A time-series study of particulate matter export in the North Pacific Subtropical Gyre based on ^{234}Th : ^{238}U disequilibrium

Claudia Benitez-Nelson[a,*], Ken O. Buesseler[b], David M. Karl[a], John Andrews[b]

[a] *Department of Oceanography, University of Hawaii, 1000 Pope Road, Honolulu, HI 96822, USA*
[b] *Department of Marine Chemistry and Geochemistry (MS 25), Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA*

Abstract

Depth profiles of total ^{234}Th (dissolved + particulate) were collected at Station ALOHA (22°45N, 158°00W) in the North Pacific Subtropical Gyre during 9 cruises from April 1999 to March 2000. Samples were collected and processed by a new 2 L technique that enables more detailed depth resolution then previous ^{234}Th studies. Significant zones of particle export (^{234}Th deficiency) and particle remineralization (^{234}Th excess) were measured both temporally and with depth. ^{234}Th derived particulate carbon (PC) and nitrogen (PN) fluxes were determined with steady-state and non-steady-state models and PC/^{234}Th and PN/^{234}Th ratios measured with both in situ pumps and free-drifting particle interceptor traps deployed at 150 m. ^{234}Th based export estimates of 4.0 ± 2.3 mmol C m^{-2} d^{-1} and 0.53 ± 0.19 mmol N m^{-2} d^{-1}, were approximately 60% higher than those measured in PIT style sediment traps from the same time period, 2.4 ± 0.2 mmol C m^{-2} d^{-1} and 0.32 ± 0.08 mmol N m^{-2} d^{-1}. Most of this difference is attributable to two large export events that occurred during October and December 1999, when traps undercollected for ^{234}Th by a factor of 2 to 4. ^{234}Th export (*ThE*) ratios based on ^{234}Th derived PC flux/^{14}C based primary production ranged from 4% to 22% (average = 8.8%). Our results confirm the recent estimates of C export by Emerson et al. (Nature 389 (1997) 951) and Sonnerup et al. (Deep-Sea Research I 46 (1999) 777) and indicate that C export from the oligotrophic ocean must be considered when discussing C sequestration in global climate change. © 2001 Elsevier Science Ltd. All rights reserved.

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*Corresponding author. Tel.: + 1-808-956-7625; fax: + 1-808-956-9516.
E-mail address: cbnelson@soest.hawaii.edu (C. Benitez-Nelson).

1. Introduction

The world's subtropical gyres cover close to 40% of the earth's surface, but are often considered to have minimal contributions to C sequestration. Nonetheless, because of their large area, temporal variations in these habitats may have significant impacts on global primary production and particulate matter export. The North Pacific Subtropical Gyre (NPSG) is of particular interest because it appears to have undergone a transition from nitrogen (N) to phosphorus (P) limitation due to an increasing abundance of N_2-fixing cyanobacteria (Karl et al., 1995, 1997, 2001; Letelier and Karl, 1996; Karl and Tien, 1997). The ecological implications of such habitat variations remain largely unexplored. On the one hand, the NPSG ecosystem may be expected to support enhanced primary production concurrent with a more intense recycling of components (Karl, 1999; Karl et al., 2001; Michaels and Capone, 2000). This would result in a decrease in the relative export of particulate matter as smaller plankton dominate the food web. On the other hand, increasing the amount of available N, via enhanced N_2 fixation, may further augment the secondary growth of other, larger plankton, such as diatoms, and hence, increase carbon export. In fact, a significant export of diatoms in the NPSG during the late summer period has recently been detected (Scharek et al., 1999).

Several studies indicate that carbon export may be significantly higher in the NPSG than previously thought (Martin et al., 1987; Karl et al., 1995, 1996). The most comprehensive data set has been collected with particle interceptor sediment traps (PITS) as part of the Hawaii Ocean Times-series (HOT) program at Station ALOHA (22°45N, 158°00W). Between 1988 and 1999, particulate carbon (PC) export rates were $2.3 \pm 0.8 \, \text{mmol} \, C \, m^2 \, d^{-1}$ (e.g. Karl et al., 1996; Christian et al., 1997). Recent estimates of total C export based on the mass balances of oxygen and inorganic and organic carbon are over two times higher (Emerson et al., 1997). Higher total C export fluxes have been further confirmed from CFC based oxygen utilization rates and assumed C/O_2 ratios by Sonnerup et al. (1999). Much of this increase has been attributed to the accumulation of dissolved organic C (DOC), rather than to sinking particles (Emerson et al., 1997). Thus, gross primary production, new production, and export production would be out of balance. If these more recent studies are correct, then the NPSG could contribute up to 50% of the global carbon export of the world's oceans. This would have a significant impact on current understanding of the C cycle, especially if these revised estimates are due to shifts in ecosystem community structure resulting from changes in global climate (Karl, 1999; Karl et al., 2001).

In this study, we utilize the disequilibrium between ^{234}Th and its parent, ^{238}U, to quantify particulate matter export over a 1-yr period at Station ALOHA. ^{234}Th is produced from the radioactive decay of ^{238}U ($t_{1/2} = 4.47 \times 10^9 \, \text{yr}$). Since the half-life of ^{234}Th is 24.1 d and this element is very particle reactive, the disequilibrium between its soluble parent ^{238}U and the measured ^{234}Th activity reflects the net rate of particle export from the upper ocean on time scales of days to weeks (e.g. Buesseler, 1998). In the upper ocean, both the formation of fresh particle surfaces and the packaging of particles into sinking aggregates are reflected in the observed ^{234}Th distribution. The ability to measure ^{234}Th from small seawater samples (Buesseler et al., 2001; Benitez-Nelson et al., 2001) has enabled us to obtain high-resolution, high-precision depth profiles of ^{234}Th at this site for the first time.

2. Methods

2.1. Study site and sample collection

The majority of samples was collected during HOT cruises (4-d duration on approximately monthly intervals) to Station ALOHA (22°45N, 158°00W) from April 1999 (HOT 104) to March 2000 (HOT 112). In July 1999, samples were also collected at Station ALOHA during a 2-week cruise that immediately followed the July (HOT 106) cruise. For total ^{234}Th measurements, 21 samples were collected from 121 Niskin-like bottles throughout the water column to a depth of 3500 m. Selected replicate samples were also collected from paired bottles to estimate sampling precision.

In order to estimate a C (and N)/^{234}Th ratio for sinking particles at 150 m, we compared particles collected by PIT style sediment traps with in situ large volume pumps. Sediment traps were deployed on every HOT cruise according to the protocol developed by the HOT program (Karl et al., 1996). In general, 6 PIT sample tubes were deployed at a depth of 150 m for approximately 48–60 h. After recovery, samples were screened with 335 μm size Nitex mesh to remove swimmers and filtered onto either 25 mm glass fiber filters (Whatman GF/F) or microquartz filters (MQ, nominal pore size ~1 μm) and dried at 60°C for 8 h. MQ filters are preferable as they have a significantly lower gross beta radioactivity blank. PC contamination from swimmers that pass through the 335 μm mesh contributes an average of $12 \pm 8.4\%$ to the total PC flux ($n = 19$; Karl et al., 1996). We verified this result by carefully picking swimmers after screening from two sediment trap samples taken in November and analyzing the PC in the isolated swimmer fraction and the remaining sediment trap sample (swimmers ~13.6% of the total PC). For ^{234}Th, typically one sediment trap sample was processed for beta counting as described below.

In situ Challenger Oceanic Mark II pumps were also deployed to collect particulate ^{234}Th. The pump utilized in this study is similar to those (McLane pumps) used in the JGOFS process studies in the Equatorial Pacific, Arabian Sea, and Southern Ocean (Bacon et al., 1996; Buesseler et al., 1995, 1998, 2001). In general, pumps were deployed over the side and particulate matter samples collected at 150 m. Greater than 2001 of seawater were pumped at a rate of $4-61 \text{min}^{-1}$ through either a 53 or 10 μm Nitex screen followed by a 142 mm MQ filter (~1 μm pore size). The filter housings used in this study result in an even distribution of filtered material across the filter (e.g. Buesseler et al., 1995, 1998).

2.2. Analyses

The 2 L technique for the measurement of total ^{234}Th in seawater has been described in detail by Buesseler et al. (2001) and Benitez-Nelson et al. (2001). Briefly, unfiltered water samples were collected and reagents added to form a MnO_2 precipitate, which preferentially scavenges ^{234}Th, leaving its parent, ^{238}U, in the dissolved phase. The precipitate was allowed to form for 8–16 h before being filtered onto a 25 mm diameter, 1.2 μm pore sized silver filter. Silver filters were chosen as they have higher counting efficiencies with respect to ^{234}Th. Alternatively, GF/F or MQ filters may be utilized instead. The silver mesh filters were allowed to air dry for several hours, and prepared for counting by mounting onto a plastic counting ring and covered with mylar and foil.

Large particulate samples collected on Nitex screens were rinsed with 0.2 μm prefiltered surface seawater onto precombusted 25 mm silver filters immediately after collection. Samples were allowed to air dry and prepared for beta counting as above. Similar procedures were used in the JGOFS process studies (Buesseler et al., 1995, 1998, 2001). The 142 mm MQ filters collected with the Nitex screens were dried in a 60°C oven for $\sim$ 8 hours. A PVC holder and stainless-steel cutter were used to cut out 20 subsamples, each with a diameter of 25 mm. The subsamples were stacked into a 25 mm plastic counting ring and compressed to a constant height/geometry under 1 metric ton of pressure with a sample press. This is identical to the procedure used by Buesseler et al. (1998, 2001) in the Arabian Sea and Southern Ocean.

All ^{234}Th samples were covered with mylar and foil before being directly counted on a 5 sample, gas-flow proportional low-level RISØ beta counter that measured the beta activity of the high energy ^{234}Th daughter, ^{234m}Pa ($E_{max} = 2.3$ MeV). Counting efficiencies varied by less than 2% between detectors and averaged 35.9 ± 1.8%. Each sample was recounted after > 150 d had passed since collection to precisely determine background count rates, which averaged 0.48 ± 0.24 cpm ($\sim$ 25% of the total measured count rate). The detector was calibrated for each cruise with 3500 m deep water samples (assumed to be in radioactive equilibrium) that were collected from 5 different water bottles from the same cast. Replicate deep water samples varied by less than 5% (avg. $= 2.38$ dpm kg^{-1}, Fig. 1). Detector calibration for the stacked MQ and particulate samples was carried out with known ^{234}Th activities in the same sample geometries (Buesseler et al., 1998, 2001a, b).

Particulate C and N (PN) analyses were determined for each filter type with a Europa CN autoanalyzer according to the HOT protocols, which do not include fuming HCl or distilled water rinsing pretreatments (Karl et al., 1991). For the MQ samples (1.0–53 μm), 8 mm subsamples were cut with a stainless steel cutter. For the Nitex screens rinsed onto 25 mm silver filters, the entire sample was analyzed after ^{234}Th analysis. Upon closer examination, a trend towards high C/N ratios was found for the Nitex screens compared with sediment traps. A similar result was observed in the equatorial Pacific and was presumably from a C-rich blank derived from oils or soot particles from the ship that were picked up by our filters during the pump deployment (Buesseler et al., 1995). Each Nitex screen sample was corrected for a C blank, such that the mean C/N molar ratio was 7.8 ± 0.6, the same as that found in sediment traps over the same time period. The average C blank derived from rinsing the Nitex screen was 5.7 ± 2.8 μmol C ($\sim$ 16% of the total). The C blank for the MQ samples was significantly lower ($<$ 10% of the total) and a molar C/N ratio of 8 ± 1 was found. The Nitex screen and MQ N blanks were less than 0.1 μmol N ($<$ 5% of the total).

2.3. Results

Total ^{234}Th activities varied both with depth and from cruise to cruise ranging from a low of 1.28 ± 0.12 dpm kg^{-1} to a high of 3.08 ± 0.29 dpm kg^{-1} (Fig. 1). In December 1999 ($n = 3$ pairs, HOT 110) and February 2000 ($n = 9$ pairs, HOT 111) replicate samples were obtained throughout the water column from separate water bottles in the same cast and were indistinguishable, within the processing/counting error ($<$ 5%). In general, the largest disequilibrium between ^{234}Th and its parent ^{238}U occurred in the upper 100 m, where particle formation rates and sinking are highest. Activities greater than secular equilibrium were typically found between 100 and 200 m, and can
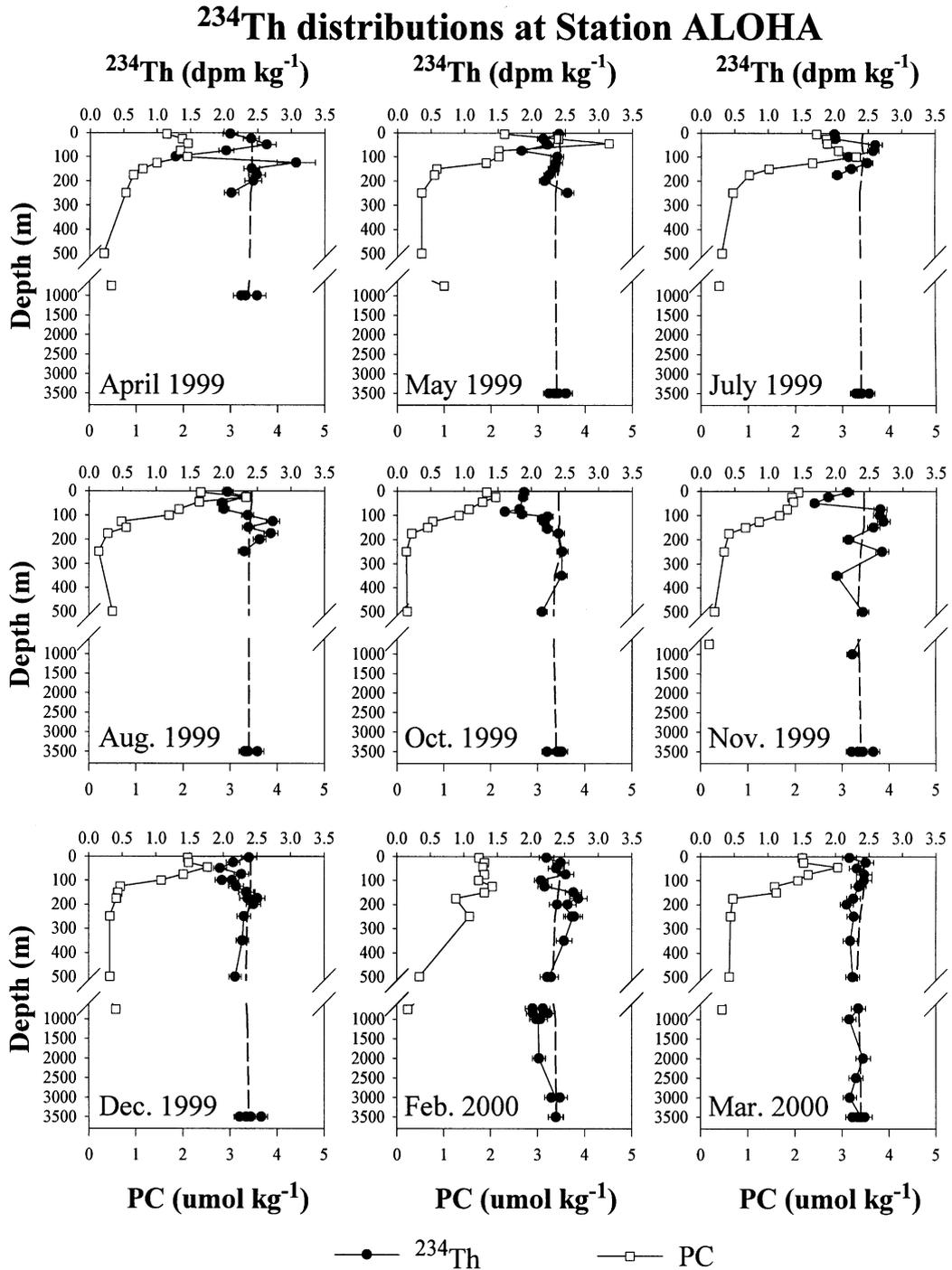
^{234}Th distributions at Station ALOHA

Fig. 1. Total ^{234}Th activities (closed circles) and PC (open squares) versus depth for all 9 cruises. In July, PC and ^{234}Th measurements were conducted on separate cruises ∼ 2 weeks apart. The vertical dashed line is the ^{234}Th expected from ^{238}U (derived from salinity). All ^{234}Th error bars were determined from counting statistics and the errors associated with efficiency calibration and water sampling. All ^{234}Th activities are decay corrected to the midpoint of collection.
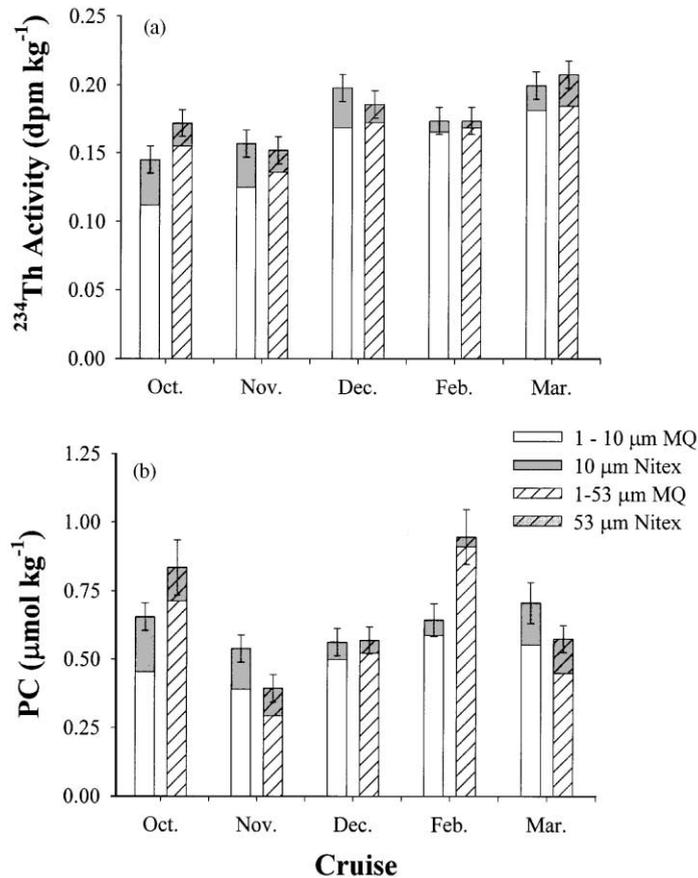
^{234}Th and PC in Nitex and MQ Filters at 150 m

Fig. 2. PC (μmol kg^{-1}) and particulate ^{234}Th (dpm kg^{-1}) in seawater at 150 m obtained with the in situ pump. White and hatched white bars are for the 1–10 and 1–53 μm MQ samples, respectively. The gray and hatched gray bars are for the > 10 and 53 μm Nitex samples, respectively. Error bars represent the error on the total particulates (e.g. 1–10 μm MQ + > 10 μm Nitex).

be achieved via particle remineralization. In many of the cruises, significant deviations from equilibrium were measured between 300 and 1000 m.

Particulate ^{234}Th samples at 150 m ranged from 0.005 dpm kg^{-1} to 0.033 dpm kg^{-1} on large particles collected on the > 10 and > 53 μm Nitex screens and between 0.112 and 0.185 dpm kg^{-1} on smaller particles collected on the 1–10 and 1–53 μm MQ (Fig. 2a). The > 10 μm Nitex screens had ^{234}Th activities that were either slightly higher than, or the same as those measured on the larger > 53 μm Nitex screens. The MQ filters showed more variability, but tended to have a corresponding trend (1–53 > 1–10 μm).

Sediment trap ^{234}Th fluxes ranged from 214 $\pm$ 8 to 611 $\pm$ 20 dpm m^{-2} d^{-1} and showed no seasonal trend. In November 1999 and February 2000, duplicate sediment trap sampling tubes were processed for ^{234}Th and ^{234}Th fluxes and were found to be within $\pm$ 2%. This is significantly

less than the error associated with PIT PC fluxes, which showed intersampling tube variability of 21% and 12% during those months. This is most likely due to differences in the number of swimmers, although hydrodynamics may also play a role (Michaels et al., 1990; Buesseler, 1991; Buesseler et al., 2000).

PC measured on >10 and $>53\,\mu m$ Nitex screens ranged from 0.03 to $0.20\,\mu mol\,C\,kg^{-1}$, whereas PC measured on the 1–10 and 1–53 μm MQ samples was two to ten times higher and ranged from 0.29 to $0.91\,\mu mol\,C\,kg^{-1}$ (Fig. 2b). Replicate analyses of PC and PN on the MQ subsamples had an error of less than 5% ($n = 4$ sets). Again, PC found on the $>10\,\mu m$ Nitex screens was either higher than or the same, within error, as that found on the $>53\,\mu m$ Nitex screens. The MQ filters showed more variability, but tended to have an opposite trend. PN followed the same general patterns as that found with PC. PN measured on >10 and 53 μm Nitex screens ranged from 0.004 to $0.025\,\mu mol\,N\,kg^{-1}$. PN measured on the 1–10 and 1–53 μm MQ samples was 3–10 times higher and ranged from 0.02 to $0.17\,\mu mol\,N\,kg^{-1}$.

3. Discussion

At Station ALOHA, most of the ^{234}Th particle scavenging occurred within the upper 100 m, coinciding with maxima in PC concentrations (Fig. 1) as found in other areas (Bacon et al., 1996; Buesseler et al., 1995, 1998, 2001; Baskaran et al., 1996). This depth distribution is consistent with ^{234}Th removal associated with biological formation of fresh particles and their subsequent removal from the euphotic zone, i.e. export production via the biological pump. Total ^{234}Th activities greater than disequilibrium were found between 100 and 200 m and are indicative of particle remineralization or accumulation. Such features have been found previously in the equatorial Pacific and are also consistent with the biological pump paradigm (Bacon et al., 1996).

In December 1999 and February 2000, a large deficit in ^{234}Th activities at depths below 300 m also occurred (Fig. 1). Similar ^{234}Th deficiencies have been found in the equatorial Pacific, where particulate ^{234}Th activity at $\sim 300\,m$ increased to 15–35% of the total ^{234}Th activity measured (Bacon et al., 1996). In the Gulf of Mexico, deficits in ^{234}Th activity were measured down to depths of 1500 m, possibly due to bottom or boundary scavenging by resuspended sediments (Baskaran et al., 1996). Unfortunately, there is a general lack of information regarding ^{234}Th within the mesopelagic (200–1000 m), as most investigators have not measured ^{234}Th activities between the euphotic zone and the deep ocean. This is because particle scavenging has been assumed to occur primarily in the surface layer.

One possible explanation for a deeper ^{234}Th : ^{238}U disequilibrium is the advection of water masses that have experienced scavenging in the recent past ($\sim 35\,d$). The water column at Station ALOHA consists of several different water mass features (Chen et al., 1987). However, the time scales over which each of these water masses are formed and subducted prior to transport to Station ALOHA are quite long, several months to decades (e.g. Sonnerup et al., 1999). Thus, this mechanism is unlikely to have caused the observed ^{234}Th distribution patterns.

Biologically mediated particle formation is a more likely cause of the ^{234}Th deficits observed within the deeper water column. Karl and Knauer (1984) found a substantial increase in the number of fecal pellets in sediment traps deployed at depths below 600 m in the northeastern Pacific Ocean. They attributed this phenomenon to both migrating zooplankton and indigenous

populations. There is a significant population of mesozooplankton that permanently reside below 400 m (23–32% of total biomass in upper 150 m), indirectly influenced by upper ocean production through the migration of their prey (Maynard et al., 1975; Al-Mutairi and Landry, 2001). There is also evidence that suspended particles may be repackaged at these deeper depths into larger sinking aggregates by organisms, such as salps and appendicularians (e.g. Davoll and Silver, 1986; Davoll and Youngbluth, 1990; Alldredge and Jackson, 1995). Such processes may explain the total ^{234}Th disequilibria measured at depth.

In order to determine the flux of ^{234}Th from the upper ocean, and hence the extent of particulate matter export, the following ^{234}Th activity balance equation is used:

$$dA_{Th}/dt = (A_U - A_{Th})\lambda - P + V, \tag{1}$$

where dA_{Th}/dt is the change in ^{234}Th activity with time, A_U is the ^{238}U activity (^{238}U (dpm kg^{-1}) = 0.0686 × salinity; Chen et al., 1986), A_{Th} is the total measured ^{234}Th activity, λ is the decay constant for ^{234}Th (= 0.0288 d^{-1}), P is the net removal flux of ^{234}Th on particles, and V is the sum of the advective and diffusive terms. In the open ocean, the magnitude of P is determined mostly by the extent of the ^{234}Th/^{238}U disequilibrium. Steady state is often assumed ($dA_{Th}/dt = 0$) and V is assumed to be negligible.

The assumption of steady state for ^{234}Th can be directly tested by the relatively high temporal resolution of our measurements. ^{234}Th fluxes were determined over the upper 150 m with both a steady state (SS) and non-steady state (NSS) model (Table 1; see Buesseler et al., 1995 for details). Each point in the calculated NSS ^{234}Th flux represents the midpoint between cruises. The NSS model assumes that the same water is being sampled between cruises. Although there is significant cruise to cruise variability, the relative difference between the average SS and NSS derived ^{234}Th fluxes is low (Table 1).

We can compare the ^{234}Th export determined from water column ^{234}Th disequilibrium with that measured in the PIT (Fig. 3). PITS undercollected for ^{234}Th during two periods of high particulate export flux that occurred in October and December 1999 by factors of 4 and 2 (compared to the SS model). During the remainder of the observation period, the ^{234}Th flux measured in the PITS is comparable to that calculated from the water column profiles. A similar pattern in the timing and magnitude of ^{234}Th under collection during periods of high ^{234}Th particle flux has been found in a 3 yr comparison of water column versus PIT derived ^{234}Th export at the oligotrophic Bermuda Atlantic Time-series Study (BATS) (Buesseler et al., 2000). At BATS, sediment traps were found to overcollect ^{234}Th during periods of low export, a tendency that is not observed at Station ALOHA. One possible reason for the undercollection is due to the timescales over which the two methods are valid. ^{234}Th fluxes are integrated over ∼ 35 d, whereas sediment traps were only deployed for ∼ 2 d. Thus, it is possible that the sediment trap deployments may have 'missed' these two large export events. The general similarity of the two estimates of ^{234}Th in this habitat suggests that sediment traps are generally representative of particulate matter export. It should be noted that in the equatorial and Subarctic Pacific, two areas of typically higher export, PITs tend to overcollect for ^{234}Th (Murray et al., 1996; Charette et al., 1999; Dunne et al., 2000).

An interesting pattern arises in the waters just below the euphotic zone in August 1999, November 1999 and February 2000. There appears to be a transient remineralization peak, or excess ^{234}Th (negative ^{234}Th flux in Table 1), below 150 m. In July 1999, there is substantial export

Table 1
Steady-state (SS) and non-steady-state (NSS) ^{234}Th fluxes and ^{234}Th derived PC export

Cruise and depth interval	SS ^{234}Th flux (dpm m^{-2} d^{-1})	Error $\pm$	NSS ^{234}Th flux[a] (dpm m^{-2} d^{-1})	Error $\pm$	SS C flux[b] (mmol C m^{-2} d^{-1})	Error $\pm$	NSS C flux[c] (mmol C m^{-2} d^{-1})	Error $\pm$
0–150 m								
April 1999	643	266	N/A		1.30	0.59	N/A	
May	806	147	921	152	1.30	0.29	1.68	0.36
July	374	146	397	104	2.04	0.97	1.41	0.53
Aug.	621	144	1016	103	0.78	0.21	3.41	0.55
Oct.	2311	125	1724	96	4.09	0.33	2.61	0.21
Nov.	374	145	268	192	0.77	0.34	0.51	0.38
Dec.	1066	173	1434	173	1.82	0.42	2.70	0.55
Feb. 2000	313	188	111	128	0.44	0.28	0.17	0.20
March	411	187	252	133	0.71	0.35	0.40	0.22
Average	765	562	769	591	4.0	2.9	4.3	2.9
150–300 m								
April 1999	571	99	N/A					
May	58	257	−302[d]	258				
July	1091	172	678	309				
Aug.	−380[d]	266	−880[d]	272				
Oct.	127	202	995	334				
Nov.	−511[d]	240	−810[d]	314				
Dec.	59	249	356	395				
Feb. 2000	−937[d]	291	−1104[d]	384				
March	591	257	1038	257				

[a] NSS fluxes are determined for the midpoint between sampling cruises.
[b] ^{234}Th derived SS PC export fluxes using C/^{234}Th ratios measured in sediment traps.
[c] ^{234}Th derived NSS PC export fluxes are derived using the average of the sediment trap C/^{234}Th ratios measured in the preceeding and following cruises.
[d] Negative fluxes between 150–300 m indicate net remineralization (see text for discussion).

below 150 m that appears to be the source of the August 1999 remineralization peak, whereas in November 1999 and February 2000, excess ^{234}Th at depth is due to high ^{234}Th export from the euphotic zone in the preceeding cruises. To a first approximation, the magnitude of the 0–300 m integrated ^{234}Th export is in balance with the decay corrected ^{234}Th excess measured at 150–300 m in the subsequent cruise, regardless of whether a SS or NSS model is used (Table 1). To our knowledge, this is the first time that such transient ^{234}Th remineralization peaks have been identified. Concurrent with the November 2000 peak in remineralization is an increase in heterotrophic bacteria coupled with a small decrease in dissolved O_2. Similar features are not seen in February, but this may be due to the long time period between cruises.

To translate ^{234}Th fluxes into PC and PN export, the C (and N)/^{234}Th ratio of sinking particles must be measured. The bulk ratios of C/^{234}Th in sediment trap and in situ pump samples are surprisingly similar (Table 2). The ratio of C/^{234}Th in sediment traps averages $4.8 \pm 0.6 \,\mu$mol dpm^{-1} from October 1999 to March 2000 when we have both trap and filter data. The average value is well within the range of that found in the North Atlantic Bloom Experiment,

^{234}Th Export (0 -150 m)
Calculated vs. Measured Export Fluxes
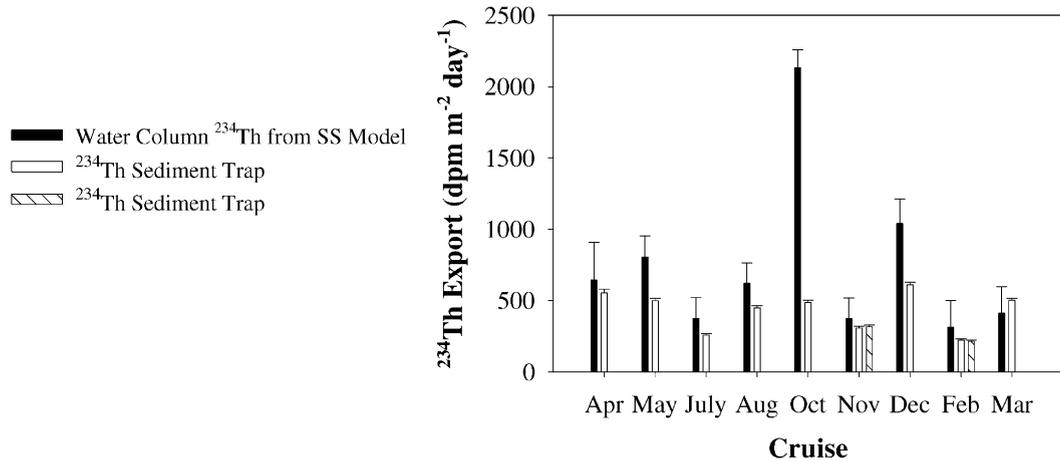

Fig. 3. Comparison of calculated ^{234}Th export over the upper 150 m from a steady state model (dark bars) with measured sediment trap ^{234}Th fluxes (white and dashed bars). Replicate sediment trap samples were measured in November 1999 and February 2000.

Table 2
C/^{234}Th (μmol dpm^{-1}) ratios measured at 150 m by in situ filtration and with sediment traps deployed for $\sim$48 h

Cruise	1–10 μm MQ	Error $\pm$	> 10 μm Nitex	Error $\pm$	1–53 μm MQ	Error $\pm$	> 53 μm Nitex	Error $\pm$	Sediment Trap	Error $\pm$
April 1999	—	—	—	—	—	—	—	—	5.54	1.05
May	—	—	—	—	—	—	—	—	4.43	0.59
July	—	—	—	—	—	—	—	—	14.96	4.08
Aug.	—	—	—	—	—	—	—	—	3.44	0.43
Oct.	4.05	1.04	6.02	0.75	4.58	1.17	7.35	0.92	4.85	0.28
Nov.	3.12	0.80	4.62	0.57	2.16	0.55	6.12	0.77	5.64	1.23
Dec.	2.96	0.39	2.19	2.50	3.02	0.77	3.61	1.45	4.67	0.77
Feb. 2000	3.55	2.50	7.40	0.96	5.40	2.45	7.14	0.95	3.87	0.79
March	3.05	0.78	8.53	2.57	2.44	0.62	5.47	1.38	4.74	0.82
Average	3.4	0.4	5.8	2.2	3.5	1.3	5.9	1.4	4.8[a]	0.6

[a] Average calculated from Oct. 1999 to March 2000. The average increases to 5.8 ± 3.5 when the entire data set is used due to the July 1999 value.

BATS, and the equatorial, subarctic, and North Pacific (Murray et al., 1989; Buesseler et al., 1992, 1995; Michaels et al., 1994; Murray et al., 1996; Charette et al., 1999; Dunne et al., 2000). The average C/^{234}Th ratios found on the > 10 and 53 μm Nitex screens are also similar and slightly higher than those found in the 1–10 and 1–53 μm MQ (Table 2). Higher C/^{234}Th ratios in the larger particle size class have also been found to occur in the Arabian Sea (Buesseler et al., 1998)

and Southern Ocean (Buesseler et al., 2001). The similarity in $C/^{234}Th$ ratios between the different in situ pump size classes and sediment traps suggests that the particles being sampled are representative of sinking aggregates.

We have chosen to use the ratio of C (and N)$/^{234}$Th measured in each sediment trap with the calculated ^{234}Th SS flux from each cruise ($n = 9$) to determine a mean annual export flux of 4.0 ± 2.3 mmol C m^{-2} d^{-1} and 0.53 ± 0.19 mmol N m^{-2} d^{-1} at the 150 m reference depth. This is identical, within error, to the value determined from the MQ and Nitex screens taken from the in situ pump or from a NSS ^{234}Th model (range: 3.4 ± 0.4–5.9 ± 1.4 mmol C m^{-2} d^{-1} and 0.37 ± 0.10–0.70 ± 0.26 mmol N m^{-2} d^{-1}, respectively, see Table 1). Our ^{234}Th derived PC and PN export is $\sim 60\%$ higher than the 2.4 ± 0.2 mmol C m^{-2} d^{-1} and 0.32 ± 0.08 mmol N m^{-2} d^{-1} determined from the PIT style sediment traps during the same time period.

Most of this difference is due to undercollection of PC by sediment traps during October and December 1999 (Fig. 4). When October and December are ignored, a ^{234}Th derived PC export flux
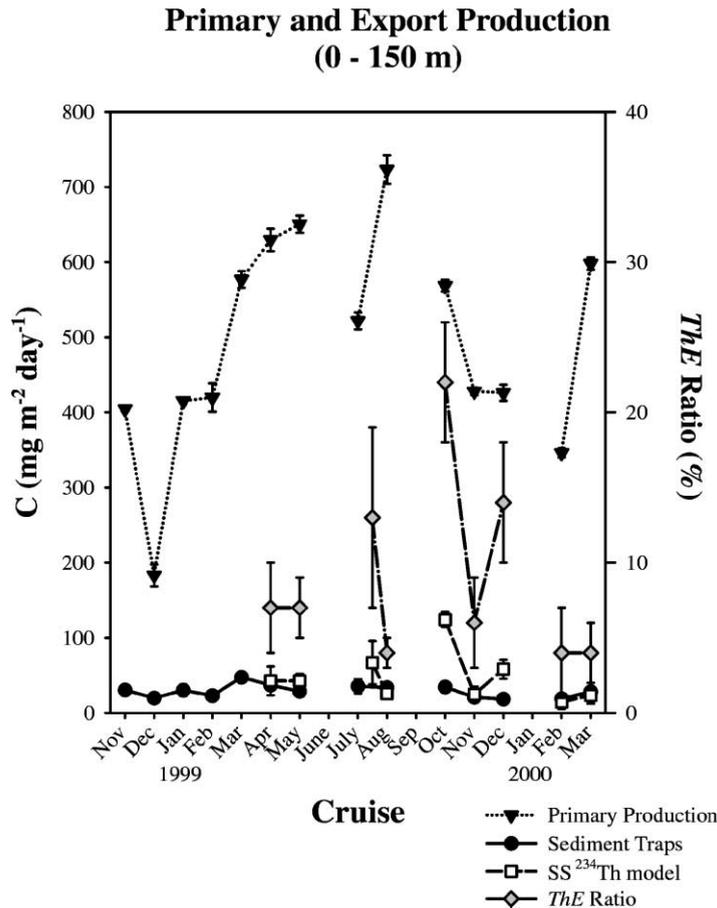

Fig. 4. Comparison of ^{234}Th derived PC export (open squares) over the upper 150 m with PC export measured in sediment traps (closed circles) and ^{14}C based primary production (closed triangles). *ThE* ratios (see text) are also depicted (gray diamonds).

of 2.9 ± 0.5 mmol $C\,m^{-2}\,d^{-1}$ is determined. Subtracting 0.3 mmol $C\,m^{-2}\,d^{-1}$ attributed to migrating zooplankton (Al-Mutairi and Landry, 2001), reduces this flux to the same, within error, as determined from sediment traps over the same time period (2.4 mmol $C\,m^{-2}\,d^{-1}$). Thus, PITs match the ^{234}Th derived PC export throughout most of the year. However, higher PC export events, which are key to understanding the C cycle at Station ALOHA, appear to be systematically underestimated by the monthly cruise frequency. This conclusion is supported by results obtained using continuously bottom-moored sediment traps that capture both the sustained and aperiodic pulsed export events (Scharek et al., 1999).

Although the PC export found in this study is higher than that measured by sediment traps, it is within the range determined by a variety of techniques in previous studies in the NPSG (Table 3). We define the ratio of ^{234}Th derived PC export to primary production as the "*ThE*" ratio (e.g. Buesseler, 1998). *ThE* ratios ranged from 4% to 22% (Fig. 4). Ratios less than 10% are consistent with the small measured disequilibrium between ^{234}Th and ^{238}U and are expected from a tightly coupled food web characteristic of oligotrophic regimes (Karl et al., 1996). In October and December, however, *ThE* ratios were 22% and 14%. High *ThE* ratios have also been found at BATS, where they exceeded 25% and even approached 50%, but only at times of extremely low primary productivity (Buesseler, 1998). The cause of these high export events is unclear, but they may be related to episodic injections of nutrient rich deep waters or to changes in community structure (Karl et al., 1996, 2001; Letelier et al., 1993; McGillicuddy et al., 1998; Karl, 1999). Scharek et al. (1999) determined a late summer PC export peak at Station ALOHA due to diatom blooms. There is no direct evidence of a late summer diatom bloom in this study. However, it is highly likely that this event may have been missed because there was no HOT cruise during the month of September 1999. The PC export flux measured in October 1999 may be due to the remnants of diatom activity and subsequent sinking. The smaller peak in PC export in December 1999 may have been caused by a small upwelling event of nutrient rich waters into the surface. Similar events have been found to typically occur during the late winter months (Letelier et al., 2000). There was no increase in the PC export measured in sediment traps for either of the two periods (Fig. 4).

The lack of correlation between primary production and ^{234}Th derived PC export in this study (e.g. Fig. 4) has also been demonstrated between primary production and PITs by Karl et al. (1996) at Station ALOHA and by Michaels and Knap (1996) at BATS. Some of this lack of coherence is due to the delay between primary production (a function of nutrients and light) and export (a function of plankton speciation and zooplankton grazing). These differences lead to a temporal offset between C uptake and export. The fact that traps and ^{234}Th are not correlated with primary production in this study also suggests that organisms responsible for the majority of primary production (i.e. phototrophic bacteria of the genera *Prochloroccus* and *Synechococcus*) are not the same as those involved in PC export (i.e. diatoms). At present, the relationship between these variables, as well as the role of episodic events, are still poorly understood.

The magnitude of PC export at Station ALOHA has large implications for understanding the C budget of the NPSG and the role of oligotrophic oceans in C sequestration. Emerson et al. (1997) determined that total C sequestration at station ALOHA was on the order of 5.5 ± 2.7 mmol $C\,m^{-2}\,d^{-1}$ ($4.4 \pm 2.5 - 7.4 \pm 4.6$ mmol $C\,m^{-2}\,d^{-1}$) at 100 m based on mass balances of O_2, and inorganic and organic C. A similar estimate of 6.0 ± 1.4 mmol $C\,m^{-2}\,d^{-1}$ at 100 m was calculated by Sonnerup et al. (1999) using CFC based O_2 utilization rates. We can also determine the total

Table 3
PC export measured at 150 m in the NPSG

Study site	Date of measurement	Method	Average (mmol C m^{-2} d^{-1})	Range (mmol C m^{-2} d^{-1})	Reference
VERTEX (28°N 155°W)	July 1983–Aug. 1983	Sediment trap	2.2		Martin et al. (1987)
VERTEX (33°N 139°W)	July 1987–May 1988	Sediment trap	7.8[a]	4.9–12.9	Knauer et al. (1990)
Sta. ALOHA (22°45N 158°W)	Dec. 1988–Oct. 1993	Sediment trap	2.3±0.6	0.9–4.8	Karl et al. (1996)
Sta. ALOHA (22°45N 158°W)	Dec. 1988–Oct. 1993	N/P diffusion model	2.2		Christian et al. (1997)
Sta. ALOHA (22°45N 158°W)	Apr. 1999–Mar. 2000	^{234}Th (SS model)	4.0±2.3	1.2–10.4	This study

[a] In this study, sediment trap samples were acid fumed to remove particulate inorganic C.

Table 4
Total C mass balance integrated over the upper 150 m in the NPSG (see text for details)

	mmol C m^{-2} d^{-1}	Timescale of estimate	Reference
Downward diffusion of DOC	-1.2 ± 1.1	1988–1999	This study
DOC accumulation	-0.7 ± 0.2	1993–1999	Church et al. (2001)
DIC accumulation	-0.8 ± 0.3	1988–1999	This study
PC export	-4.0 ± 2.3	April 1999–March 2000	This study
Migrating zooplankton and associated processes	-0.6 ± 0.1	1994–1996	Al-Mutairi and Landry (2001)
Total C output	-7.3 ± 2.6		
C and O$_2$ based C export	-4.4 ± 2.5 to -7.4 ± 4.6 at 100 m	1990, 1992, 1995	Emerson et al. (1997)
CFC based C export[a]	-6.0 ± 1.3 at 100 m		
	-4.1 ± 0.8 at 150 m	1991	Sonnerup et al. (1999)
Upward diffusion of DIC	3.9 ± 3.5	1988–1999	This study
Atmospheric CO$_2$ uptake	2.7 ± 0.9	1988–1995	Winn et al. (1998)
Total C input	6.6 ± 3.6		

[a] This estimate does not include particulate inorganic C export.

magnitude of C sequestration from the euphotic zone using a simple mass balance (Table 4). Church et al. (2001) integrated DOC over the upper 175 m and determined that DOC was accumulating in the NPSG surface waters. Here, we recalculated the rate of DOC accumulation to be 0.7 ± 0.2 mmol C m^{-2} d^{-1} for the upper 150 m. DIC is also accumulating over this depth horizon at a rate of 0.8 ± 0.3 mmol C m^{-2} d^{-1}. A downward diffusive flux of DOC across 150 m using the 5-yr mean DOC profile from the HOT program and an average vertical eddy diffusivity, K_z, of 0.9×10^{-4} m^{-2} s^{-1} (average of Li et al., 1984 and Ledwell et al., 1993 K_z estimates) is 1.2 mmol C m^{-2} d^{-1}. For comparison, Emerson et al. (1997) determined a mean downward transport of DOC as high as 1.6 ± 1 mmol C m^{-2} d^{-1}, based on the change in the ratio of DOC/O$_2$ across 100 m.

Al-Mutairi and Landry (2001) determined that migrating zooplankton contribute an additional 0.3 ± 0.1 mmol C m^{-2} d^{-1} based on models that incorporated the difference in zooplankton biomass and community structure between 150 m depth integrated day and night tows. This zooplankton mediated flux increases by 0.25 mmol C m^{-2} d^{-1} when migrant mortality, organic C excretion, and fecal pellet production at depth are also considered. When all of these pathways of C removal are summed, a total C export of 7.3 ± 2.6 mmol C m^{-2} d^{-1} is determined, similar to that estimated previously (Table 4). This again suggests that C sequestration in the NPSG is substantial, and these areas of the world's oceans need to be considered more fully in all models which seek to emulate global C export.

This total C export is balanced, within error, by the rate of CO$_2$ uptake from the atmosphere, 2.7 ± 0.9 mmol C m^{-2} d^{-1} (Winn et al., 1998), and the upward diffusion of DIC into the euphotic zone from below, 3.9 ± 3.5 mmol C m^{-2} d^{-1} (calculated from the 11 yr mean DIC profile across 150 m from the HOT program and an average vertical eddy diffusivity of 0.9×10^{-4} m^{-2} s^{-1}). It is

important to note that both the influx of DIC and the outflux of DOC from the upper 150 both depend on the same vertical eddy diffusivity (see above) and these two terms have opposite signs in the C budget. Our mass balance estimate indicates that while the C cycle at Station ALOHA is presently balanced, individual components have changed with time, indicating a dynamic non-steady-state regime.

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