Estuarine, Coastal and Shelf Science (1998) **46,** 351–358

Particle Scavenging in the Upper Water Column off Mindoro Island, Philippine: $^{234}Th/^{238}U$ Disequilibria

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Received 17 June 1996 and accepted in revised form 30 September 1997

Vertical profiles of dissolved and particulate ^{234}Th in the upper water column of four stations in the narrow channel adjacent to Mindoro Island, Philippine were determined during November 1991. Calculated from the degree of disequilibrium between particle-reactive ^{234}Th and soluble parent, ^{238}U, the residence times of dissolved and particulate ^{234}Th range from 20 to 42 days and from 9 to 17 days, respectively. Vertical ^{234}Th fluxes of 4300–7000 dpm m^{-2} day^{-1} from the upper 200 m are required to balance the deficiency of ^{234}Th.

Keywords: thorium-234; scavenging; vertical fluxes; Philippine

Introduction

It is well known that ‘ particle-reactive ’ elements are removed from the ocean by adsorption onto particle surfaces followed by particle settling. It is this process, referred to as chemical scavenging, that controls the distribution of many elements in the ocean (Goldberg, 1954). Naturally occurring radionuclides are useful for tracing particle transport processes in various oceanographic regimes. Among the radionuclides produced from uranium–thorium decay series, thorium isotopes have been suggested as a powerful analogue metal for ‘ particle-reactive ’ elements to predict their geochemical behaviour in the ocean.

The compatible time scale of the radioactive life time of ^{234}Th (34·8 days) and the residence time of marine particulate matter has made ^{234}Th a very useful tracer in studying scavenging phenomena in the upper layer of the open ocean (Coale & Bruland, 1985, 1987; Buesseler *et al.*, 1995) and in coastal waters (Minagawa & Tsunogai, 1980; Kaufman *et al.*, 1981; McKee *et al.*, 1984, 1986; Coale & Bruland, 1985; Wei & Murray, 1992). The only source of ^{234}Th in seawater is radioactive decay of ^{238}U, a conservative-type element due to its strong complexing tendency towards carbonate ions. With an exactly known source function and the degree of deviation from the secular equilibrium, one can delineate the rates of particle scavenging and removal if both dissolved and particulate phases of ^{234}Th in seawater were measured.

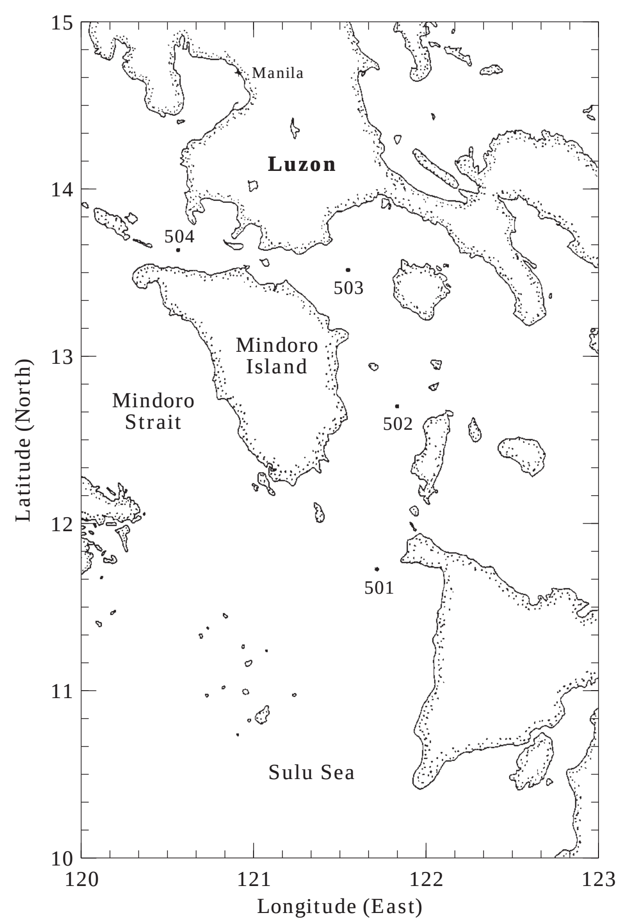

FIGURE 1. Locations of four large-volume sampling stations.

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TABLE 1. Depth distribution of total suspended material (TSM), dissolved and particulate ^{234}Th at four stations around Mindoro Island, Philippines during 2–4 November 1991

Station	Depth (m)	TSM (mg kg^{-1})	Diss. ^{234}Th (dpm kg^{-1})	Part. ^{234}Th (dpm kg^{-1})
501	0	0·42	0·818 ± 0·037	0·517 ± 0·035
	10	0·39	0·851 ± 0·050	0·172 ± 0·012
	20	0·42	0·869 ± 0·045	0·259 ± 0·016
	30	0·34	1·018 ± 0·050	0·215 ± 0·012
	50	0·23	0·868 ± 0·131	0·327 ± 0·022
	80	0·13	1·042 ± 0·049	0·290 ± 0·019
	130	0·12	1·593 ± 0·081	0·439 ± 0·023
	200	0·00	1·792 ± 0·097	0·382 ± 0·036
502	0	0·54	0·926 ± 0·055	0·363 ± 0·021
	10	0·22	1·270 ± 0·076	0·205 ± 0·014
	20	0·32	1·037 ± 0·051	0·193 ± 0·012
	30	0·24	1·181 ± 0·063	0·291 ± 0·022
	50	0·30	1·055 ± 0·061	0·191 ± 0·015
	60	0·21	1·116 ± 0·059	0·528 ± 0·044
	80	0·15	1·128 ± 0·059	0·174 ± 0·017
	130	0·10	1·057 ± 0·050	0·324 ± 0·022
	200	0·11	1·613 ± 0·076	0·762 ± 0·058
503	0	0·38	0·699 ± 0·038	0·189 ± 0·010
	10	0·34	0·718 ± 0·036	0·204 ± 0·013
	20	0·33	0·735 ± 0·039	0·127 ± 0·008
	30	0·27	0·714 ± 0·038	0·134 ± 0·009
	50	0·41	0·600 ± 0·040	0·151 ± 0·010
	60	0·34	0·778 ± 0·039	0·184 ± 0·012
	80	0·12	0·896 ± 0·045	0·273 ± 0·014
	130	0·11	0·959 ± 0·047	0·365 ± 0·020
	200	0·14	0·985 ± 0·054	0·597 ± 0·030
504				
	0	0·24	0·890 ± 0·069	0·422 ± 0·028
	10	0·02	1·123 ± 0·088	0·085 ± 0·007
	20	0·16	0·937 ± 0·108	0·292 ± 0·022
	30	0·03	0·955 ± 0·100	0·223 ± 0·018
	50	0·19	0·955 ± 0·074	0·183 ± 0·011
	60	0·30	0·569 ± 0·065	0·505 ± 0·029
	80	0·21	0·773 ± 0·058	0·369 ± 0·031
	110	0·14	1·151 ± 0·090	0·263 ± 0·018
	150	0·16	1·027 ± 0·077	0·368 ± 0·030
	200	0·09	1·082 ± 0·081	0·738 ± 0·060

Standard deviations are based on propagated counting error ($\pm 1\sigma$).

Because of terrestrial influences, the coastal waters have higher productivity, higher suspended particle load and more dynamic characteristics. Consequently, the scavenging rate of ^{234}Th by particles in coastal waters is much faster than that in the open ocean. In a previous paper (Wei & Hung, 1992), we presented evidence that the scavenging rate constant of ^{234}Th correlates positively with total particle loads in the northern Luzon Strait. In this paper, we report the ^{234}Th distribution in the water column of the narrow channel connecting the South China Sea and the Sulu Sea. We have determined dissolved and particulate ^{234}Th activities in the upper 200 m at four stations in the east region of Mindoro Island.

Materials and methods

Seawater samples were collected at four stations around Mindoro Island (Figure 1) during 2–4 November 1991, onboard RV *Ocean Researcher I* (cruise No. 300). About 20 l of seawater were collected using 20 l Go-Flo bottles mounted on hydrowire. A CTD system, with a fluorescence sensor attached, was deployed immediately before or after

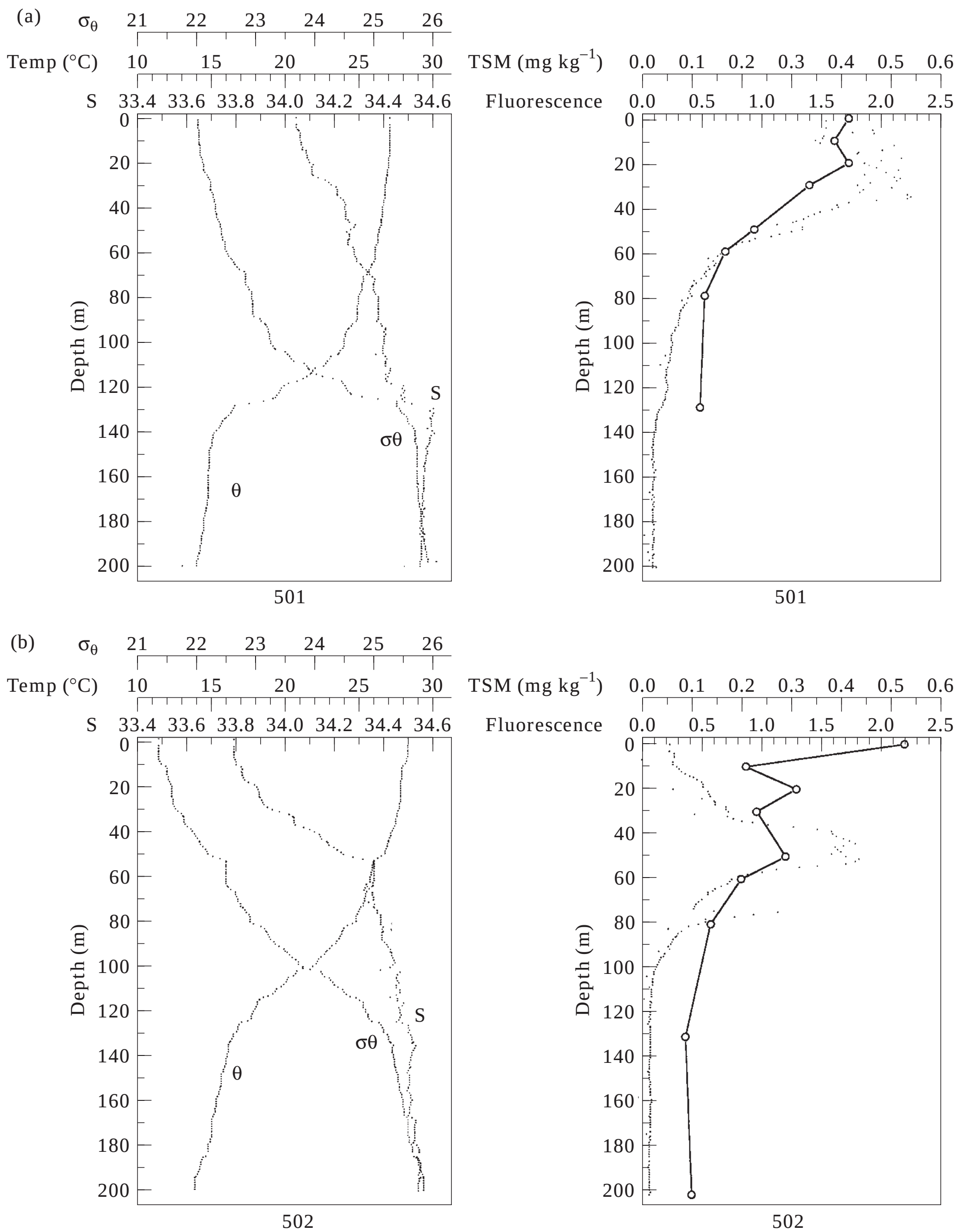

FIGURE 2. (a) and (b)

the large-volume hydrocasts to obtain hydrographic data. Seawater samples were filtered through a pre-weighed 142 mm Nuclepore filter (0·45 μm) placed in a Plexiglas filter holder. After filtration, the filter was rinsed with about 10 ml deionized distilled water, stored in a Petri dish, and returned to the laboratory. Preconcentration and separation of uranium and thorium from the filtered seawater samples were carried out on board ship. Detailed procedures for ^{234}Th sample handling can be found in Wei and Murray (1991, 1992) and Wei and Hung (1992).

The activities of ^{234}Th were counted by a low background (<0·3 cpm) anticoincidence counter (Tennelec LB-5100) via its β-emitting daughter ^{234}Pa. The purity of samples was checked by counting through a time span of about two months to confirm that the radioactive decay curve was followed (Wei, 1991). Blank contribution of all reagents and filter

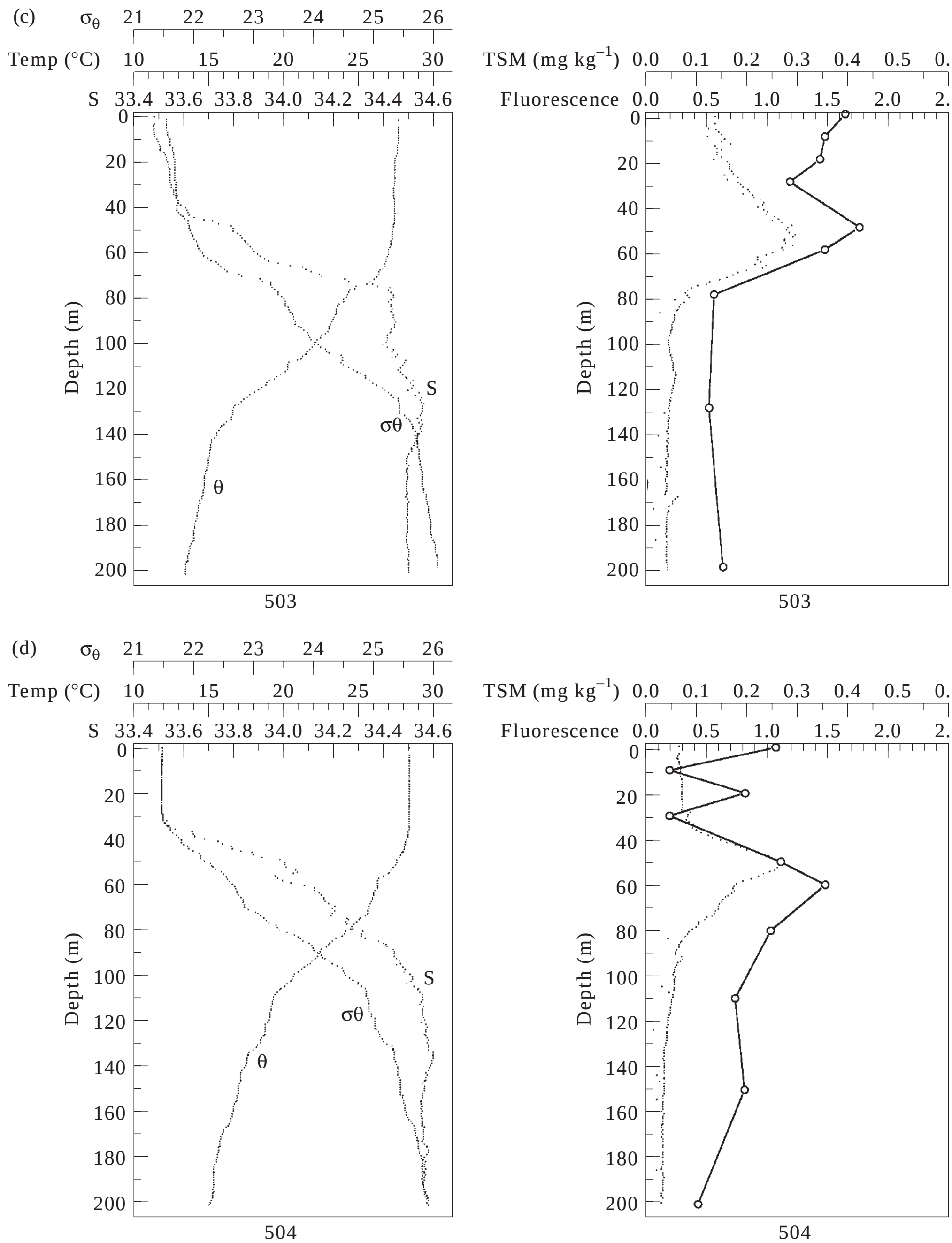

FIGURE 2. (c) and (d)

FIGURE 2. Vertical profiles of hydrographic parameters [temperature, salinity (S) and potential density], fluorescence and total suspended matter (TSM) concentration at the four stations.

paper used for this study was determined to be negligible. Chemical yield of thorium was estimated by counting ^{230}Th with silicon surface-barrier detectors (EG&G Ortec 576). The counting efficiencies of the detectors were calibrated against NIST traceable ^{241}Am (Isotope Products Laboratory 387-67-2-2) and ^{230}Th (Isotope Products Laboratory 387-67-3) standard plates. Activities of ^{234}Th reported here were corrected back to the sampling time, after the ingrowth of ^{234}Th from ^{238}U was subtracted.

Results

Concentrations of total suspended matter (TSM), dissolved (DTh) and particulate (PTh) ^{234}Th

TABLE 2. Inventories and residence times of dissolved (τ_D) and particulate (τ_P) ^{234}Th in the upper 200 m water column of four sampling stations

Station	^{238}U (dpm cm^{-2})	DTh (dpm cm^{-2})	PTh (dpm cm^{-2})	J flux (dpm m^{-2} day^{-1})	P flux (dpm m^{-2} day^{-1})	τ_D (day)	τ_P (day)
501	48·65	26·47	7·14	6380	4326	42	17
502	48·53	24·33	7·50	6961	4804	35	16
503	48·33	17·71	6·52	8808	6932	20	9
504	48·45	20·00	7·48	8184	6032	25	12

activities at each sampling depth of four stations around Mindoro Island are given in Table 1. Uncertainties of all radioisotope data listed were calculated according to the propagation of counting error ($\pm 1\,\sigma$).

The vertical distributions of hydrographic data (salinity, temperature, and potential density), fluorescence and TSM concentration at stations 501, 502, 503 and 504 are shown in Figure 2. Inflow from the South China Sea through the channel off Mindoro Island is the main source of seawater in the Sulu Sea (Broecker *et al.*, 1986). As can be seen in Figure 2, a fresher and warmer water resides in the upper portion of the water column at the four stations. Stations 501 and 502 located at the northern outskirts of the Sulu Sea, have higher surface salinity, indicating less terrestrial influence in the region. Resemblance of total suspended matter and fluorescence profiles for station 501 implies that biological particles dominate the particulate pool in the euphotic zone. Chlorophyll *a* concentrations at our sampling stations were calculated from fluorescence measured by a Sea Tech fluorometer according to the relationship obtained by Gong *et al.* (1993). Standing stock of chlorophyll *a* in the upper 200 m are 73·3, 47·7, 47·2 and 34·5 mg m^{-2} for stations 501, 502, 503 and 504, respectively.

Dissolved and particulate ^{234}Th at the four stations are shown in Figure 3. Total ^{234}Th activities calculated from the sum of dissolved and particulate ^{234}Th were also included in the figure. A dotted line drawn at 2·35 dpm kg^{-1} in the figure represents ^{238}U activity calculated from the S-^{238}U relationship from Ku *et al.* (1977). Error bars represent uncertainties based on propagated counting error ($\pm 1\,\sigma$). In most cases, error bars are smaller than the symbols for particulate samples. Both dissolved and particulate ^{234}Th activities show a large deficiency with respect to ^{238}U, indicating active scavenging and removal phenomena in the upper water column. Th-234 is generally enriched in the dissolved phase, ranging from 50% to >90% of total ^{234}Th. Vertical profiles of dissolved and total ^{234}Th at stations 501 and 502, located to the east of Mindoro Island, were characterized by a large deficiency in the top 80–100 mm then sharply elevated to the secular equilibrium value at the depth of the pycnocline. At the two stations to the north of the island, stations 503 and 504, the disequilibrium between total ^{234}Th and ^{238}U was still evident at the deepest sampling depth (200 m). Particulate ^{234}Th profiles showed a mild increasing trend with depth but with less vertical variation than the dissolved profiles at all four stations.

Discussion

With one isotope available, residence times of ^{234}Th with respect to scavenging and particle removal processes can only be estimated from the irreversible scavenging model (Coale & Bruland, 1985, 1987; Wei & Murray, 1991, 1992). It is noted that the irreversible model may not be applicable in some environments because of its debatable steady-state assumption and the ignorance of diffusion–advection terms. However, with limited data available, the model can still provide a first-order information on the scavenging phenomena in the study area. Time-series experiments on ^{234}Th scavenging revealed that the steady-state assumption is valid in Funka Bay (Tanaka *et al.*, 1983) and in Dabob Bay (Wei & Murray, 1992) because the turn-over rate of ^{234}Th is relatively fast in those environments.

According to the model, differences of dissolved and total ^{234}Th and ^{238}U activities represent the degree of scavenging and removal rates, respectively, imposed on the system, i.e.

$$J = \lambda\,(\mathrm{U} - \mathrm{DTh}) \tag{1}$$

$$P = \lambda\,(\mathrm{U} - \mathrm{TTh}) \tag{2}$$

Where λ, U, DTh, TTh are the decay constant of ^{234}Th, activity of ^{238}U, dissolved ^{234}Th, and total

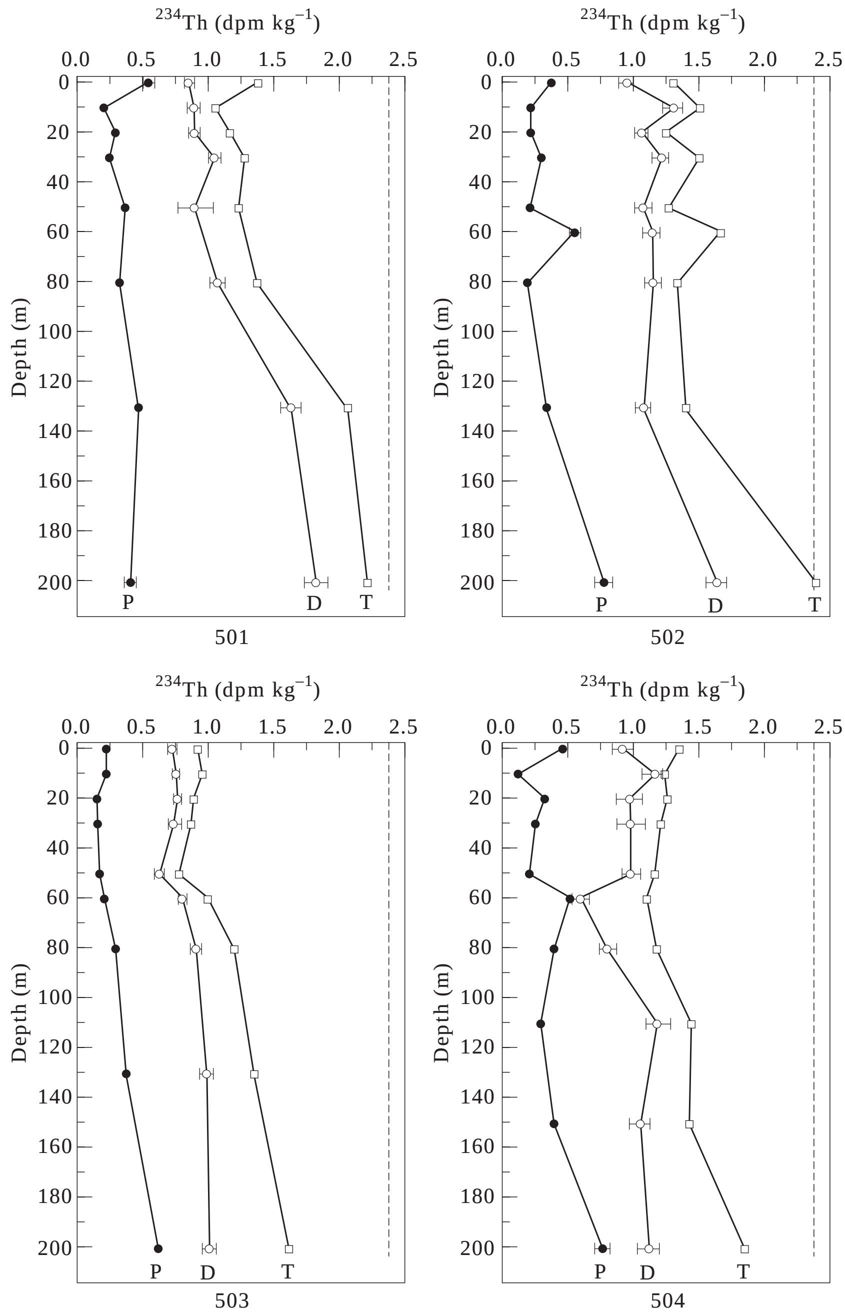

FIGURE 3. Vertical profiles of total (□), dissolved and (○) and particulate (●) ^{234}Th at the four stations. The vertical dashed line at 2·39 dpm kg^{-1} represents ^{238}U activity calculated from S − ^{238}U relationship. Error bars represent uncertainties based on propagated counting error.

^{234}Th activities, respectively. Residence times of ^{234}Th with respect to scavenging (τ_D) and particle removal (τ_P) processes can easily be calculated from dividing dissolved and particulate by *J* and *P*, respectively, i.e.

$$\tau_D = \mathrm{DTh}/J \qquad (3)$$

$$\tau_P = \mathrm{PTh}/P \qquad (4)$$

Table 2 summarizes the results of model calculation. As seen in the table, dissolved and particulate ^{234}Th in the upper water column has a residence time of 20–42 days and 9–17 days, respectively. Generally, the two stations to the east of Mindoro Island, stations 501 and 502, have longer ^{234}Th residence time, implying a different degree of terrestrial influence in the two regimes. A particle settling velocity, in the range of

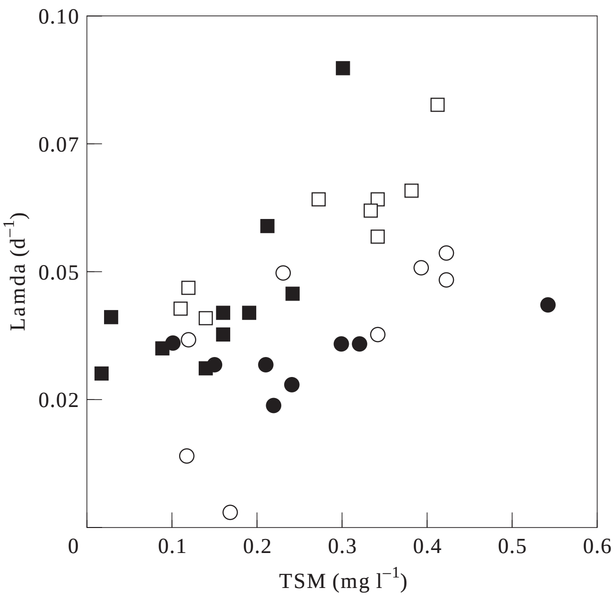

FIGURE 4. Correlation of scavenging rate constant (τ_D^{-1}) and total suspended matter concentration. Station 501, ○; station 502, ●; Station 503 □; station 504, ■.

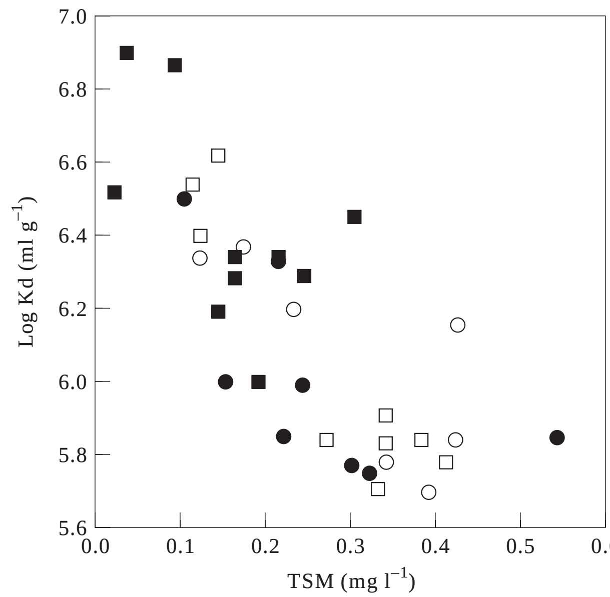

FIGURE 5. Correlation of partitioning coefficient (K_{day}) and total suspended matter concentration. Station 501, ○; station 502, ●; station 503, □; station 504, ■.

10–20 m day^{-1}, is needed to accomplish such a short residence time of particulate ^{234}Th in the upper 200 m. Comparing with sinking rates of fecal pellets (Bruland & Silver, 1981), this relatively slow settling velocity implies that the upper water column was dominated by small-size particles.

Equation (2) was used to calculate the vertical ^{234}Th flux at 200 m depth and the results show that relatively high ^{234}Th fluxes of 4300–7000 dpm m^{-2} day^{-1} are needed to maintain the large deficiencies of ^{234}Th. A higher ^{234}Th flux was found in the region to the north of Mindoro Island (Table 2). It should be noted that ^{234}Th fluxes higher than 4000 dpm m^{-2} day^{-1} are rarely seen except in a region with substantial terrestrial influence like Funka Bay (Tanaka *et al.*, 1983) and Dabob Bay (Wei & Murray, 1992).

Vertical distributions of TSM (Figure 2) and total ^{234}Th (Figure 3) tend to be antithetical, indicating scavenging is strongly affected by particle concentration. A relatively good correlation of scavenging rate constant (τ_D^{-1}) and TSM concentration is shown in Figure 4. An increasing trend of scavenging rate constant with increasing TSM concentration was also observed in the northern Luzon Strait (Wei & Hung, 1991) and in the deep ocean (Bacon & Anderson, 1982). Based on these observations, a pseudo first-order reaction can be attributed to the ^{234}Th scavenging phenomenon. Overall, stations 501 and 502 have a higher scavenging rate constant for a given TSM concentration. Higher scavenging rates observed in the northern channel of Mindoro Island may be a result of enhanced adsorption by terrestrial particles. For example, manganese oxides can serve as an efficient scavenger for thorium in coastal environments (Hunter *et al.*, 1988).

The effect of particle concentration is also shown in the partitioning of ^{234}Th between particulate and dissolved phases. The distribution coefficient, K_d, has been used as a geochemical index of the degree of the reactivity of elements towards particulate matters. The distribution coefficient of ^{234}Th calculated as

$$K_d = \frac{PTh}{DTh} \frac{1}{[TSM] \cdot \rho}$$

where ρ = seawater density (g ml^{-1}) is plotted against TSM concentration in Figure 5. It can be seen that the K_d of ^{234}Th shows large variation (by larger than an order of magnitude) from $10^{5.7}$ to $10^{6.9}$ ml g^{-1} and decreases with increasing TSM concentration. Based on the argument of Honeyman *et al.* (1988) lower K_d is expected when particle concentrations and scavenging rates are higher.

Conclusion

Scavenging phenomenon in the upper water column off Mindoro Island, Philippine was investigated based on the vertical distribution of dissolved and particulate ^{234}Th at four stations. Thorium-234 is found to be deficient relative to its parent throughout the upper 200 m water column. Residence times of ^{234}Th with respect to scavenging and particle removal processes were estimated based on the irreversible scavenging model. Unusually high vertical fluxes of ^{234}Th (4300–7000 dpm m^{-2} day^{-1}) were calculated.

Acknowledgements

This research was supported by the National Science Council, Republic of China under grants NSC84-2611-M002A-005 and NSC-85-2611-M002A-022. We are grateful to K.-L. Chang and C.-C. Yang for measuring dissolved oxygen and nutrients. We would like to thank the crew of the RV *Ocean Researcher I* for their assistance in the sample collection. Comments made by anonymous reviewers substantially improved the manuscript.

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