

## Accumulation of Th, Pb, U, and Ra in marine phytoplankton and its geochemical significance<sup>1</sup>

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### Abstract

The bioaccumulation of U, Th, Ra, and Pb in four diverse nanoplanktonic algal species and a picoplanktonic blue-green alga was determined with radiotracers. Among the nanoplankton, differences of 1-2 orders of magnitude in volume/volume concentration factors (VCFs) were observed for a given nuclide, but larger differences were observed among the four nuclides, with VCF values of  $\text{Th} > \text{Pb} > \text{Ra} \approx \text{U}$ . The picoplankton cells, with greater surface: volume ratios, had significantly higher VCF values. The mean VCF values in the nanoplankton of Th and Pb were  $1.5 \times 10^5$  and  $3.6 \times 10^4$  in the light and  $2.8 \times 10^5$  and  $7.3 \times 10^4$  in the dark. The VCFs of Th and Pb in the picoplankton were both about  $2 \times 10^6$ , irrespective of light. Retention half-times of  $^{228}\text{Th}$  and  $^{210}\text{Pb}$  in fecal pellets of *Artemia salina*, fed radiolabeled diatoms, were 20-50 d, but  $> 120$  d for  $^{228}\text{Th}$  at 4°C. The results suggest that sinking plankton and their debris could account for most of the natural series radionuclides sedimenting out of oceanic surface waters.

It is well established that several natural radionuclides,  $^{234}\text{Th}$ ,  $^{228}\text{Th}$ ,  $^{210}\text{Pb}$ , and  $^{210}\text{Po}$ , have very short residence times in oceanic surface waters (Cochran 1982; Broecker and Peng 1982). The rapid removal of these nuclides has led to the suggestion that they are transported from surface to deep waters through biologically mediated processes (Rama et al. 1961; Bhat et al. 1969; Broecker et al. 1973; Matsumoto 1975). The recent observations that the fluctuations in the settling fluxes of  $^{228}\text{Th}$  in the deep waters of the Sargasso Sea (Bacon et al. 1985) are strongly correlated with the primary productivity in the euphotic zone and that the scavenging rate of  $^{234}\text{Th}$  is proportional to primary production in the California Current (Coale and Bruland 1985) support these earlier suggestions. However, direct measurements of Th isotopes and  $^{210}\text{Pb}$  in "net plankton" yielded low concentrations of these nuclides in this material, leading to the suggestion that biological uptake may be unimportant in the transport of these nuclides from surface to deep waters of the

open ocean (Krishnaswami et al. 1976; Nozaki and Tsunogai 1976; Turekian 1977).

We have examined this problem in more detail, since critical evaluation of the role of marine organisms in mediating the distribution of these nuclides in surface waters requires knowledge of their concentration in the primary producers. The net plankton used for calculating the export fluxes of these nuclides out of the euphotic zone would be dominated by zooplankton and larger phytoplankton and hence would not be representative of the preponderance of marine phytoplankton. However, collection of sufficient quantities of pure phytoplankton from natural waters for radiochemical analysis is difficult. We therefore approached the problem by experimentally studying the accumulation of U-Th series nuclides in different species of marine phytoplankton maintained in laboratory cultures. We have included *Synechococcus* sp., a picoplanktonic cyanophyte. The picoplankton, relatively little studied to date, have been shown to be an important component of phytoplankton communities (Platt et al. 1983) and may significantly influence the movement of particle reactive metals in oceanic surface waters (Fisher 1985).

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#### Materials and methods

Experiments assessing the accumulation of U, Th, Ra, and Pb in algal cultures used the centric marine diatom *Thalassiosira pseudonana* (clone 3H), the chlorophyte *Dunaliella tertiolecta* (clone Dun), the coccolithophore *Emiliania huxleyi* (clone MCH No. 1), the filamentous cyanophyte *Oscillatoria woronichinii* (clone Osc N4), and the picoplanktonic cyanophyte *Synechococcus* sp. (clone L1602). Cell dimensions, experimental procedures for media preparation, sampling, and isotope handling are all described elsewhere (Fisher et al. 1983a; Fisher 1985). Cultures were incubated in constant light or constant darkness. Two replicate cultures (three replicates for clone L1602) and appropriate controls, with no cells, were examined for each treatment. Volume/volume concentration factors (VCFs) were calculated (Fisher et al. 1983a) for all nuclides and algal species at each sample time. The activity per cell volume was calculated by subtracting appropriate control filter values (from uninoculated "cultures") from the measured filterable activities in the inoculated samples. The *Synechococcus* sp. culture was axenic, but the other cultures had some bacterial contamination as indicated by epifluorescence microscopy. However, in none of the cultures did the bacterial biomass exceed a few percent of the algal biomass. Moreover, most of these bacteria pass through the 1- $\mu\text{m}$  Nuclepore filters used to filter the nanoplankton.

Interference from multiple gamma emissions during measurements was minimized by conducting experiments with either a single tracer [ $^{232}\text{U}$  in equilibrium with its daughters (see Fig. 1), or  $^{210}\text{Pb}$ ] or a double tracer ( $^{210}\text{Pb}$  and  $^{228}\text{Ra}$ ) per culture. All tracers were added as nitrates. No attempts were made to determine the speciation of the tracers after their introduction to the seawater. The time-zero water concentrations in different experiments ranged between:  $^{232}\text{U}$ , 1.2 and 11 pM (0.23–2.1 Bq ml $^{-1}$ );  $^{228}\text{Th}$ , 0.085 and 0.8 pM (0.6–5.7 Bq

ml $^{-1}$ );  $^{228}\text{Ra}$ , 0.43 pM (1 Bq ml $^{-1}$ );  $^{210}\text{Pb}$ , 15 pM (10 Bq ml $^{-1}$ ). Surface seawater concentrations of U are about  $10^4$  pM, of Th  $\leq 0.3$  pM, of Ra about  $2 \times 10^{-4}$  pM, and of Pb about 100 pM (Cochran 1982; Bruland 1983). The  $^{232}\text{U}$  and  $^{210}\text{Pb}$  were obtained from the C.E.A., Gif-sur-Yvette, France, and the  $^{228}\text{Ra}$  was milked from  $^{232}\text{Th}$  and was provided by R. Bojanowski. The pH of the cultures immediately after tracer addition was between 7.4 and 8.0.

An additional experiment was conducted to measure the retention of Th and Pb in zooplankton fecal pellets. Several hundred brine shrimp (*Artemia salina*) were fed diatoms (clone 3H) that had been "double-labeled" with  $^{210}\text{Pb}$  and  $^{228}\text{Th}$  for 3 d and then resuspended into unlabeled filtered seawater (Fisher et al. 1983a). After 6 h of feeding on a suspension of  $2 \times 10^5$  cells ml $^{-1}$ , the animals were transferred to a liter of unlabeled filtered seawater contained in a modified fecal pellet collector (La Rosa 1976). The average fecal pellet produced was  $361 \pm 95$   $\mu\text{m}$  long and  $148 \pm 35$   $\mu\text{m}$  in diameter (measurements of 80 pellets).

The pellets were gently collected by large-bore pipet and placed on a 43- $\mu\text{m}$  nylon mesh fixed to the bottom of a polyethylene tube of 1-cm length and diameter. The polyethylene capsule containing the pellets (50–100 pellets per capsule) was then sealed at the top with 43- $\mu\text{m}$  nylon mesh. Twenty such capsules were made and assayed for their 46 keV radiation from  $^{210}\text{Pb}$  within about 2 h of collection. Three of the capsules were preserved as controls in a counting tube, and the remaining capsules were held immersed in filtered seawater contained in a glass beaker at  $4^\circ\text{C} \pm 1^\circ$  or  $14^\circ\text{C} \pm 1^\circ$  for various periods up to 120 d. The water in the beaker was changed at intervals of 1–3 d. The nuclide retention was measured following two approaches. In the first, a marked capsule from the set was taken out of suspension at frequent intervals, assayed for its  $^{210}\text{Pb}$  activity, and resuspended in fresh, filtered seawater. In the second approach, one of the capsules was taken out of suspension permanently at defined intervals. This capsule was immediately assayed for its  $^{210}\text{Pb}$  activity and after a few months for its  $^{228}\text{Th}$  activity.

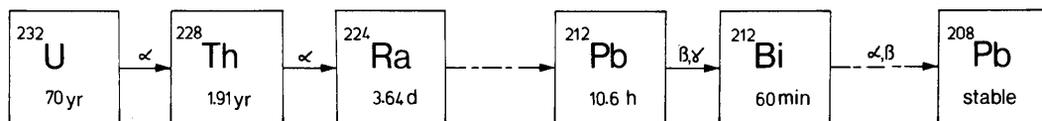


Fig. 1.  $^{232}\text{U}$  decay series. Nuclides with half-lives  $\geq 1$  h are shown.

The concentrations of radionuclides in all samples (i.e. water, filters, and *Artemia* fecal pellets) were measured by alpha and gamma spectrometric methods.  $^{232}\text{U}$  was measured by alpha spectrometry with  $^{238}\text{U}$  as tracer. Uranium was separated from the samples and purified by standard ion exchange procedures, electro-deposited, and measured with a solid-state detector (Bhat et al. 1969).  $^{228}\text{Th}$ ,  $^{210}\text{Pb}$ , and  $^{228}\text{Ra}$  were measured by nondestructive gamma ray spectrometry.  $^{228}\text{Th}$  was determined by counting its progeny,  $^{212}\text{Pb}$  (220–260 keV), to avoid the time-consuming analytical separations for purifying  $^{228}\text{Th}$ . The intermediate daughters between  $^{228}\text{Th}$  and  $^{212}\text{Pb}$  are all short-lived, except for  $^{224}\text{Ra}$  which has a half-life of 3.64 d (Fig. 1). The growth of  $^{212}\text{Pb}$  from  $^{228}\text{Th}$  would be governed by the Bateman equation (Fricdlander et al. 1966) and to a large extent dictated by the half-life of  $^{224}\text{Ra}$ . The  $^{212}\text{Pb}$  and  $^{228}\text{Th}$  activities would nearly attain radioactive equilibrium after about 5–6 half-lives of  $^{224}\text{Ra}$  (around 20 d) and the  $^{212}\text{Pb}$  activity of the sample after this period would be nearly the same as that of  $^{228}\text{Th}$ . (This approach would not be valid if the uptake of Ra in the cultures exceeded that of Th, although none of our samples falls in this category.)

We counted the samples periodically over 15–20 d and calculated the  $^{228}\text{Th}$  and  $^{224}\text{Ra}$  activities in the samples at the time of their filtration by analyzing  $^{212}\text{Pb}$  time-series count rates with the Bateman equation. The calculations assume that there is no loss of  $^{220}\text{Rn}$  from the samples. The observation that in each of the 20 time-zero samples the  $^{212}\text{Pb}$  count rate remained nearly constant (C.V. = 3–7%) throughout the 20-d counting period suggests that  $^{220}\text{Rn}$  loss from the samples was negligible.  $^{210}\text{Pb}$  was measured by counting its 46 keV photon emissions (35–55 keV) and  $^{228}\text{Ra}$  via the photons of its daughter  $^{228}\text{Ac}$  (865–1,010 keV). The  $^{228}\text{Ra}$  samples were counted 1–2 d after their

filtration to ensure radioactive equilibrium between  $^{228}\text{Ra}$  and  $^{228}\text{Ac}$  ( $t_{1/2} = 6.1$  h). All phytoplankton samples were counted with a Packard 5650 Autogamma counter [with a NaI(Tl) crystal] under identical counting conditions. The  $^{228}\text{Th}$  assay (via  $^{212}\text{Pb}$ ) in the fecal pellets was performed with an Ortec intrinsic gamma-X germanium detector. Whenever a double tracer was used, necessary corrections for interference in the peak regions were made by counting appropriate standards.

### Results

The growth of the cells and their accumulation of  $^{228}\text{Th}$  and  $^{210}\text{Pb}$  are shown in Figs. 2 and 3. The uptake of  $^{232}\text{U}$  and  $^{228}\text{Ra}$  by the phytoplankton was extremely low (<2% of the activity in the water column, throughout the course of the experiments). The fractions of filterable radionuclide in the uninoculated control samples were very low (<1%) for all nuclides except  $^{228}\text{Th}$ , for which it averaged about 23% with the nanoplankton experiments and <10% with the picoplankton experiment (Figs. 2, 3).

Equilibrium with respect to fractionation between the dissolved and the particulate phases of the radionuclides was generally achieved in 1 d. The nuclide concentration per cell at 1 d was generally within a factor of two of its value after a 3-d exposure for all isotopes and algal species except for the  $^{210}\text{Pb}$  contents per 3H cell in the light after a 3-d exposure, where it was 5–6 times lower than those after exposure for 1 d. This observation probably resulted from a cell division rate of 3H that exceeded the  $^{210}\text{Pb}$  adsorption rate. Thus, the VCF values did not change appreciably after 1 d, except for  $^{210}\text{Pb}$  in illuminated 3H cells (Figs. 2, 3). Generally, algal uptake followed the pattern  $^{228}\text{Th} > ^{210}\text{Pb} > ^{232}\text{U} \approx ^{228}\text{Ra}$ . Concentration factors after exposure for 3–6 d are given in Table 1. The differences between the VCF values for the different algal species

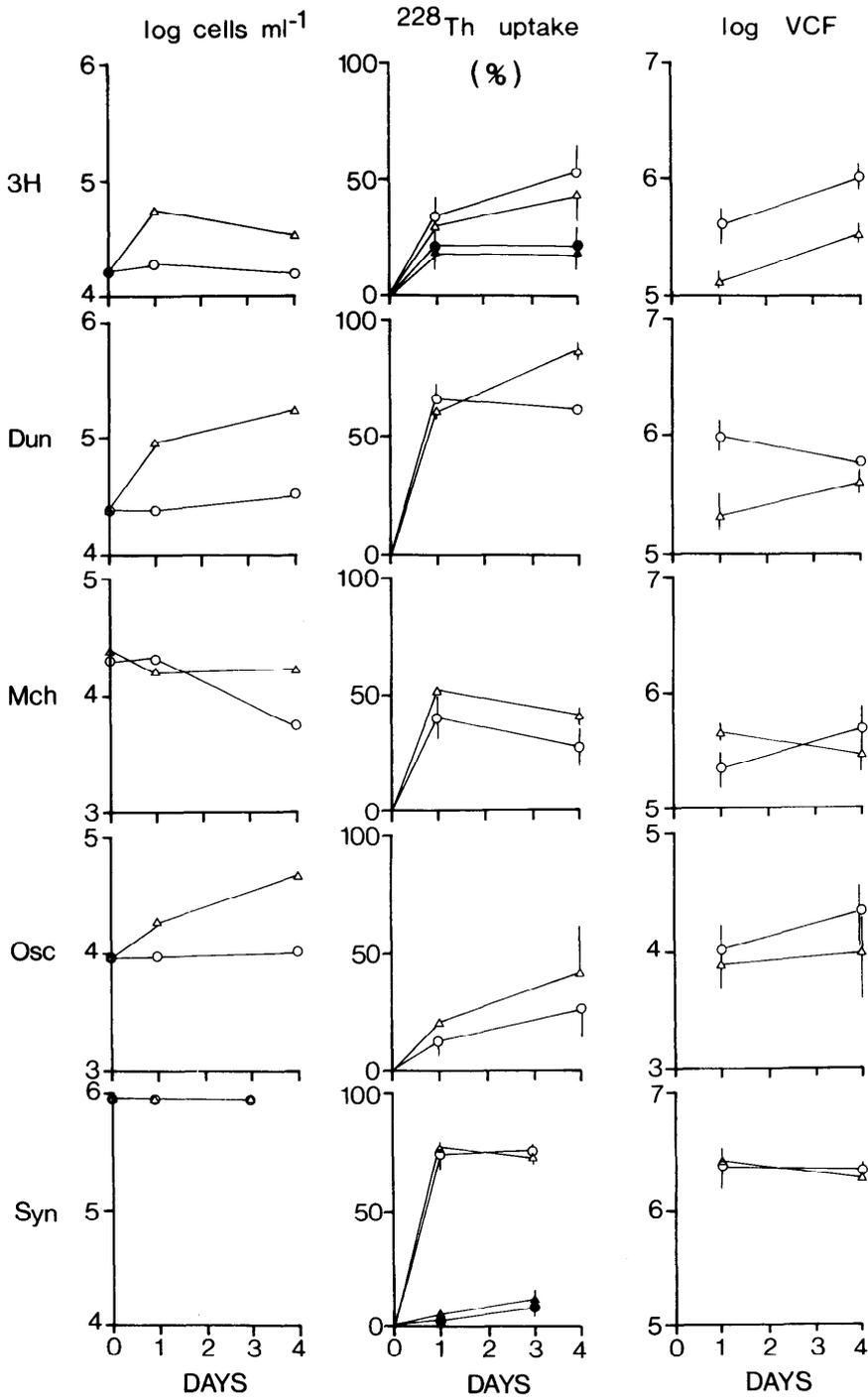


Fig. 2. Growth of cells (3H: *Thalassiosira pseudonana*; Dun: *Dunaliella tertiolecta*; Mch: *Emiliana huxleyi*; Osc: *Oscillatoria woronichinii*; Syn: *Synechococcus* sp.) and accumulation of <sup>228</sup>Th under light (Δ) and dark (O) conditions. The percent <sup>228</sup>Th uptake represents the percent of the water column <sup>228</sup>Th caught on a 1-μm Nuclepore filter (0.2-μm filter for Syn). <sup>228</sup>Th uptake by control filters (from uninoculated water) shown with solid symbols; controls for 3H, Dun, Mch, and Osc identical. The <sup>228</sup>Th VCF values take into account the <sup>228</sup>Th content of blank (control) filters. Data points are means ± 1 SD of two replicate cultures (three replicates for Syn).

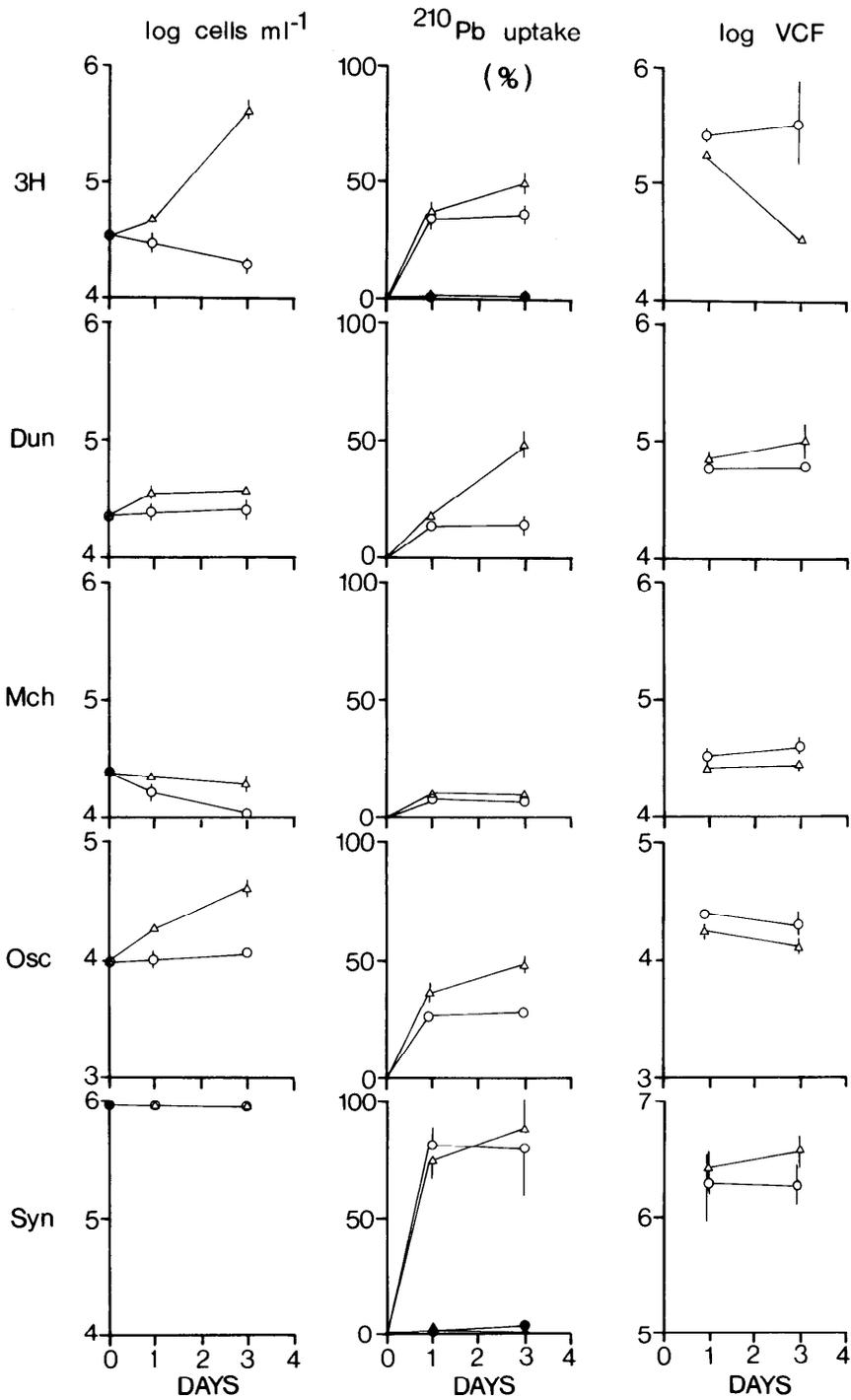


Fig. 3. As Fig. 2, but of <sup>210</sup>Pb.

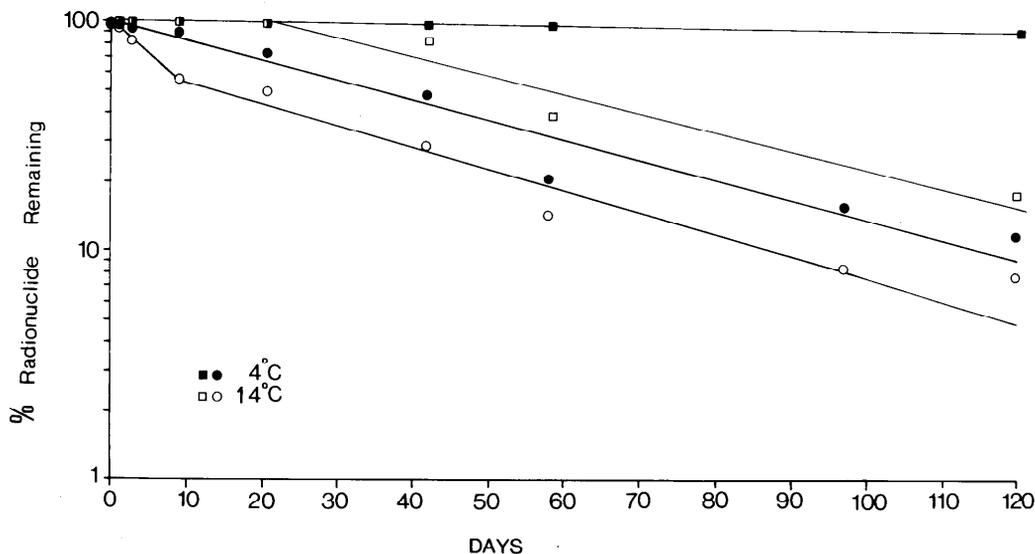


Fig. 4. Retention of  $^{210}\text{Pb}$  (O, ●) and  $^{228}\text{Th}$  (□, ■) by *Artemia salina* fecal pellets maintained in unlabeled seawater at 4°C and 14°C.

for any one nuclide were smaller than the differences among the nuclides for any one species. The highest VCF value measured was  $\sim 2 \times 10^6$  for  $^{228}\text{Th}$  and  $^{210}\text{Pb}$  in *Synechococcus* sp. (Table 1). The VCF values for  $^{210}\text{Pb}$  and  $^{228}\text{Th}$  in algae incubated under light and dark conditions were generally similar (Table 1; Figs. 2, 3).

In the illuminated *D. tertiolecta* and *O. woronichinii* cultures, pH increased considerably as the cells divided, going from about 7.9 after 1 d to about 9.0 after 3 d. Since the VCF values for  $^{210}\text{Pb}$  and  $^{228}\text{Th}$  in light and dark cultures were similar (Table 1), this pH increase apparently had no major effect on nuclide uptake by these species.

The retention of  $^{210}\text{Pb}$  in *A. salina* fecal pellets contained in the repeatedly sampled capsules is shown in Fig. 4. Both at 4°C and 14°C,  $\sim 90\%$  of the  $^{210}\text{Pb}$  in the pellets is lost within 120 d. The loss curve at 4°C is nearly exponential with a single rate constant, which yields a retention half-time ( $tb_{1/2}$ ) of  $36 \pm 3$  d for  $^{210}\text{Pb}$  in the pellets. The loss curve at 14°C seems to show two components, characterized by a rapid loss during the initial stages ( $tb_{1/2} = 10 \pm 0$  d) followed by a more gradual loss ( $tb_{1/2} = 32 \pm 4$  d). If we combine the  $^{210}\text{Pb}$  loss data from different capsules for the same temperature and

time, the loss curves show greater scatter; the  $tb_{1/2}$  values for the pooled data are then  $45 \pm 6$  d at 4°C and  $23 \pm 2$  d at 14°C. The fecal pellets retained  $^{228}\text{Th}$  more than  $^{210}\text{Pb}$ , as there was no discernible loss of  $^{228}\text{Th}$  at 4°C, while at 14°C the  $tb_{1/2}$  was 30–44 d. The differential retention of  $^{228}\text{Th}$  and  $^{210}\text{Pb}$  in fecal pellets held at 4°C suggests that physical breakup of the pellets was not solely responsible for the measured loss of radionuclides (at least at 4°C).

#### Discussion

The concentration factors of the nuclides in the algal species studied generally followed the trend  $\text{Th} > \text{Pb} > \text{Ra} \approx \text{U}$ . Comparison of the concentration factors with those measured for transuranic elements in these cells (Fisher et al. 1983a; Fisher and Fowler in press) shows that the accumulation of Th is similar to the particle-reactive elements Am, Pu, Cm, and Cf. The minor influence of light on the accumulation of U-Th series nuclides in these species was similar to earlier findings for other metals by Fisher et al. (1983a, 1984) and Fisher (1985). These earlier studies concluded that metal association with phytoplankton proceeds by adsorption to cell surfaces. Lead

Table 1. Volume/volume concentration factors (VCFs) obtained from phytoplankton in culture. Means  $\pm$  1 SD,  $n = 2$  for all cells except L1602 ( $n = 3$ ). (Not determined—nd.)

Clone	Condition	VCF ( $\times 10^4$ )			
		$^{228}\text{Th}^*$	$^{210}\text{Pb}^\dagger$	$^{232}\text{U}^*$	$^{228}\text{Ra}^\ddagger$
3H (diatom)	Light	39 $\pm$ 11	3.7 $\pm$ 0.4	<0.02	<0.03
	Dark	106 $\pm$ 23	47 $\pm$ 6	<0.06	nd
Dun (green)	Light	41 $\pm$ 7	10 $\pm$ 4	<0.04	nd
	Dark	57 $\pm$ 7	6.3 $\pm$ 2	<0.02	nd
Mch (coccolithophore)	Light	31 $\pm$ 12	3.4 $\pm$ 0.6	<0.01	<0.03
	Dark	49 $\pm$ 23	4.7 $\pm$ 0.9	<0.06	nd
Osc (blue-green)	Light	1.1 $\pm$ 0.7	1.3 $\pm$ 0.2	<0.004	<0.006
	Dark	2.1 $\pm$ 1.1	1.9 $\pm$ 0.6	<0.002	nd
L1602 (blue-green)	Light	190 $\pm$ 12 $\ddagger$	264 $\pm$ 61	nd	nd
	Dark	199 $\pm$ 24 $\ddagger$	178 $\pm$ 46	nd	nd

\* Equilibration time of 96 h.

† Equilibration time of 70 h.

‡ Equilibration time of 144 h.

and americium have been shown to associate principally with the cell walls of marine phytoplankters (Fisher et al. 1983c), and presumably other particle-reactive, nonessential metals like Th would do the same.

The high affinity of Pb and especially Th for phytoplankton suggests that they are particle-reactive in general, consistent with their known marine geochemical behavior and their long retention in *Artemia* fecal pellets. The association of Th with marine particulate matter has been shown to be reversible and in equilibrium with adsorption/desorption processes (Nozaki et al. 1981; Bacon and Anderson 1982). In open ocean waters, the residence times of Th isotopes in marine suspended matter have been calculated to be in the range of 2–10 months (corresponding to a  $tb_{1/2}$  of about 45–200 d), based on vertical profiles of dissolved Th isotopes in open ocean waters (Nozaki et al. 1981; Bacon and Anderson 1982).

We have observed that the  $tb_{1/2}$  of  $^{228}\text{Th}$  in *Artemia* fecal pellets held at 4°C is >120 d. The retention of  $^{210}\text{Pb}$  and  $^{228}\text{Th}$  in the fecal pellets was comparable to that of  $^{241}\text{Am}$ —a particle-reactive transuranic nuclide—in euphausiid fecal pellets (Fisher et al. 1983b). The scatter in the  $^{210}\text{Pb}$  retention data derived from different fecal pellets (i.e. different capsules) probably was more a function of different physical characteristics, including degradation rates, among the different batches of pellets than of varia-

tions in the desorption rates for the nuclides. The influence of biological and physical degradation of the fecal pellets, if any, on retention of radionuclides warrants further study. It can be surmised from our data that the desorption of these elements from sinking fecal pellets would proceed slowly in nature, and fast-sinking fecal pellets would be expected to transport these elements, like the particle-reactive transuranic elements, to deep waters and sediments (Higgo et al. 1977; Fisher and Fowler in press). Consistent with this idea, Coale and Bruland (1985) concluded that zooplankton fecal pellets were responsible for the transport of Th in the California current.

Table 2 presents a comparison of concentration factors of Th, Pb, Ra, and U in the phytoplankton cultures with those in various types of suspended particulates in seawater. Concentration factors were also calculated on dry weight bases (DWCFs) to facilitate comparisons with available field data. The geometric mean DWCFs in the phytoplankton cultures studied here are  $8.7 \times 10^5$  for Th and  $2.9 \times 10^5$  for Pb. If we exclude the *D. tertiolecta* and *O. woronichinii* data to avoid any possible pH artifacts, these geometric means are not altered appreciably (in fact, they increase about twofold). The geometric mean DWCFs in phytoplankton cultures are comparable to those measured in surface ocean particulates and in sediment trap materials (Table 2). Field data of Krishnaswami et al. (1976)

Table 2. Comparison of dry weight concentration factors (DWCFs) obtained from laboratory culture experiments with those determined from measurements of marine particulate matter.

Sample	DWCF ( $\times 10^4$ )				Reference
	Th	Pb	Ra	U	
Algal cultures					
<i>T. pseudonana</i>	106	10	<0.08	<0.06	Present work
<i>D. tertiolecta</i>	244	60	—	<0.2	Present work
<i>E. huxleyi</i>	89	10	<0.09	<0.03	Present work
<i>O. woronichinii</i>	2.2	3	<0.01	<0.008	Present work
<i>Synechococcus</i> sp.	975	1,100	—	—	Present work
Surface water particles					
Atlantic Ocean	200	—	2	—	Krishnaswami et al. 1976
Indian Ocean	80	—	—	—	Krishnaswami et al. 1981
Geosecs No. 48, S. Atlantic	—	10	—	—	Somayajulu and Craig 1976
Deep water particles					
Panama and Guatemala basins	2,000	—	—	—	Bacon and Anderson 1982
Sediment trap material					
N. Atlantic (389 m)	200	50	3	0.05	Brewer et al. 1980
N. Atlantic (1,000 m)	450	100	7	0.05	Brewer et al. 1980
Net plankton					
Phytoplankton	—	10	—	—	Shannon et al. 1970
Phytoplankton	—	—	2–16	—	Shannon and Cherry 1971
Mixed plankton	—	—	0.18	—	Szabo 1967
Mixed plankton	—	—	0.7	0.12	Knauss and Ku 1983
Zooplankton (copepods and crab larvae)	0.6	0.2	—	0.01	Krishnaswami et al. 1985
Zooplankton (salps)	2	1	—	0.03	Krishnaswami et al. 1985
Zooplankton (calanoids and cyclopoids)	2	2	0.5	0.02	Kharkar et al. 1976

indicate that  $^{234}\text{Th}$  concentration factors in marine particulate matter decrease with increasing suspended particulate load. Since the particulate load in our experiments ( $\geq 0.3 \text{ mg liter}^{-1}$ ) exceeded that of all but the most productive waters, it may be expected that the measured concentration factors (and subsequent flux estimates) in the phytoplankton cultures represent lower limits. The high concentration factors of Th and Pb in phytoplankton suggest that these organisms could be important sequestering agents for these nuclides in surface waters and that the flux of organic material out of euphotic waters, either by direct sinking of phytoplankton cells or packaged into zooplankton fecal pellets, could appreciably influence the vertical flux of these nuclides.

Table 3 presents a range of estimates of organic carbon exported from the euphotic zones of different oceans together with an estimate, based on mean DWCFs of Th and Pb derived in our laboratory experiments,

of the flux of  $^{234}\text{Th}$  and  $^{210}\text{Pb}$  associated with sinking phytoplankton (in whatever form). The flux of radionuclides should be a function of the sinking particulate load, which is in turn a function of the primary production in the euphotic zone (Honjo 1982; Deuser et al. 1983; Jickells et al. 1984), provided that the radionuclide:C ratios in the primary producers and settling organic matter are identical. However, if the radionuclides are not recycled in surface waters as efficiently as carbon, then the nuclide fluxes presented in Table 3 would be lower limits. The estimates of  $^{234}\text{Th}$  and  $^{210}\text{Pb}$  fluxes on an oceanwide basis via sinking phytoplankton (Table 3) can be compared with the measured fluxes of these nuclides from the euphotic zone.

Data on the  $^{234}\text{Th}$  removal rate from surface waters are obtained from  $^{234}\text{Th} : ^{238}\text{U}$  ratios. On the basis of a mean value of 0.8 for the  $^{234}\text{Th} : ^{238}\text{U}$  activity ratio in surface waters ( $\sim 100 \text{ m}$ ) of the mid-Arabian Sea,

Wharton Sea, and North Pacific, the  $^{234}\text{Th}$  removal is calculated to be  $\sim 50 \times 10^4 \text{ dpm m}^{-2} \text{ yr}^{-1}$  (Bhat et al. 1969; Matsumoto 1975). For oligotrophic waters such as the Sargasso Sea, an estimate of  $^{234}\text{Th}$  removal can be obtained from  $^{228}\text{Th}$  data. The residence times of  $^{228}\text{Th}$  are  $< 6 \text{ yr}$  in the upper 100 m of these waters and  $< 29 \text{ yr}$  in the upper 350 m, corresponding to removal rate constants of  $> 0.167 \text{ yr}^{-1}$  and  $> 0.035 \text{ yr}^{-1}$  (Li et al. 1980). If we assume that  $^{234}\text{Th}$  and  $^{228}\text{Th}$  have the same residence time (Kaufman et al. 1981) and a  $^{234}\text{Th}$  standing crop of  $2 \times 10^5 \text{ dpm m}^{-2}$  (at 100 m), then the  $^{234}\text{Th}$  removal flux can be calculated to be  $0.7$  to  $3.3 \times 10^4 \text{ dpm m}^{-2} \text{ yr}^{-1}$ . We estimate the removal flux of  $^{234}\text{Th}$  in oligotrophic waters via sinking phytoplankton to be  $1.1 \times 10^4 \text{ dpm m}^{-2} \text{ yr}^{-1}$ , using a new production rate of  $1.54 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Eppley and Peterson 1979) and the mean DWCF of  $8.7 \times 10^5$  in phytoplankton cultures.

For waters of high productivity such as in the Antarctic, there are no water-column data for calculating the  $^{234}\text{Th}$  removal flux, although an upper limit can be set by assuming the removal rate  $\approx$  production from  $^{238}\text{U} \approx 200 \times 10^4 \text{ dpm m}^{-2} \text{ yr}^{-1}$ . For  $^{210}\text{Pb}$ , the removal flux is about  $5\text{--}20 \times 10^3 \text{ dpm m}^{-2} \text{ yr}^{-1}$  (Table 3). A major problem associated with calculating  $^{210}\text{Pb}$  removal flux is the paucity of data on its atmospheric deposition. When estimated  $^{234}\text{Th}$  and  $^{210}\text{Pb}$  removal fluxes via phytoplankton are compared with those calculated from their surface water ( $\sim 100 \text{ m}$ ) inventories, both in oligotrophic waters (such as the central subtropical regions) and in highly productive waters (e.g. upwelling regions, neritic waters, Antarctic waters), we find that  $> 50\%$  of the  $^{234}\text{Th}$  sedimenting out at 100 m probably is associated with the phytoplankton or their debris. Further, the estimates in Table 3 show that the phytoplankton and their debris could be a significant pathway for removing  $^{234}\text{Th}$  and  $^{210}\text{Pb}$  from surface ocean waters.

Support for these suggestions comes from studies (Bacon et al. 1985; Coale and Bruland 1985) showing positive correlations between  $^{228}\text{Th}$  and  $^{234}\text{Th}$  fluxes and primary production in various surface waters of the North Atlantic and the North Pacific. Com-

Table 3. Estimates of fluxes of  $^{234}\text{Th}$  and  $^{210}\text{Pb}$  influenced by phytoplankton in different waters.

Ocean	Flux from the euphotic zone		
	Org. C* ( $\text{g C m}^{-2} \text{ yr}^{-1}$ )	$^{234}\text{Th}\dagger$ ( $\times 10^4 \text{ dpm m}^{-2} \text{ yr}^{-1}$ )	$^{210}\text{Pb}\ddagger$ ( $\times 10^3 \text{ dpm m}^{-2} \text{ yr}^{-1}$ )
Atlantic	27	18.8	6.3
Pacific	8	5.6	1.9
Indian	18	12.5	4.2
Arctic	0	0	0
Antarctic	146	102	33.9
Flux at $\sim 100 \text{ m}$		0.7–3.3§; 50	5–20#

\* Assumes equal to "new" primary production (from Eppley and Peterson 1979).

† Using geometric mean DWCF of  $8.7 \times 10^5$  (Table 2) and surface water  $^{234}\text{Th}$  of  $2 \text{ dpm liter}^{-1}$  (Coale and Bruland 1985); assumes  $C = 0.25$  dry wt.

‡ Using geometric mean DWCF of  $2.9 \times 10^5$  (Table 2) and surface water  $^{210}\text{Pb}$  concentration of  $0.2 \text{ dpm liter}^{-1}$  (Cochran 1982); assumes  $C = 0.25$  dry wt.

§ For oligotrophic waters such as the Sargasso Sea (from Li et al. 1980); assumes  $^{234}\text{Th}$  and  $^{228}\text{Th}$  removal rate constants are equal (Kaufman et al. 1981).

|| Calculated from Bhat et al. 1969 and Matsumoto 1975.

# From Bacon et al. 1976 and Nozaki and Tsunogai 1976.

parison of measured  $^{234}\text{Th}$  fluxes at specific oceanic sites with fluxes predicted for these waters using our laboratory-derived concentration factors and available data on new production rates shows good agreement. For example, in the California Current ( $36^\circ 50' \text{N}$ ,  $123^\circ 00' \text{W}$ ; MLML Pit Cruise-2) our data would predict a removal flux of  $8 \times 10^5 \text{ dpm m}^{-2} \text{ yr}^{-1}$  for a new production rate of  $116 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Coale and Bruland 1985). This estimate compares with the value of  $\sim 7.3 \times 10^5 \text{ dpm m}^{-2} \text{ yr}^{-1}$  based on water column inventories and sediment trap flux of  $^{234}\text{Th}$  (Coale and Bruland 1985). Similarly in the VERTEX-1 station ( $36^\circ 36' \text{N}$ ,  $123^\circ 48' \text{W}$ ) our data would predict a  $^{234}\text{Th}$  removal flux of  $5.7 \times 10^5 \text{ dpm m}^{-2} \text{ yr}^{-1}$  for a new production rate of  $82 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Knauer et al. 1984). The  $^{234}\text{Th}$  flux at this location based on its deficiency in the water column is  $5.5 \times 10^5 \text{ dpm m}^{-2} \text{ yr}^{-1}$  (Coale and Bruland 1985). For  $^{210}\text{Pb}$  a similar comparison can be made for the MLML Pit Cruise-2 station. Based on a DWCF of  $2.9 \times 10^5$ , a new production rate of  $116 \text{ g C m}^{-2} \text{ yr}^{-1}$ , and a  $^{210}\text{Pb}$  concentration of  $0.2 \text{ dpm liter}^{-1}$ , we would predict a removal flux of  $2.7 \times 10^4 \text{ dpm m}^{-2} \text{ yr}^{-1}$ . The measured flux at this station is  $1.9 \times 10^4 \text{ dpm m}^{-2} \text{ yr}^{-1}$  (Coale and Bruland 1985).

In light of these findings, the suggestions

of Nozaki and Tsunogai (1976) and Tur-ekian (1977) that biological removal of  $^{210}\text{Pb}$  and  $^{234}\text{Th}$  would account only for a minor fraction of their flux from surface waters need re-evaluation. The lower  $^{210}\text{Pb}$  and  $^{234}\text{Th}$  enrichment factors these workers reported for plankton probably result from measurements of comparatively large, net plankton, dominated by zooplankton. We would speculate that particle-reactive elements like Th and Pb should show a direct correlation between enrichment factors and surface: volume ratio of the particles (or organisms), as seen for Am, Cm, Pu, and Cf (Fisher and Fowler in press), thereby resulting in higher concentration factors in the smaller phytoplankton than in the larger phytoplankton and the zooplankton. The data for Th and Pb (this paper) and other metals (Fisher 1985) in the picoplankton further support this idea. The data of Shannon et al. (1970) on  $^{210}\text{Pb}$  in net phytoplankton yield a DWCF of  $1 \times 10^5$ , comparable to the mean value based on our experiments. It is recognized, however, that there is considerable scatter in the available field data.

The close similarity in the dissolved profiles of  $^{226}\text{Ra}$  and Si in the world ocean suggests that  $^{226}\text{Ra}$  distribution in the oceans is affected by the same processes that affect the Si distribution (Ku et al. 1970, 1980; Chung 1980). Sediment trap data on the settling fluxes of  $^{226}\text{Ra}$  and biogenic  $\text{SiO}_2$  show a very strong positive correlation with a slope of  $26 \text{ dpm } ^{226}\text{Ra g}^{-1} \text{ SiO}_2$  (Brewer et al. 1980). Given a typical  $^{226}\text{Ra}$  concentration of  $0.2 \text{ dpm liter}^{-1}$  in seawater and a biogenic  $\text{SiO}_2$  content of 50% in siliceous organisms, the sediment trap data yield a DWCF of about  $6 \times 10^4$  in siliceous organisms. Attempts to identify  $^{226}\text{Ra}$ -concentrating organisms have thus far not been successful, except for the observation of high concentrations of  $^{226}\text{Ra}$  in *Rhizosolenia* sp. (Shannon and Cherry 1971). Our results on Ra uptake by *T. pseudonana*, another centric diatom, failed to show substantial bioaccumulation of this element. Ra has been shown to be concentrated heavily by zooxanthellae associated with coral reefs, with a DWCF of about  $3 \times 10^6$  (Flor and Moore 1977). Similarly, Ra concentrates in

highly calcified macroalgae, presumably by coprecipitation with the calcium carbonate matrix (Edgington et al. 1970). However, in our study no pronounced differences were observed between the concentration of Ra in the coccolithophore *E. huxleyi* and in the noncalcareous phytoplankton. Analogous to Ra, the distribution of Ba in the sea appears to be linked to that of Si (Li et al. 1973; Collier and Edmond 1984). As with Ra, the major siliceous carrier phase for Ba has not been identified (Bankston et al. 1979; Collier and Edmond 1984). It is likely that the cycling of Ra and Ba are governed by the same process(es), such as the biologically mediated formation of barite crystals in the water column (Dehairs et al. 1980).

The low concentration of U in the phytoplankton may be a result of the speciation of U in an anionic complex— $\text{UO}_2(\text{CO}_3)_3^{4-}$ —in seawater (Stumm and Brauner 1975). This complex may be generally unreactive for suspended marine particulates (such as phytoplankton) which carry a negative surface charge (Myers et al. 1975; Neihof and Loeb 1972). Moreover, the affinity of U for dissolved carbonate may greatly exceed its affinity for ligands on algal surfaces. Consistent with this hypothesis, algal uptake of U, which was attributed to U adsorption to cell surfaces, was found to be maximal at pH 5, being markedly inhibited by the presence of carbonate (Sakaguchi et al. 1978; Horikoshi et al. 1979). Analyses of sediment trap samples yield a U concentration of about  $1.1 \text{ dpm g}^{-1}$  dry biogenic matter (Brewer et al. 1980; Anderson 1982), corresponding to a DWCF of about 500. This value is consistent with the results obtained from the phytoplankton cultures (Table 2), suggesting that the phytoplankton uptake of U in surface waters could account for the measured fluxes of this element through the water column.

In summary it would appear that Th and Pb are very reactive for marine particulate matter, including phytoplankton and zooplankton fecal material. Their flux from surface waters should be governed by association with the surfaces of sinking particulate matter and therefore be a function of primary productivity in the euphotic zone. By contrast, U and Ra behave relatively con-

servatively with respect to association with biogenic particulates. We note, however, that these conclusions are based on experimental laboratory studies with only a few algal species. It is difficult to judge how far these laboratory culture experiments can be used to predict natural marine biogeochemical processes. However, the observation that our results are consistent with available field data is certainly encouraging. Further research with many more species and varying experimental conditions should help to quantify the role of organisms in mediating the distribution of these nuclides in marine systems.

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