}Th in the particulate form; $A_{\text{Th}}^{\text{p}}:A_{\text{U}} = 0.23 \pm 0.09$ in the surface layer. This observed ratio leads to a mean residence time of particulate ^{234}Th of 18 days.

CEROP I—This 1-week sampling period was characterized by a 50-m mixed layer with relatively depleted nitrate levels averaging $0.5 \mu\text{M}$. In the surface layer, $A_{\text{Th}}^{\text{d}}:A_{\text{U}} = 0.58 \pm 0.04$ with no significant variation in A_{Th}^{d} during the week. This activity ratio yields a τ_{d} of 47 days. The suspended particle concentration averaged only $66 \mu\text{g liter}^{-1}$ in the surface layer, and $A_{\text{Th}}^{\text{p}}:A_{\text{U}} = 0.028 \pm 0.016$. This low particulate ^{234}Th activity yields a mean particulate ^{234}Th residence time, τ_{p} , of only 2.4 days.

An intense swarm of salps (mainly *Salpa*

fusiformis and to a lesser extent *Pegea socia*) was present in the California Current during CEROP I. Salp appearance correlated to the surfacing of a strong deep scattering layer observed with the ship's PDR. Silver and Bruland (1981) showed that the frequency of various size classes of food items in fecal pellets produced by these salps reflected the sizes available in the water column, indicating that the salps were indiscriminately packaging the suspended particulate material into large fecal pellets (even bacterial size particles of the order of 0.2–2 μm were seen). The average sinking rates of the salp fecal pellets were of the order of 1,000 m day^{-1} , with maximum sinking rates of 2,700 m day^{-1} (Bruland and Silver 1981). The short particulate ^{234}Th residence time of 2.4 days reported here and the low suspended particulate load are consistent with intense grazing and packaging activity by these animals.

CEROP II—During this week-long period, upwelling was occurring, with surface nitrate values of 5–6 μM . There was also a shallowing of the mixed layer to 20 m. This was a more transient system with substantial variation in dissolved ^{234}Th ; the $A^{\text{d}}_{\text{Th}}:A_{\text{U}} = 0.39 \pm 0.11$ in the surface 50 m. This yields a mean τ_{d} of 22 days.

The net phytoplankton was dominated by diatoms, the net zooplankton by copepods. The average suspended particulate concentration in the surface layer was 200 $\mu\text{g liter}^{-1}$. The $A^{\text{p}}_{\text{Th}}:A_{\text{U}} = 0.12 \pm 0.05$ which yields a mean τ_{p} of 8 days.

CEROP III—CEROP III provided a horizontal transect across the low salinity California Current (sta. 1–3) and then, a week later, the occupation of a station within the current (sta. 12) for 1 week. The mean surface activity ratios for the horizontal transect stations in the California Current were $A^{\text{d}}_{\text{Th}}:A_{\text{U}} = 0.45 \pm 0.10$ and $A^{\text{p}}_{\text{Th}}:A_{\text{U}} = 0.18 \pm 0.10$. These ratios yield a mean τ_{d} of 28 days and τ_{p} of 17 days. At station 12, where a detailed vertical profile was obtained, the surface mixed layer was from 60 to 70 m deep with an average nitrate concentration of 3 μM . $A^{\text{d}}_{\text{Th}}:A_{\text{U}} = 0.46 \pm 0.10$, yielding a mean τ_{d} of 30 days, whereas $A^{\text{p}}_{\text{Th}}:A_{\text{U}} = 0.14 \pm 0.09$, yielding a mean τ_{p} of 12

days. The average suspended particulate load was 115 $\mu\text{g liter}^{-1}$.

MLML Pit, cruise-1—Near-surface samples were collected from a station 30 km off Monterey Bay during a period of upwelling and high primary productivity: 68 $\text{mmol C m}^{-2} \text{d}^{-1}$ (Knauer et al. 1979). The surface $A^{\text{d}}_{\text{Th}}:A_{\text{U}}$ averaged 0.31, corresponding to a dissolved ^{234}Th residence time of 15 days.

MLML Pit, cruise-2—Samples from this cruise were collected from a station about 80 km off the Monterey Peninsula. The primary production was $57 \pm 10 \text{mmol C m}^{-2} \text{d}^{-1}$ over a 6-day period (Knauer and Martin 1981) with a 1% light level at 60 m. Modeling of the dissolved ^{234}Th activity ratio, $A^{\text{d}}_{\text{Th}}:A_{\text{U}} = 0.45 \pm 0.04$, required a 31-day residence time for dissolved ^{234}Th with respect to scavenging onto particles. $A^{\text{p}}_{\text{Th}}:A_{\text{U}} = 0.095 \pm 0.005$, indicating a particulate ^{234}Th residence time of 8 days. The average suspended particulate load was 210 $\mu\text{g liter}^{-1}$.

CC III, cruise-1—At this coastal upwelling station, only 20 km offshore, in the center of Monterey Bay, the surface $A^{\text{d}}_{\text{Th}}:A_{\text{U}}$ dropped to 0.19 yielding τ_{d} of only 8 days. The suspended particulate load was 600 $\mu\text{g liter}^{-1}$.

CC III, cruise-2—This station provided one more example of a high-productivity coastal upwelling region. CC III, cruise-2 was about 20 km from shore in the center of Monterey Bay. $A^{\text{d}}_{\text{Th}}:A_{\text{U}} = 0.14 \pm 0.06$, yielding a mean τ_{d} of 5.7 days, while $A^{\text{p}}_{\text{Th}}:A_{\text{U}} = 0.27$, yielding a mean τ_{p} of 16 days. An intense phytoplankton bloom was evident. The suspended particulate load in the surface waters was of the order of 2,000 $\mu\text{g liter}^{-1}$ and was dominated by chain diatoms.

Discussion

Various studies have demonstrated a tendency for the scavenging rate of thorium to be greater in coastal surface waters than in oceanic surface waters. This trend has been accounted for by the increased concentration of suspended particles encountered as the continental shelf is approached. Because direct uptake at the sediment–water boundary could also account for the decreased res-

idence time in coastal or shelf waters, we deliberately avoided nearshore shelf waters with their large terrigenous particulate component and, instead, chose as a study area the California Current in which biological processes are the predominant source of particulate material.

Suspended particulate material in the surface waters of the California Current is a mixture of organisms ranging from picoplankton to macroplankton and of detritus, primarily of biogenic origin. Rates of particle production in these waters are relatively fast. Phytoplankton assimilates nutrients at rates equivalent to a doubling of its biomass every 1–5 days (Eppley et al. 1983). Yet the particle flux due to sinking of individual phytoplankters and detrital particles is too slow ($\leq 1 \text{ m d}^{-1}$; Bienfang 1980) to account for a significant portion of steady state particle removal. Herbivorous copepods and gelatinous zooplankton, in the course of grazing, can rapidly package this material into fecal pellets (Dagg and Grill 1980; Madin 1974) with sinking rates from 100 to 1,000 m d^{-1} (Komar et al. 1981; Bruland and Silver 1981). In this way, particles are produced and removed from the surface waters relatively quickly. We interpret the scavenging and removal of thorium as a response responding to the intensity of these biological processes.

In applying the surface water scavenging model, we assume uniform production of dissolved ^{234}Th , with essentially irreversible scavenging of dissolved ^{234}Th onto suspended (or fine) particulate material, followed by particle packaging and subsequent large particle removal. In the surface waters of the California Current the scavenging of dissolved ^{234}Th occurs on time scales of 1–6 weeks. The suspended particulate ^{234}Th is then packaged into rapidly sinking large particles in about 1 week; this time scale is too short for significant desorption to occur, and the assumption of irreversible scavenging is valid to a first approximation. These surface water conditions are markedly different from those in the deep sea, where fine particles have residence times in the water column of 5–10 years, and a reversible exchange model best explains the distribu-

tions of the three radiogenic thorium isotopes (^{234}Th , ^{228}Th , ^{230}Th) in dissolved and particulate form (Nozaki et al. 1981; Bacon and Anderson 1982). Bacon and Anderson (1982) suggested that thorium isotopes in the deep sea are repeatedly exchanged between seawater and particle surfaces during the 5–10-year lifetime of the fine particles in the deep sea. Their model indicated an adsorption rate constant for thorium of $K_{+1} \approx 1 \text{ yr}^{-1}$ and a desorption rate constant $K_{-1} \approx 3 \text{ yr}^{-1}$. Thorium would spend a mean life of 4 months on suspended particles before reversible desorption back into solution. However, in surface waters of the California Current the bulk of the particulate ^{234}Th would be removed by large particle sedimentation rather than by desorption back into solution. Thorium scavenging rates calculated by ^{234}Th : ^{238}U and ^{228}Th : ^{228}Ra disequilibria should be equivalent only if the scavenging process is primarily irreversible. Limited results obtained from these separate isotope pairs on the same unfiltered surface samples yield similar scavenging rates (Knauss et al. 1978; Kaufman et al. 1981), supporting this assumption.

A summary of the results from the California Current over the temporal and spatial scales sampled is presented in Table 3. The mean life of dissolved thorium with respect to particle removal, τ_d , varies by close to an order of magnitude: from 6 days under highly productive coastal upwelling conditions (CC III-1) to 47 days under less productive conditions (CEROP I). Integrated primary production for the surface photic zone was determined by ^{14}C uptake at VERTEX I and MLML Pit cruise-2. For MLML Pit cruise-1, Knauer et al. (1979) reported an estimate of primary productivity. We have estimated primary production at the other stations, and the assigned values together with the rationale used in these estimates are also given in Table 3.

In Fig. 3 the calculated first-order scavenging rate constant ($1/\tau_d$) for dissolved ^{234}Th with respect to removal onto particles is plotted vs. primary production. Within the limits of the data, the scavenging rate appears to be proportional to the primary productivity. The lowest scavenging rate

Table 3. Results and model calculated τ_d , τ_p , J_{Th} , and P_{Th} for various California Current surface waters.

	Avg $A_{Th}^d:A_U$	τ_d (days)	Avg $A_{Th}^p:A_U$	τ_p (days)	Avg A_U^*	Surface layer depth (m)	J_{Th}	P_{Th}	^{234}Th sediment trap flux	Primary productivity (mmol C $m^{-2} d^{-1}$)
							(dpm $m^{-2} d^{-1} \times 10^{-3}$)			
VERTEX I	0.33±0.06	17	0.23±0.09	18	2.359	50	2.3	1.5	0.8–2.1	47±7†
CEROP I	0.58±0.04	47	0.028±0.016	2.4	2.329	50	1.4	1.3	0.9	23±11‡
CEROP II	0.39±0.11	22	0.12±0.05	8	2.380	50	2.1	1.7	2.0	68±34§
CEROP III sta. 12	0.46±0.10	30	0.14±0.09	12	2.346	65	2.4	1.7	1.3	23±11‡
MLML Pit cruise-1	0.31±0.01	15	—	—	2.398	50	2.3	—	—	≈68
MLML Pit cruise-2	0.47±0.04	31	0.95±0.005	8	2.374	60	2.2	1.8	2.2	57±10¶
CC III cruise-1	0.19±0.03	8	—	—	2.394	35	2.0	—	—	150±50#
CC III cruise-2	0.14±0.06	5.7	0.27	16	2.393	35	2.1	1.4	—	150±50#

* Calculated value, based on the U : salinity relationship of Ku et al. 1977 (units in dpm liter⁻¹).

† Measured; Martin et al. 1984.

‡ Estimated; based on Ryther 1969, Knauer et al. (1979) assigned this value to coastal nonupwelling waters in this area. This is equivalent to the values observed by Eppley et al. (1979) for this type of water off southern California. It is assigned a ±50% error.

§ Estimated; based on Ryther 1969, Knauer et al. (1979) assigned this value to upwelling waters in this area. This is midrange for the values Eppley et al. (1979) observed in similar waters off southern California. It is assigned a ±50% error.

|| Estimated; Knauer et al. 1979.

¶ Measured; Knauer and Martin 1981.

Estimated; this value represents the range of primary production for intense coastal upwelling observed by Eppley et al. (1979) off southern California.

constant (0.021 d⁻¹) corresponds to the low productivity conditions (23 ± 11 mmol C m⁻² d⁻¹) observed at CEROP I during a time of nutrient depletion and lack of upwelling. The highest scavenging rate constant (0.18 d⁻¹) corresponds to the high productivity conditions observed at CC III (150 ± 50 mmol C m⁻² d⁻¹). The line in Fig. 3 suggests that the scavenging rate constant is roughly equivalent to 1 × 10⁻³ times the primary production.

Eppley and Peterson (1979) estimated the primary production rate of central gyre surface waters to be of the order of 6 mmol C m⁻² d⁻¹. The extrapolated estimate of a first-order scavenging rate from Fig. 3 would be of the order of 0.005 d⁻¹ or a mean life of dissolved ²³⁴Th of roughly 200 days in oligotrophic gyres. This estimate is in agreement with earlier work in which total Th isotopes were used to obtain estimates of thorium residence times in open ocean surface waters of the order of hundreds of days and with our own observations in the surface waters of the North and South Pacific Gyre systems (Bruland and Coale in prep.).

Particle residence times

The mean life of the particulate ²³⁴Th in the surface waters of the California Current ranged from 2.4 to 18 days. The low value of 2.4 days coincided with a period of an intense salp swarm in the California Cur-

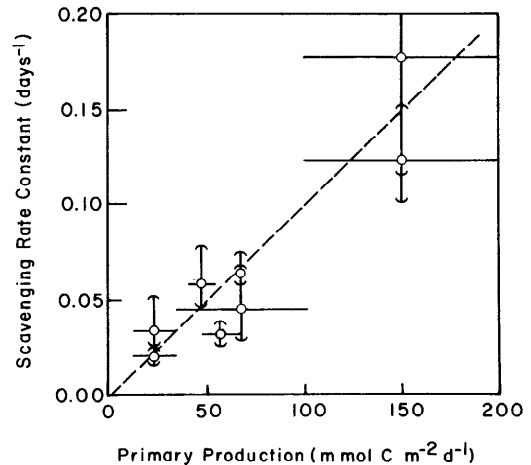


Fig. 3. Model-derived first-order dissolved ²³⁴Th scavenging rate constant vs. primary production.

Table 4. Production terms and fluxes for the 6-day study on MLML Pit cruise-2. The errors are those associated with daily variations at the sediment trap site.

Primary productivity* (mmol C m ⁻² d ⁻¹)	57±10 (60 m)
New productivity† (mmol C m ⁻² d ⁻¹)	26.5±9.6 (60 m)
Sediment trap flux* (mmol C m ⁻² d ⁻¹)	12.6–18 (65 m)
Sediment trap mass flux* (g m ⁻² d ⁻¹)	1.34 (65 m)
Sediment trap flux of ^{234}Th (dpm m ⁻² d ⁻¹)	2.2×10 ³ (65 m)
P_{Th} , model calculated flux of ^{234}Th (dpm m ⁻² d ⁻¹)	1.8×10 ³ (60 m)

* Knauer and Martin 1981.

† Eppley et al. 1983.

rent. Salps and doliolids are periodically the dominant zooplankton in these waters and salps can swarm at densities of 700–4,200 individuals m⁻², with the populations covering 200,000 to 450,000 km² for a period of at least several months (Berner 1967). If, for example, we chose a value of 1,000 ind m⁻² as representative of the CEROP I salp swarm, a conservative filtration rate of 1 liter h⁻¹ for an individual salp (Madin 1974; Harbison and Gilmer 1976) leads to a 50-m surface layer being completely filtered once every 2 days. This estimate is consistent with the observed removal rate of particulate thorium. In addition, in sediment trap material collected at 58 and 580 m at the CEROP I site >90 percent of the mass flux was composed of fecal pellets from these animals. In contrast to the salp-dominated CEROP I cruise, VERTEX I in the same general area was conspicuously devoid of salps or other macrozooplankton. Amorphous organic detritus dominated the sediment trap contents at all depths during this period (Martin et al. 1984) and fluxes of elliptical and cylindrical fecal pellets, as determined by surface layer sediment trap counts, were 19 and 37 times lower during VERTEX I than for other times in the same area (M. Tuel pers. comm.). These observations are consistent with a lower zooplankton grazing pressure. The relatively long particle residence time of 18 days fits with this low grazing pressure.

Table 5. Residence times of particulate phases for the 6-day study on MLML Pit cruise-2.

Residence time of	Days	Mixed depth layer (m)
Total particles (from suspended particulate load and trap flux)	9.3	65
Particulate ^{234}Th , τ_p (from model)	8	60
Particulate ^{234}Th , τ_p (from trap flux)	6.5	65
POC, τ_{POC} (from new production)	13	60
POC, τ_{POC} (from sediment traps)	19–28	65
POC turnover time (from regenerated production)	15	60
POC loss with respect to sinking loss and regeneration (from total production)	7	60

Eppley et al. (1983) suggested that new production and sinking of organic particles are coupled and that it is possible to calculate the residence time of organic particles and their recycling time via consumption and decomposition in the surface layer. The MLML Pit cruise-2 is one of the sites to which Eppley and coworkers have applied their model. Table 4 presents the various production terms and fluxes determined during this 6-day study. Table 5 presents the residence times within the surface zone of the different particulate phases with respect to their inputs or outputs. The residence time of POC is estimated as either the quotient (POC concentration)/(new production rate) or as the quotient (POC concentration)/(sediment trap flux). The rate of POC turnover is estimated as the quotient (POC concentration)/(regenerated production rate) where regenerated production = (total – new production).

The residence time of particulate ^{234}Th at this site is 6.5 days calculated from the sediment trap flux or 8 days from the water column ^{234}Th disequilibria model. These values are only half of the residence time of POC with respect to new production or of the turnover time of POC. However, if we calculate the residence time of POC with respect to total productivity (i.e. new plus regenerated production), we get a value of 7 days. This is similar to that observed for particulate ^{234}Th and is consistent with the

greater degree of recycling of organic carbon than of particulate ^{234}Th , which does not appear to be appreciably regenerated within the surface layer. The residence time of total particles in the surface zone as measured by suspended particulate load relative to the measured trap flux is intermediate between the ^{234}Th and POC-derived flux estimates, since the "total" particles include both organic matter and more refractory phases such as biogenic opal, calcium carbonate, etc.

J_{Th} and P_{Th}

Our estimates for J_{Th} , the rate of removal of dissolved ^{234}Th to particulate form in the surface zone, vary from 1.4 to 2.3×10^3 dpm $\text{m}^{-2} \text{d}^{-1}$. P_{Th} , the rate at which ^{234}Th is transported out of the surface layer by particle flux, varies from 1.3 to 1.8×10^3 dpm $\text{m}^{-2} \text{d}^{-1}$ (these values are 40–60% of the dissolved ^{234}Th production rate from ^{238}U decay in the surface layer). During VERTEX I, J_{Th} was 2.27×10^3 dpm $\text{m}^{-2} \text{d}^{-1}$ whereas P_{Th} was 1.50×10^3 . In this case 33% of the initial dissolved ^{234}Th produced was lost by radioactive decay during its life in the dissolved form, with 67% removed to the particulate form; 34% of the ^{234}Th scavenged to the suspended particulate form was then lost by radioactive decay during the 18-day mean life of the particles before their transport out of the surface layer. Thus, 44% of the dissolved ^{234}Th produced in the surface water was removed from the surface zone by particulate transport. During CER-OP I, J_{Th} was only 1.41×10^3 dpm $\text{m}^{-2} \text{d}^{-1}$ and P_{Th} was 1.31×10^3 . In this case, with efficient filtering and packaging by the salps, only 7% of the ^{234}Th scavenged onto particles was lost by radioactive decay before it was removed from the surface layer.

The model-derived P_{Th} values can be compared with direct measurements of the particulate flux of ^{234}Th from sediment trap collections located beneath the surface zone of intense scavenging and packaging activity. Available water column and sediment trap data are compared in Table 3. In general, the two approaches agree within 20–40%. This agreement puts an added degree of confidence on both the ^{234}Th model approach and the sediment trap studies.

The P_{Th} values of 1.3 – 1.8×10^3 dpm $\text{m}^{-2} \text{d}^{-1}$ are orders of magnitude greater than those of any other radionuclide. As an example, activities of ^{234}Th on particles collected at the base of the euphotic zone during the MLML Pit cruise-2 were 1,600 dpm g^{-1} , compared to 38 for ^{210}Pb and 48 for ^{210}Po . Activities of other thorium or uranium isotopes were no more than a few dpm g^{-1} at most.

Conclusions

The naturally occurring radiogenic pair ^{234}Th : ^{238}U is a powerful tracer of scavenging and particulate transport processes occurring in oceanic surface waters. By modeling the ^{234}Th : ^{238}U disequilibrium in dissolved and particulate phases, we were able to determine scavenging rates and particulate ^{234}Th residence times and draw the following conclusions.

The first-order scavenging rate constant of thorium from dissolved to particulate phase varies as a function of primary productivity from 0.005d^{-1} in oligotrophic gyres to $\sim 0.2 \text{d}^{-1}$ in areas of high primary production. These scavenging rate constants correspond to τ_d of 200 to 5 days.

The residence time of the particles is a function of grazing pressure by herbivorous zooplankton and varies from ~ 2 days under intense grazing by gelatinous zooplankton to ~ 20 days where zooplankton populations are relatively sparse.

Model-derived estimates of particulate thorium fluxes can be made. These estimates agree to within 20–40% with particulate thorium fluxes measured directly with sediment traps located beneath the surface euphotic zone.

References

- BACON, M. P., AND R. F. ANDERSON. 1982. Distribution of thorium isotopes between dissolved and particulate forms in the deep sea. *J. Geophys. Res.* **87**: 2045–2056.
- BERNER, L. D. 1967. Distribution atlas of *Thalassia* in the California Current region. Calif. Coop. Ocean. Fish. Invest. Atlas 8. 322 p.
- BHAT, S. G., S. KRISHNASWAMI, D. LAL, RAMA, AND W. S. MOORE. 1969. Th-234/U-238 ratios in the ocean. *Earth Planet. Sci. Lett.* **5**: 483–491.
- BIENFANG, P. K. 1980. Phytoplankton sinking rates in oligotrophic waters off Hawaii, U.S.A. *Mar. Biol.* **61**: 69–77.

- Broecker, W. A., A. Kaufman, and R. M. Trier. 1973. The residence time of thorium in surface sea water and its implications regarding the fate of reactive pollutants. *Earth Planet. Sci. Lett.* **20**: 35-44.
- Bruland, K. W., and M. W. Silver. 1981. Sinking rates of fecal pellets from gelatinous zooplankton (salps, pteropods, doliolids). *Mar. Biol.* **63**: 295-300.
- Dagg, M. J., and D. W. Grill. 1980. Natural feeding rates of *Centropages typicus* females in the New York Bight. *Limnol. Oceanogr.* **25**: 597-609.
- Eggemann, D. W., and P. R. Betzer. 1976. Decomposition and analysis of refractory oceanic suspended materials. *Anal. Chem.* **48**: 886-890.
- Eppley, R. W., and B. J. Peterson. 1979. Particulate organic matter flux and planktonic new production in the deep ocean. *Nature* **282**: 677-680.
- , E. H. Renger, and P. R. Betzer. 1983. The residence time of particulate organic carbon in the surface layer of the ocean. *Deep-Sea Res.* **30**: 311-323.
- , ———, and W. G. Harrison. 1979. Nitrate and phytoplankton production in southern California coastal waters and its role in the growth of phytoplankton. *Limnol. Oceanogr.* **24**: 483-494.
- Feely, H. W., G. W. Kipphut, R. M. Trier, and C. Kent. 1980. ^{228}Ra and ^{228}Th in coastal waters. *Estuarine Coastal Mar. Sci.* **11**: 179-205.
- Goldberg, E. D., and M. Koide. 1962. Geochronological studies of deep sea sediments by the ionium/thorium method. *Geochim. Cosmochim. Acta* **26**: 417-450.
- Harbison, G. R., and R. W. Gilmer. 1976. The feeding rates of the pelagic tunicate *Pegea confederata* and two other salps. *Limnol. Oceanogr.* **21**: 517-528.
- Hodge, V. F., M. Koide, and E. D. Goldberg. 1979. Particulate uranium, plutonium and polonium in the biogeochemistries of the coastal zone. *Nature* **277**: 206-209.
- Kaufman, A., Y.-H. Li, and K. K. Turekian. 1981. The removal rates of ^{234}Th and ^{228}Th from waters of the New York Bight. *Earth Planet. Sci. Lett.* **54**: 385-392.
- Knauer, G. A., and J. H. Martin. 1981. Primary production and carbon-nitrogen fluxes in the upper 1,500 m of the northeast Pacific. *Limnol. Oceanogr.* **26**: 181-186.
- , ———, and K. W. Bruland. 1979. Fluxes of particulate carbon, nitrogen, and phosphorus in the upper water column of the northeast Pacific. *Deep-Sea Res.* **26**: 97-108.
- Knauss, K. G., T. Ku, and W. S. Moore. 1978. Radium and thorium isotopes in the surface waters of the East Pacific and coastal southern California. *Earth Planet. Sci. Lett.* **39**: 235-249.
- Komar, P. D., A. P. Morse, L. F. Small, and S. W. Fowler. 1981. An analysis of sinking rates of natural copepod and euphausiid fecal pellets. *Limnol. Oceanogr.* **26**: 172-180.
- Ku, T.-L., K. G. Knauss, and G. G. Matheiu. 1977. Uranium in open ocean: Concentration and isotopic composition. *Deep-Sea Res.* **24**: 1005-1017.
- Li, Y.-H., W. H. Feely, and P. H. Santschi. 1979. $^{228}\text{Th}/^{228}\text{Ra}$ radioactive disequilibrium in the New York Bight and its implications for coastal pollution. *Earth Planet. Sci. Lett.* **42**: 13-26.
- , ———, and J. R. Toggweiler. 1980. ^{228}Ra and ^{228}Th concentrations in GEOSECS Atlantic surface waters. *Deep-Sea Res.* **27**: 545-555.
- Madin, L. P. 1974. Field observations on the feeding behavior of salps (Tunicata: Thaliacea). *Mar. Biol.* **25**: 143-147.
- Martin, J. H., and others. 1984. Vertical transport and exchange of materials in the upper waters of the oceans (VERTEX): Introduction to the program, hydrographic conditions and major component fluxes during VERTEX-I. Moss Landing Mar. Lab. Tech. Publ. 84-1.
- Matsumoto, E. 1975. ^{234}Th - ^{238}U radioactive disequilibrium in the surface layer of the ocean. *Geochim. Cosmochim. Acta* **39**: 205-212.
- Nozaki, Y., Y. Horibe, and H. Tsubota. 1981. The water column distributions of thorium isotopes in the western North Pacific. *Earth Planet. Sci. Lett.* **54**: 203-216.
- Ryther, J. H. 1969. Photosynthesis and fish production in the sea. *Science* **166**: 72-76.
- Silver, M. W., and K. W. Bruland. 1981. Differential feeding and fecal pellet composition of salps and pteropods, and the possible origin of the deep-water flora and olive-green "cells." *Mar. Biol.* **62**: 263-273.
- Turekian, K. K., and L. H. Chan. 1971. The marine geochemistry of the uranium isotopes, ^{230}Th and ^{231}Pa , p. 311-320. *In* Activation analysis in geochemistry and cosmochemistry. Universitetsforlaget.
- Turner, D. R., M. Whitfield, and A. G. Dickson. 1981. The equilibrium speciation of dissolved components in freshwater and seawater at 25°C and 1 atm pressure. *Geochim. Cosmochim. Acta* **45**: 855-881.
- Wang, C. H., D. L. Willis, and W. D. Loveland. 1975. Radiotracer methodology in the biological, environmental, and physical sciences. Prentice-Hall.

Submitted: 27 December 1983

Accepted: 3 August 1984