^{234}Th scavenging and particle export fluxes from the upper 100 m of the Arabian Sea

M. M. Sarin, R. Rengarajan and V. Ramaswamy*

Physical Research Laboratory, Ahmedabad 380 009, India
*National Institute of Oceanography, Dona Paula 403 004, India

We have determined the particle scavenging rates, export fluxes of ^{234}Th and settling particles from the upper 100 m of the Arabian Sea as a part of the JGOFS (India) Programme. The spatial and temporal measurements made in the open ocean profiles reveal close similarities in the dissolved ^{234}Th : ^{238}U disequilibria, suggesting that the rates of particle-associated scavenging processes are generally uniform in the central Arabian Sea. The observed disequilibrium integrated for the upper 100 m yields a mean scavenging residence time of ~ 30 days and a removal rate of ~ 3400 dpm $m^{-2} d^{-1}$ for ^{234}Th, from dissolved to particulate phases.

The deficiency of total ^{234}Th (dissolved + particulate) relative to ^{238}U allows us to compute the vertical export flux of particulate ^{234}Th. The flux data for the upper 100 m show spatial variations with enhanced export fluxes centered around 22°N 67°E, a region characterized by higher rates of column primary productivity. Using the ^{234}Th export fluxes and the measured specific activity of ^{234}Th in the sediment traps, we have computed the particle and carbon fluxes at 100 m. These results reveal that the particle fluxes determined from sediment traps are systematically low and the estimated C export fluxes are grossly out of proportion with the column primary production.

THE reactive nuclides of the U–Th decay series, viz. ^{234}Th, ^{210}Po and ^{210}Pb serve as valuable tracers for studying the rates of particle-associated chemical scavenging processes, particle export from the euphotic zone and new production in the ocean. These tracers are introduced in the water column as dissolved species (by radioactive decay of their parent nuclides dissolved in seawater) and are redistributed between the dissolved and particulate phases depending on their particle reactivity and availability of particle surfaces. The latter depends on the rates of primary production, particle transformation and their net downward export. Bhat *et al.*[1] were the first to demonstrate the application of ^{234}Th–^{238}U disequilibrium to study the particle scavenging processes in oceanic surface waters. These studies were later expanded by Coale and Bruland[2,3] and suggested that the scavenging rates of reactive elements may vary as a function of new production rather than total primary production. Recently, Buesseler *et al.*[4,5] have used the profiles of ^{234}Th and a non-steady state scavenging model

to quantify the particulate ^{234}Th fluxes and to derive export fluxes of particulate carbon and nitrogen from the euphotic zone. Likewise, the ^{210}Po–^{210}Pb disequilibrium in surface waters and the particulate release of ^{210}Po at ~ 100 m have been modelled to derive the new production rates in the Arabian Sea[6].

Measurements of particle export fluxes using sediment traps in the top few hundred meters of the water column have also been compared with those derived based on the ^{234}Th : ^{238}U disequilibrium studies[7-9]. These studies have shown significant discrepancy for the trap fluxes suggesting that the shallow traps do not always provide a reliable measure of the particle export. We report here our results on the ^{234}Th scavenging and particle export fluxes in the eastern-central Arabian Sea during the JGOFS (India) cruises. We have used the ^{234}Th and ^{238}U isotope data from unfiltered (total) samples and the specific activity of ^{234}Th in the sediment trap material to derive the particle export fluxes.

Samples and analyses

Samples were collected during ORV *Sagar Kanya* cruises No. 91 (April–May 1994), No. 99 (February–March 1995) and No. 104 (July–August 1995) in the Arabian sea (Figure 1). Three stations sampled during April–May 1994 at 11°N, 15°N and 22°N along the 64°E transect were reoccupied during the subsequent cruises to study the temporal and spatial variations in the export fluxes of ^{234}Th and settling particles, The hydrographic data (potential temperature, salinity and depth) were simultaneously measured at all stations. Parallel measurements of primary productivity were also made using *in-situ* incubations[10].

Unfiltered seawater samples from the upper 300 m water column were collected using 30 litre Go-Flo bottles fitted on the CTD rosette and were analysed for ^{234}Th, ^{238}U, ^{210}Po and ^{210}Pb. At selected stations, along the 64°E transect (Figure 1), samples were also filtered through 0.4 µm pore size Nuclepore filters (47 mm diameter) directly attached to the Go-Flo bottles. All these nuclides were pre-concentrated from about 20–25 litres of either filtered or unfiltered seawater with Fe(OH)$_3$ in presence of chemical yield tracers. Subsequently, radiochemical separation and purification of these

nuclides were achieved following the procedures of Sarin et al.[11].

The mass flux of settling particles at 100 and 300 m depths was measured using free-floating sediment traps deployed, during April–May 1994 (cruise-91) and February–March 1995 (cruise-99), for a period of 3–5 days at station sites 15°N, 64°E and 21.5°N, 64°E. The multi-traps (Hydrobios, Germany) consisting of a PVC cylinder (having collection area 0.01515 m² and aspect ratio of 1 : 4) fitted to six polyethylene bottles were used in this study. After recovery of the traps, supernatant water in the sample bottles was carefully decanted and 'swimmers' were removed. Samples were then filtered through 0.4 μm Nuclepore filters and dried at 40°C. One-half of the collected material was analysed for ^{234}Th, ^{210}Po and ^{210}Pb. For this, filters were acid digested (HCl + HNO$_3$) in presence of yield spikes and analytical procedures follow that of Sarin et al.[11]. The remaining half of the filters were stored for the analysis of organic carbon.

Results and discussion

In this article we present the data on the dissolved and total (dissolved + particulate) ^{234}Th concentrations; results on the ^{210}Po and ^{210}Pb will be presented elsewhere. The distribution of dissolved and total ^{234}Th activities vs depth at the three stations along the 64°E transect is shown in Figure 2. The vertical profiles of total ^{234}Th measured at stations along the coast are presented in Figure 3. The errors (± 1σ) in the ^{234}Th activities are

about ± 5% arising from counting statistics, tracer calibrations and blank corrections. The accuracy and precision of our ^{234}Th measurements were checked by analysing unfiltered seawater samples collected from 1000 to 2000 m depths. The ^{234}Th/^{238}U activity ratios measured in these samples were in close agreement to the expected equilibrium value. The ^{238}U activity (Figures 2 and 3) was calculated based on its relation with salinity [^{238}U (dpm/kg) = (0.06969) × S‰] derived for the Arabian Sea[11]. This relation is based on measured ^{238}U and salinity data for samples collected from surface to 2000 m depth including those from sub-oxic regions. The ^{238}U concentration did not show any distinct decrease in the samples from denitrification region[6,11].

^{234}Th scavenging

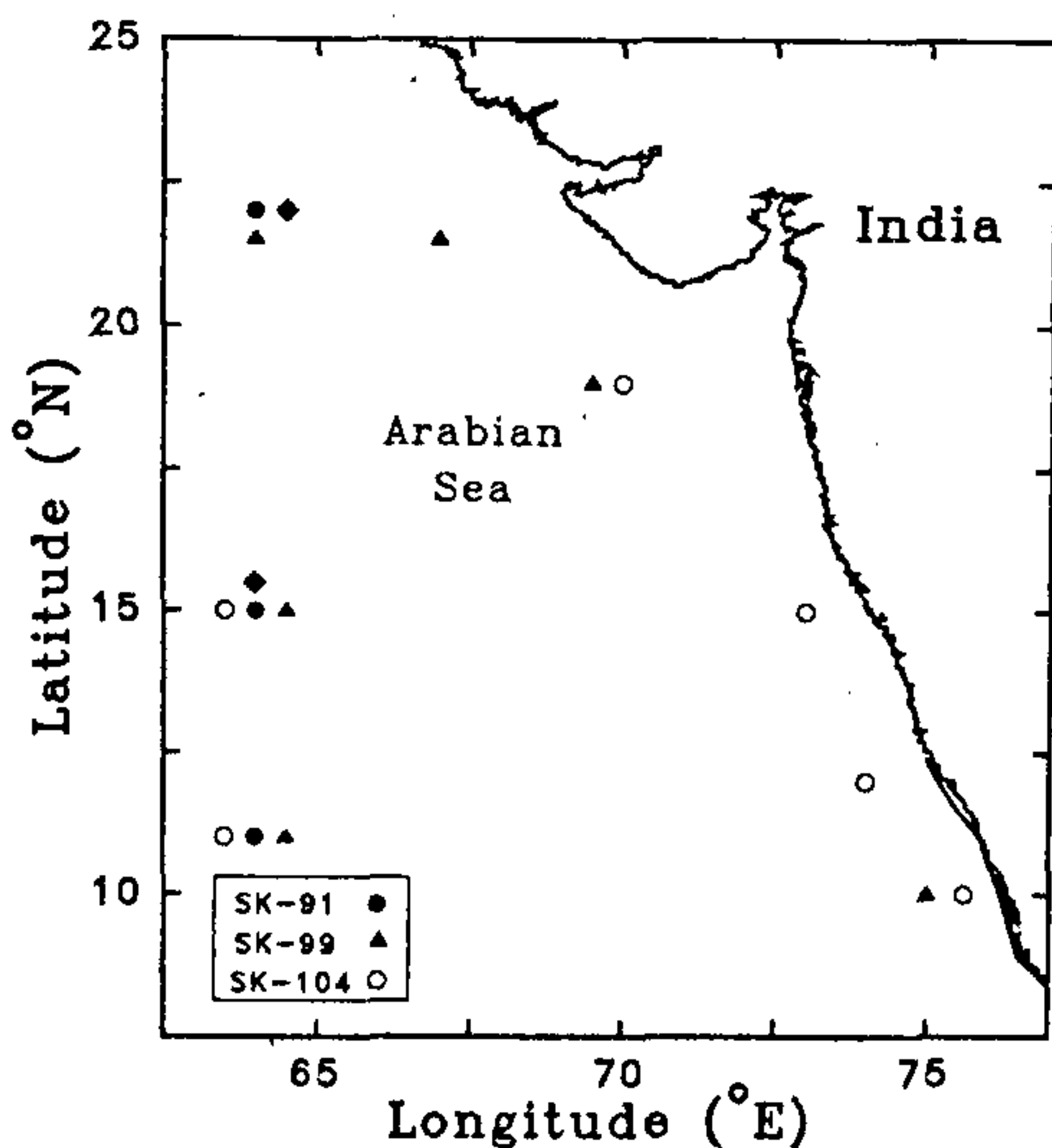The dissolved activity of ^{234}Th, at all sampling depths

Figure 1. Stations sampled during three cruises: SK-91 (April–May 1994), SK-99 (February–March 1995) and SK-104 (July–August 1995). Reoccupation of the stations during different seasons, along the 64°E transect, is shown as an offset. Locations of trap deployment is shown by diamond symbol.
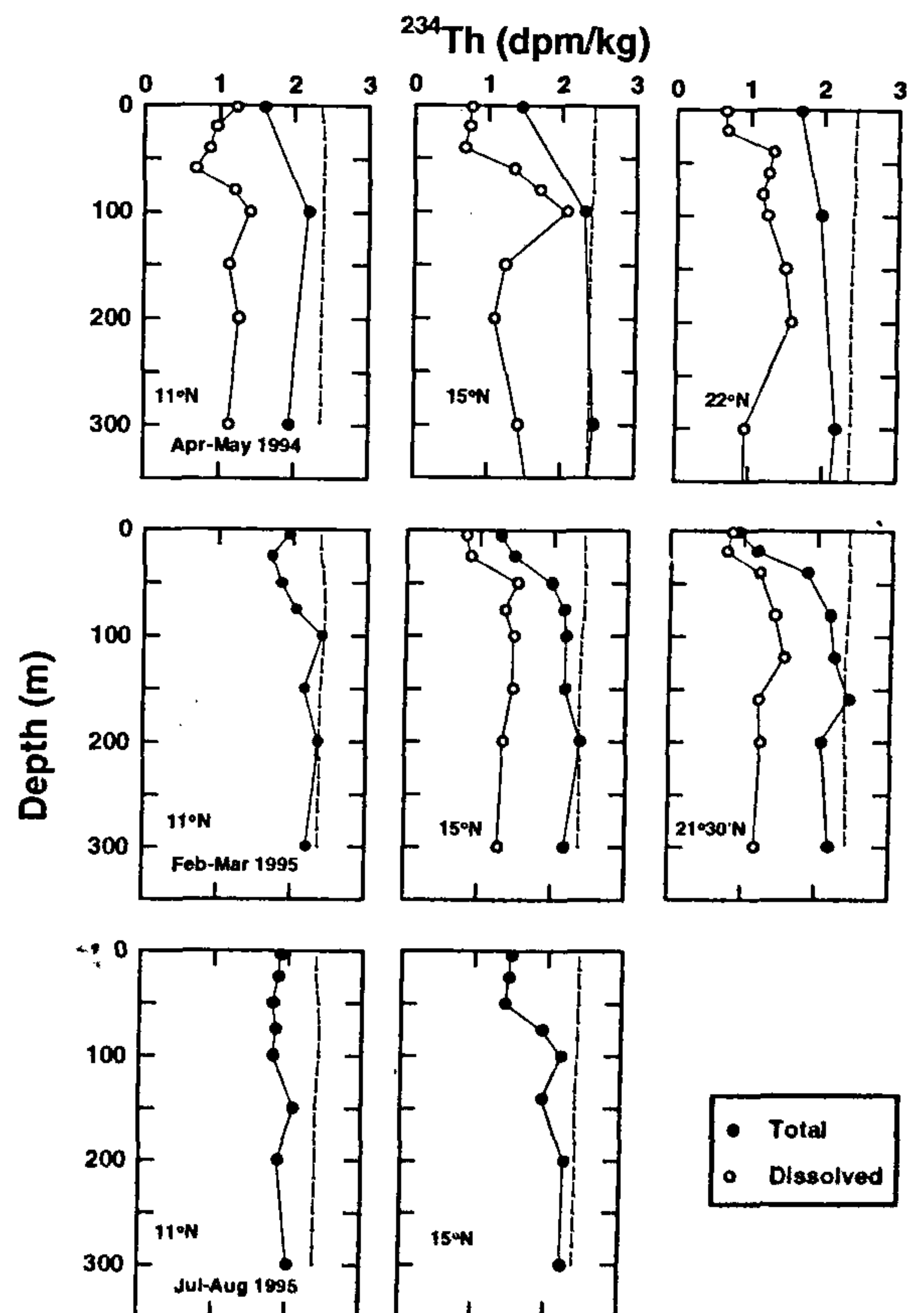

Figure 2. Vertical profiles of dissolved and total (dissolved + particulate) ^{234}Th activities in the upper 300 m at three open ocean stations along the 64°E transect. The dash line represents the dissolved activity of the parent isotope ^{238}U. A gross deficiency of ^{234}Th is clearly evident in the surface 100 m.

(Figure 2), shows a pronounced deficiency with respect to its parent [238]U whereas total [234]Th shows near-equilibrium concentration at > 100 m. The deficiency of dissolved [234]Th is attributed to its removal from the dissolved to particulate phases. The dissolved [234]Th : [238]U activity ratio in surface waters at three stations along the 64°E, during April–May (summer), ranges from 0.28 to 0.43; with lowest value occurring at the northern-most station. However, the column deficiency of dissolved [234]Th integrated over 0–100 m is quite similar at all the three stations. These results yield a mean residence time of about 30 days for dissolved [234]Th in the surface 100 m with respect to its removal onto particles. The nearly identical extent of dissolved [234]Th : [238]U disequilibrium suggests that the rates of particle-associated scavenging processes in the central Arabian Sea are quite uniform and are not resolvable based on [234]Th distribution.

These three stations along the 64°E transect were reoccupied during winter (February–March, Figure 1). The overall pattern of dissolved [234]Th distribution and the extent of [234]Th : [238]U disequilibrium during the winter

months is nearly the same as that measured during the summer. The mean dissolved [234]Th : [238]U activity ratio in the surface 100 m at these three stations is 0.49 (Figure 2), which yields [234]Th scavenging residence time of 34 days, quite similar to that observed during summer. This result is surprising considering that the water column (0–100 m) productivity[10] at these sites during winter ranged from 335 to 643 mgC m^{-2} d^{-1}, which is about 2–3 times higher than that during April–May. The scavenging residence time of [234]Th during the summer and winter seasons is quite similar to that reported by Sarin et al.[12] at nearby locations. These results imply that the temporal variations in chemical scavenging rates of [234]Th in surface waters of the central Arabian Sea are not significantly influenced by the primary production and that the steady-state conditions assumed in the tracer scavenging model are nearly valid. Furthermore, our results from the Arabian Sea do not follow the linear trend between [234]Th scavenging rate and the primary productivity as reported by Coale and Bruland[2] for the Gulf of California.

The total [234]Th activity (dissolved + particulate) measured in the unfiltered samples also shows a pronounced deficiency with respect to [238]U in the upper 100 m water column (Figures 2 and 3). This deficiency of total [234]Th is attributed to its scavenging and subsequent downward export via settling particles. The mean residence time of [234]Th, with respect to its decay and removal from the water column, is about 100 days. Below 100 m, the total activity of [234]Th at stations along the 64°E transect is close to secular equilibrium value (Figure 2). In
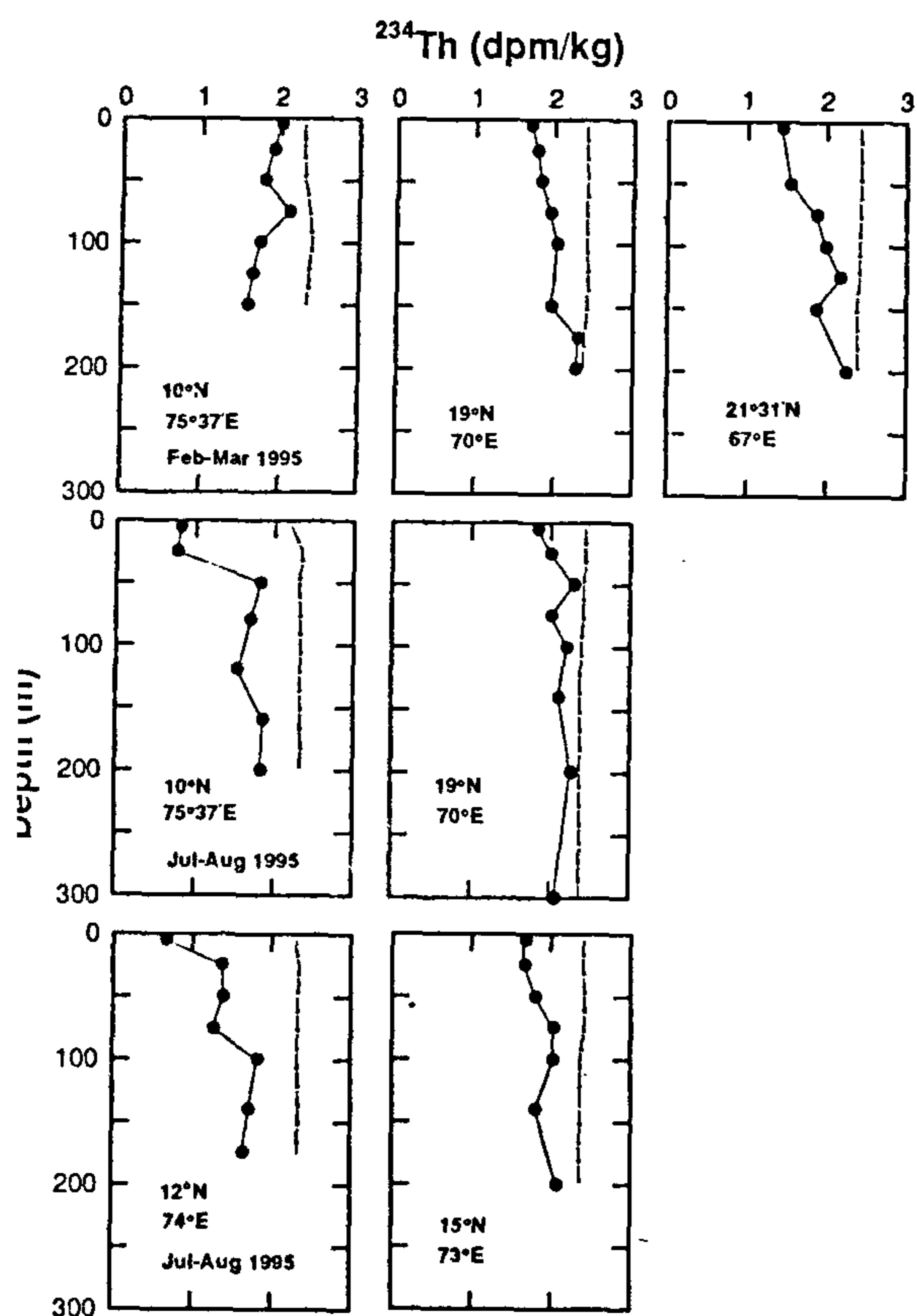

Figure 3. Activity of total [234]Th at coastal stations is plotted with respect to [238]U (dash line) indicating signficant deficiency all through the water column.

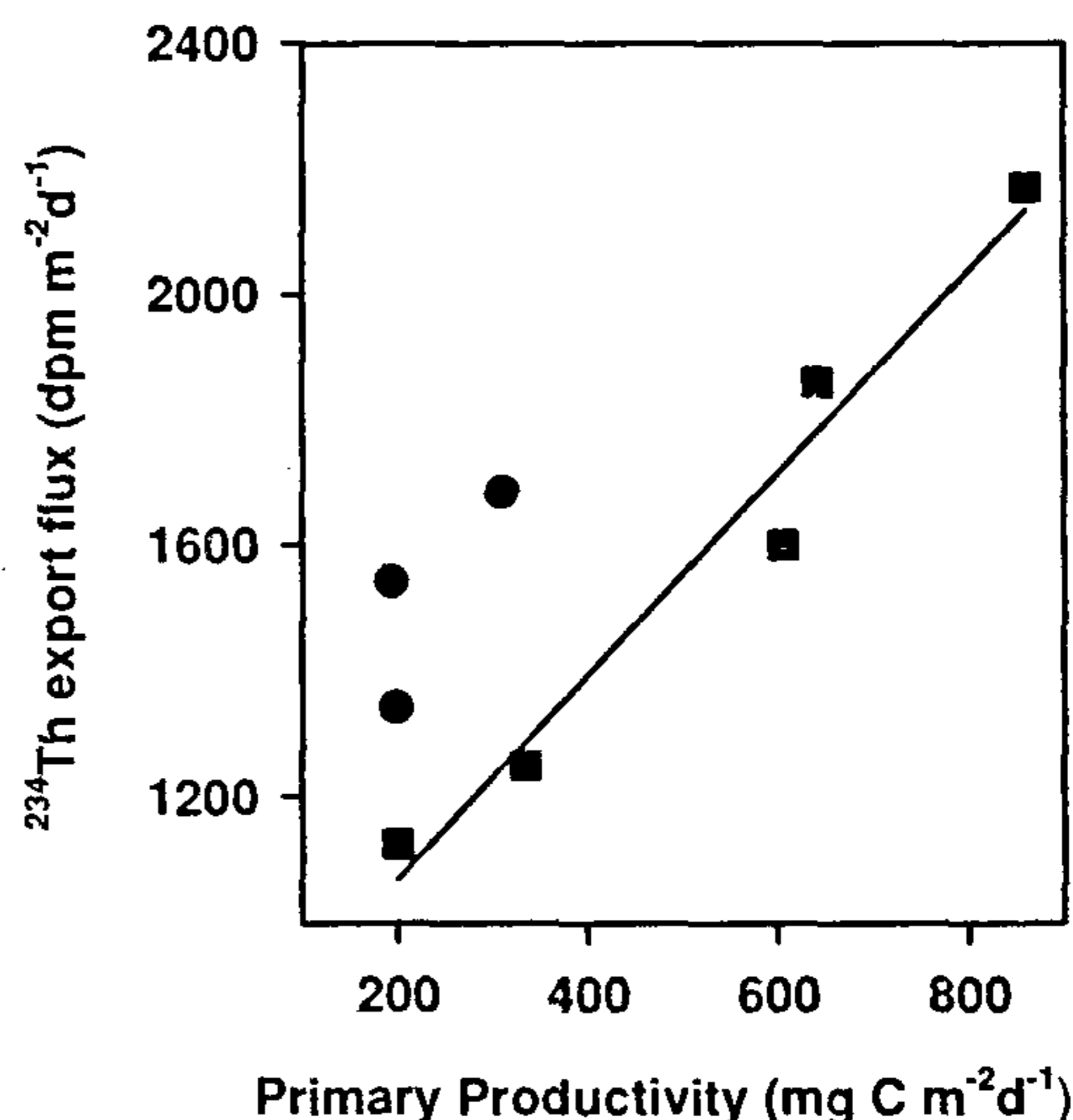Figure 4. [234]Th export fluxes computed from the water column profiles as a function of primary production rate. Linear relation is seen for the data (filled squares) during winter (February–March). Data for summer (April–May) is shown by filled circles. Primary productivity data are from Bhattathiri et al.[10].

contrast, the total ^{234}Th activity at stations along the coast shows marked deficiency down to 200 m depth (Figure 3). One possible explanation for this is the higher particulate concentration in coastal waters and the rapid uptake of ^{234}Th near the sediment–water interface. At some of the coastal stations, this deficiency is relatively enhanced all through the water column during the monsoon period (July–August).

We have computed the removal rate of ^{234}Th from dissolved to particulate phases for two stations, viz. 22°N and 15°N (along the 64°E transect) based on the dissolved activities of ^{234}Th and ^{238}U measured during April–May and February–March (Figure 2). The average rate at which dissolved ^{234}Th is scavenged onto particles in the surface 100 m is estimated to be about 3400 dpm m^{-2} d^{-1}. This rate for the central Arabian Sea is comparable to that reported for the California Current[2]. The inventories of total ^{234}Th (dissolved + particulate) in the surface 100 m for the open ocean profiles, along the 64°E transect, are quite similar $(17 \pm 1)10^4$ dpm m^{-2} during the three sampling seasons (Table 1). The total ^{234}Th inventories vary from 12.4×10^4 to 19.7×10^4 dpm m^{-2} at the coastal stations (Table 1).

^{234}Th export

The measured deficiency of total ^{234}Th with respect to dissolved ^{238}U (Figures 2 and 3) has been modelled to derive the vertical export of particulate ^{234}Th from the upper 100 m water column (Table 1). The export fluxes at the coastal stations range from 915 to 2750 dpm m^{-2} d^{-1}. At open ocean stations, ^{234}Th export rates show a north–south trend with higher values for the northern-most stations (Table 1). However, the derived export fluxes at an individual station are quite similar during

the summer (April–May) and winter (February–March) but tend to be somewhat higher during monsoon (July–August, Table 1).

The ^{234}Th export fluxes computed for the open ocean stations show a linear trend with the integrated column (0–100 m) primary productivity (Figure 4). This relationship, however, seems to be limited for the data from the same season. For example, the ^{234}Th export fluxes during February–March vary from 1125 to 2170 dpm m^{-2} d^{-1} while the column productivity varies from 200 to 860 mgC m^{-2} d^{-1}. Although these export fluxes are somewhat identical with those during April–May (Table 1), the primary productivity is about a factor of three higher during the winter cruise (February–March 1995). These results suggest that the use of ^{234}Th as a survey tool for primary productivity needs close scrutiny.

Particle export

The particulate ^{234}Th export fluxes (at 100 m) based on water column deficiency are distinctly higher than those measured directly using floating sediment traps (Table 2), particularly in the samples collected during winter. During the winter season, the ^{234}Th flux measured by traps at 100 m is about a factor of four lower than that expected (assuming no lateral transport of particulate Th) from the water column deficiency (Table 2). Similar results are obtained based on the ^{210}Pb flux measured in the trap material and that expected from the atmospheric fallout[13]. This suggests that the shallow traps underestimate the particle export flux and the carbon export fluxes determined using them, without appropriate corrections for trapping efficiency, are likely to be underestimated. Similar observations were made by Buesseler et al.[4] during the North Atlantic Bloom Experiment.

Table 1. Spatial and temporal variations in the inventory of total ^{234}Th (dissolved + particulate) and Th export fluxes at 100 m in the Arabian Sea

	Inventory (10^4 dpm m^{-2})			Export flux* (dpm m^{-2} d^{-1})		
Location	April–May 1994	February–March 1995	July–August 1995	April–May 1994	February–March 1995	July–August 1995
Open ocean stations						
21°31′N, 67°E	–	15.4	–	–	2170	–
21°30′N, 64°E	17.4	17	–	1685	1860	–
15°N, 64°E	17.9	17.4	15.7	1545	1600	2045
11°N, 64°E	18.1	18.4	17.3	1345	1250	1620
Coastal stations						
10°N, 75°37′E	–	18.2	13.1	–	1125	2535
12°N, 74°E	–	–	12.4	–	–	2750
15°N, 73°E	–	–	17.4	–	–	1540
19°N, 70°E	–	17.3	19.7	–	1715	915

*Calculated based on the observed ^{234}Th : ^{238}U disequilibrium.

For deriving the particle export rates (Table 2), we have corrected for the trapping efficiency by assuming it to be the ratio of the measured [234]Th flux in the traps to that expected from its water column deficiency. It is also implicit here that the measured [234]Th flux in the traps deployed over 3–5 days is representative of the site.

Analogous calculations for the total material fluxes, from the upper 100 m column, have been made for other sampling sites in the Arabian Sea (Table 3). The particle export fluxes, corrected for trapping efficiency, range from 1890 to 3280 mg m^{-2} d^{-1} during winter and are about a factor of 2 to 3 higher than those during summer. In each case, particle fluxes are obtained by dividing the estimated [234]Th export (Table 1) by [234]Th specific activity (dpm/g) measured in the traps (Table 2). The measured [234]Th activity in the trap material during April–May and February–March is 1856 and 662 dpm/g, respectively, and it is assumed to be representative of all the sites during the respective season. A decrease in the specific [234]Th activity by a factor of 3 during winter could be related to the dilution of trap material by the increased abundance of particles/aggregates. This is in agreement with the measured C/[234]Th ratio during February–March (Table 2) when the column productivity is 2–3 times higher than that during April–May. Buesseler et al.[4] have suggested that the temporal changes in C/[234]Th could occur as a function of local primary production and export balance. Relatively high C/[234]Th ratios were observed during bloom conditions in the North Atlantic[4]. We observe an increase in the C/[234]Th ratio from 0.24 during summer to 0.52 (mg/dpm) during winter suggesting that an enhanced vertical transport of sinking particles are [234]Th deficit. The organic carbon to total mass ratio in the traps is somewhat comparable between summer and winter, 0.43 and 0.35 respectively. This observation further reinforces the view that the dilution of trap material is most likely the cause

Table 2. Measured and estimated fluxes at sediment trap sites in the Arabian Sea

Location	Depth (m)	[234]Th export (dpm m^{-2} d^{-1}) (1)	(2)[@]	Particle export (mg m^{-2} d^{-1}) (1)	(2)[$]	C/[234]Th (mg dpm^{-1}) (1)	Carbon export (mgC m^{-2} d^{-1}) (1)	(2)[£]
April–May 1994								
15°N, 64°E	100	1225	1545	660	830	0.24	290	371
February–March 1995								
21°30'N, 64°E	130	482	1860	728	2810	0.52	251	986

(1) Measured in the sediment trap material.
(2) Estimated based on water column profiles.
[@] From Table 1.
[$] Corrected for the trapping efficiency computed as the ratio of [234]Th flux calculated from the water column deficiency to that measured in the traps.
[£] Derived from C/[234]Th ratio in the trap and calculated [234]Th export.

Table 3. Export fluxes of [234]Th, settling particles and carbon at 100 m in the central Arabian Sea

Location	Column productivity[@] (mgC m^{-2} d^{-1})	[234]Th export[$] (dpm m^{-2} d^{-1})	Particle export* (mg m^{-2} d^{-1})	Carbon export[+] (mgC m^{-2} d^{-1})
April–May 1994				
22°N, 64°E	310[†]	1685	910	404
15°N, 64°E	193	1545	830	371
11°N, 64°E	199	1345	725	322
February–March 1995				
21°30'N, 67°E	860	2170	3280	1150
21°30'N, 64°E	643	1860	2810	986
15°N, 64°E	606	1600	2420	848
11°N, 64°E	335	1250	1890	662
10°N, 75°37'E	200	1125	–	–

[@] Data from Bhattathiri et al. (this issue).
[$] From Table 1.
*Obtained by dividing estimated [234]Th export by [234]Th specific activity (dpm/g). The [234]Th activity in the trap material during April–May and February–March is 1856 and 662 dpm/g, respectively. This specific activity is taken to be the same for all locations during the respective season.
[+] Derived from C/[234]Th ratio and [234]Th export.
[†] Measured at 22°N, 68°E.

for the decrease in particulate ^{234}Th activity during winter.

As proposed by Eppley[14], the other purpose of studying ^{234}Th–^{238}U disequilibrium and particle export of ^{234}Th, in the upper 100m, is to relate it to carbon export flux out of the euphotic zone. The C export flux has been computed as a product of the ^{234}Th export flux (Table 3) and C/^{234}Th ratio for the corresponding period (Table 2). The calculated flux is distinctly higher than the measured C export at the trap site during winter (Table 2), suggesting that an appropriate correction for particle trapping efficiency is needed for the reliable estimates of C using floating sediment traps. In general, estimated C export fluxes at all stations are higher than the column primary productivity (Table 3). There could be two explanations for the estimated C fluxes being higher than the primary productivity: (i) there is an additional source of carbon via the microbial loop and that the C/^{234}Th measured in the trap material (collected over 3–5 days period) is not representative of the site and water column POC inventory, or (ii) there is a phase lag between primary production and flux out of the euphotic zone. We propose the first explanation to be more dominant as there is an evidence for active microbial pathway[15]. Also, C/^{234}Th ratio of the settling particles in the trap may not be appropriate for estimating organic C export. Indeed the direct measurement of C flux in the traps during April–May is also higher than the primary production (Table 2). These observations raise the question of differential cycling of the various components of particulate matter and ^{234}Th in the upper 100 m of the Arabian Sea.

Conclusions

The ^{234}Th : ^{238}U disequilibrium in the upper 100 m has been used to derive the chemical scavenging rates and the export fluxes of ^{234}Th and settling particles in the Arabian Sea. In the open ocean, the residence time of dissolved ^{234}Th with respect to its removal onto particles is ~ 30 days. We find that the estimated vertical export fluxes of particulate ^{234}Th (at the respective sites) are similar between summer and winter and that the export fluxes are higher in general over the regions characterized

by higher rates of column productivity. The ^{234}Th flux data are used to derive the fluxes of particulate matter and carbon at 100 m. The computed fluxes of particles are significantly higher than those measured using free-floating sediment traps. The C export fluxes are also higher than the column primary productivity suggesting that the direct comparison of these fluxes with independent estimates of new production is needed. The future studies should aim towards understanding the relationship between C and ^{234}Th on sinking particles and dynamics of carbon cycling in the Arabian Sea.

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