

Does $^{234}\text{Th}/^{238}\text{U}$ disequilibrium provide an accurate record of the export flux of particulate organic carbon from the upper ocean?

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Abstract

The magnitude of the flux of biogenic particulate organic carbon (POC) exported from the surface waters of the world ocean and remineralized at depth is critical to constraining models of the global carbon cycle, yet remains controversial. The use of upper ocean sediment traps is still one of the primary tools for determining this export flux, although trap fluxes have been shown to vary significantly because of hydrodynamic and sample collection biases. Over the past decade, ^{234}Th increasingly has been used as a tracer to estimate POC export from the euphotic zone by multiplying the depth-integrated ^{234}Th flux by the $\text{POC}/^{234}\text{Th}$ ratio of sinking particles. The accuracy of this technique is highly dependent on the natural variability in the $\text{POC}/^{234}\text{Th}$ ratio and ^{234}Th flux, yet the significance of this variability to estimates of POC export remains uncertain. Based on an analysis of new ^{234}Th and POC data from the Labrador Sea and a review of 25 previous independent field studies, we report that POC export fluxes can vary 2–10 times or more solely because of variability in the $\text{POC}/^{234}\text{Th}$ ratio and procedures used to estimate the ^{234}Th flux. Recommended improvements include studies of the biological, chemical, and physical mechanisms controlling ^{234}Th -organic matter interactions in seawater; detailed comparisons of $\text{POC}/^{234}\text{Th}$ ratios in size-fractionated and sediment trap material; increased spatial and temporal sampling density of ^{234}Th ; and more standardized procedures to calculate the ^{234}Th export flux.

The oceans are the largest sink of atmospheric carbon dioxide (CO_2) on Earth. The biological pump is a key mechanism by which oceanic CO_2 sequestered from the atmosphere is exported from the surface to the deep ocean as sinking biogenic particulate matter. Accurate measures of this export flux are critical to constraining models of the global carbon cycle and traditionally have been obtained from time series deployments of sediment traps in the upper ocean. Trap fluxes, however, have been reported to vary by as much as 3–10 times because of hydrodynamic and sample collection biases (Buesseler 1991). ^{234}Th ($t_{1/2} = 24.1$ d), a particle-reactive radionuclide produced in seawater from soluble ^{238}U ($t_{1/2} = 4.47 \times 10^9$ yr), has emerged as a primary

tracer of the downward flux of POC in the world ocean (Figs. 1, 2). The ^{234}Th method for determining POC export fluxes has the advantage of providing a temporally integrated record (days to weeks) of particle export that can be determined from ships and without the apparent biases that characterize upper ocean sediment traps.

Typically, there is a deficit of ^{234}Th in the surface ocean with respect to its production by its parent ^{238}U , which is ascribed to the uptake of ^{234}Th onto particle surfaces and subsequent sinking of particles into the water below (Bhat et al. 1969; Matsumoto 1975; Santschi et al. 1979; Coale and Bruland 1985; Bruland and Coale 1986; Coale and Bruland 1987; Murray et al. 1989). In using ^{234}Th as a tracer of POC export, it is assumed that one requires only a knowledge of the ^{234}Th deficit and the $\text{POC}/^{234}\text{Th}$ ratio of sinking particulate matter to calculate the rate at which particulate biogenic carbon is transported downward. Thus, the POC export flux (P_{POC} , $\text{mol C m}^{-2} \text{d}^{-1}$) is defined empirically as the product of the $\text{POC}/^{234}\text{Th}$ ratio, which is ideally representative of sinking biogenic particles, and the depth-integrated ^{234}Th flux

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$$P_{\text{POC}} = \left(\frac{\text{POC}}{^{234}\text{Th}} \right)_{i,w} \times \lambda \int_0^z (A_U - A_{\text{Th}}) dz \quad (1)$$

where $(\text{POC}/^{234}\text{Th})_{i,w}$ is the POC/²³⁴Th ratio ($\mu\text{mol dpm}^{-1}$) measured in sinking particulate matter of size i and collected at depth w , A_U is the activity of ²³⁸U (dpm L^{-1}), A_{Th} is the total ²³⁴Th activity (dpm L^{-1}), λ is the ²³⁴Th decay constant (0.0288 d^{-1}), and z is the lower boundary of the depth-integrated ²³⁴Th deficit. As we show however, it is difficult to rigorously define and measure both of the key parameters: the POC/²³⁴Th ratio of sinking particles and the depth-integrated ²³⁴Th flux.

In this work, we first provide a summary of previous studies that document the natural variability in the POC/²³⁴Th ratio of marine particles, the range in ²³⁴Th particle flux, and the various assumptions and criteria applied when using these observations to calculate upper ocean POC export fluxes. We then report new size-fractionated ²³⁴Th and POC data from the Labrador Sea and use these observations to quantitatively demonstrate the significance of the variability in the POC/²³⁴Th ratio and ²³⁴Th flux on the calculated export flux of POC. Finally, several recommendations are suggested to improve the accuracy of ²³⁴Th-derived export fluxes of POC from the upper ocean.

Background

The largest uncertainty in estimating P_{POC} is the POC/²³⁴Th ratio of sinking particulate matter, which ranges by three orders of magnitude: $0.5\text{--}80 \mu\text{mol dpm}^{-1}$ in the open ocean and $2\text{--}534 \mu\text{mol dpm}^{-1}$ in shelf waters (Table 1). The POC/²³⁴Th ratio of marine particles varies significantly with location and time in association with changes in primary and secondary productivity, plankton community structure, export production, particle size distribution, particle aggregation–disaggregation, and food web dynamics (Lee et al. 1993; Buesseler et al. 1995; Bacon et al. 1996; Murray et al. 1996; Charette and Moran 1999; Burd et al. 2000). The POC/²³⁴Th ratio has also been found to vary within a given station at any particular time depending on particle size and collection method, as we demonstrate. No consensus exists as to the cause of this variability; however, preferential remineralization of POC and decay of ²³⁴Th as particles age have been suggested to be major factors (Buesseler et al. 1995; Bacon et al. 1996; Murray et al. 1996; Charette and Moran 1999; Burd et al. 2000). Variability in the POC/²³⁴Th ratio might also be due to differences in methods of collection, which include water sampling with bottles, large-volume pumps, and sediment traps, each of which have unique sampling biases (Murray et al. 1996). The significance of this variability on POC fluxes has not been fully explored yet is critical to their validation.

Significant variability also exists in the criteria used to calculate the particle export flux of ²³⁴Th from the depth-integrated ²³⁴Th deficit, which typically assumes a steady state ($\partial^{234}\text{Th}/\partial t = 0$), although non–steady state models (Tanaka et al. 1983; Buesseler et al. 1992a; Wei and Murray 1992; Moran and Buesseler 1993; Buesseler et al. 1998; Kim et al. 1999; Benitez-Nelson et al. 2000; Benitez-Nelson et

al. 2001a) have been used, as well as inclusion of advective and diffusive transport of ²³⁴Th (Buesseler et al. 1994, 1995; Bacon et al. 1996; Murray et al. 1996; Gustafsson et al. 1998; Charette et al. 1999; Benitez-Nelson et al. 2000; Charette et al. 2001; Dunne et al. 2000) (Table 1). The usual intent is to measure the export of particles from the euphotic zone, where they are presumed to be formed. A number of studies have integrated the ²³⁴Th deficit down to the base of the euphotic zone (Buesseler et al. 1992a, 1995; Bacon et al. 1996; Murray et al. 1996), whereas the total ²³⁴Th deficit, which often extends down below the euphotic zone, has also been used (Michaels et al. 1994; Shimmield et al. 1995; Benitez-Nelson et al. 2001a; Foster and Shimmield 2002). There is no consensus as to what causes a deficit below the euphotic zone; it is likely that fecal pellets made below this zone and particles sinking from above continue to adsorb ²³⁴Th, whereas downward mixing of ²³⁴Th-depleted surface water could also be important. It is even less apparent what integration depth to use in shallow, shelf water environments, which are often well mixed and exhibit ²³⁴Th/²³⁸U disequilibrium throughout the water column from removal of ²³⁴Th on abiogenic particles resuspended from the ocean bottom (Cochran et al. 1995; Gustafsson et al. 1998; Benitez-Nelson et al. 2000; Moran and Smith 2000; Charette et al. 2001; Coppola et al. 2002; Foster and Shimmield 2002). Furthermore, the chemical equilibrium involved between Th and particle surfaces (Bacon and Anderson 1982; Moore and Hunter 1985; Quigley et al. 2001), the complexation of Th with colloidal matter (Baskaran et al. 1992; Moran and Buesseler 1992, 1993; Huh and Prahl 1995; Niven et al. 1995; Guo et al. 2002; Quigley et al. 2002; Santschi et al. 2003), the particle remineralization of Th (Murnane et al. 1994; Barbeau et al. 2001), and the kinetics of these reactions (Moore and Millward 1988; Moran and Moore 1992; Murnane et al. 1994) remain poorly constrained.

Methods

Water samples were collected from the upper 250 m toward the end of the spring bloom at three stations in the Labrador Sea in July 1999 (Fig. 2; Table 2). The sampling protocol was designed to collect particles that spanned a range in particle size, consisting of small ($1\text{--}10 \mu\text{m}$ for ²³⁴Th, $0.7\text{--}10 \mu\text{m}$ for POC), intermediate ($10\text{--}53 \mu\text{m}$), and large ($>53 \mu\text{m}$) particles. Large-volume in situ pumps (Challenger Oceanic Systems and Services) were used to pump seawater ($\sim 200\text{--}1,200$ liters) sequentially through 53- and $10\text{-}\mu\text{m}$ -pore-size Nitex screens (142 mm diameter), a $1\text{-}\mu\text{m}$ Hytrec II cartridge prefilter, and two MnO₂-impregnated adsorber cartridges to scavenge dissolved ²³⁴Th from seawater (Moran et al. 1997; Charette et al. 2001). Particles collected on Nitex screens were resuspended at sea into GF/F filtered seawater using an ultrasonicator ($\sim 2\text{--}5$ min) and then filtered onto precombusted GF/F filters (25 mm diameter) (Buesseler et al. 1995; Charette and Moran 1999; Charette et al. 2001). Seawater was also collected for determination of suspended POC using Go-Flo bottles by filtration onto precombusted GF/F filters. All GF/F filters were dried at 60°C and stored frozen for subsequent ²³⁴Th and

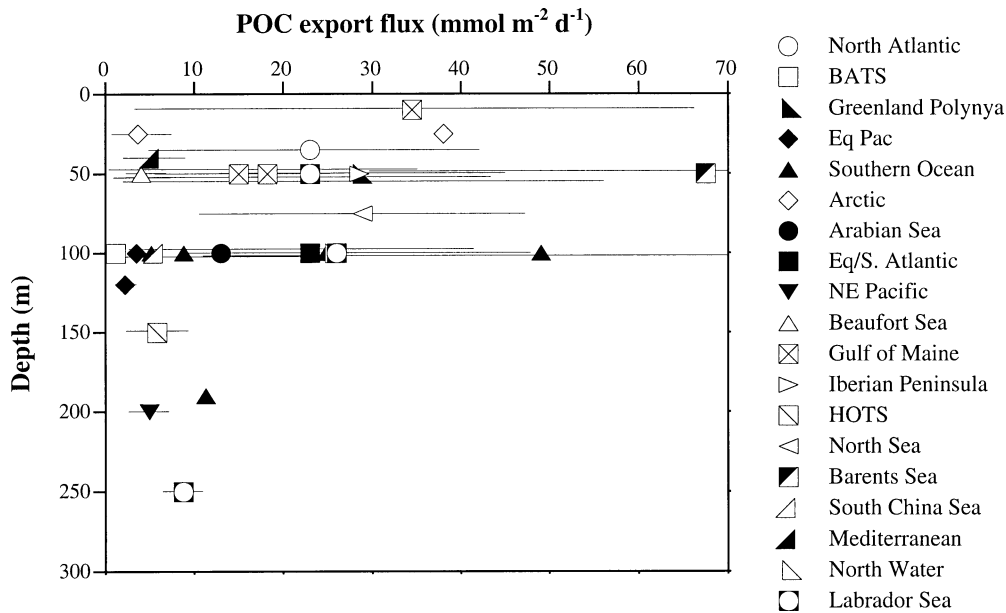


Fig. 1. ²³⁴Th-derived POC export fluxes as a function of depth for the world ocean. Symbols represent average POC flux and horizontal bars represent range for a given study. Symbol used for the Southern Ocean represents individual studies in the Ross Sea, Bellinghousen Sea, Antarctic Polar Front, and Southern Ocean-Pacific sector. Data are listed in Table 1.

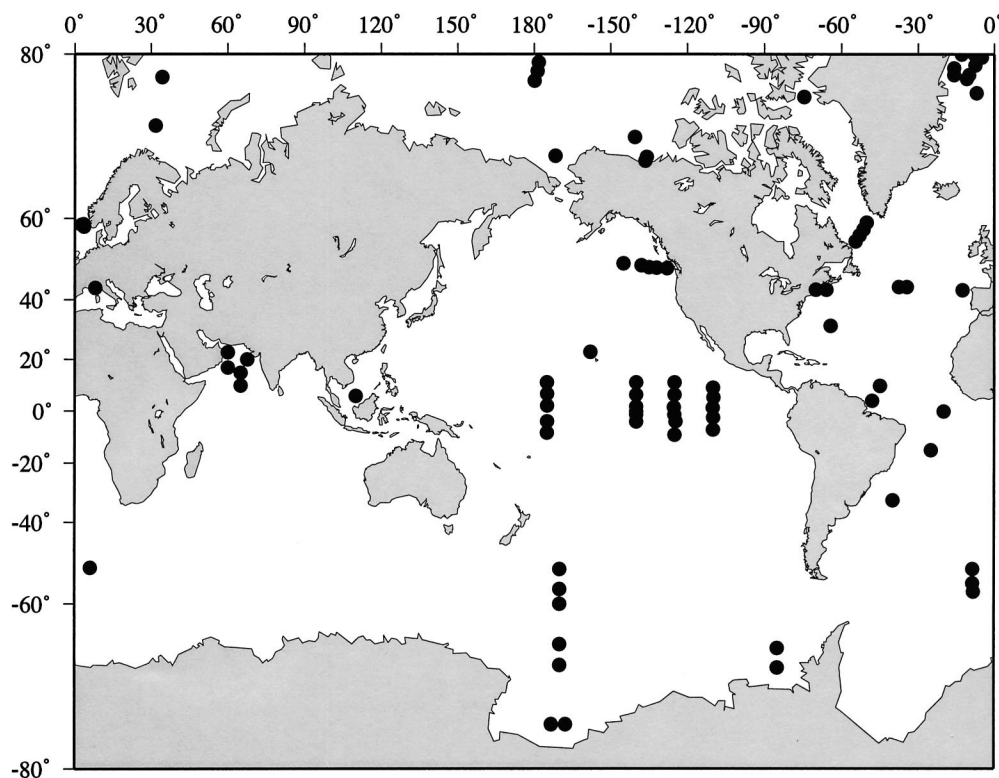


Fig. 2. Global distribution of sampling locations where upper ocean POC export fluxes have been determined using ²³⁴Th/²³⁸U disequilibrium (data plotted in Fig. 1). Also shown are stations occupied in this study in the Labrador Sea, July 1999.

POC analysis. MnO_2 cartridges and 1- μm cartridge prefilters were dried at 60°C and held for ^{234}Th analysis.

^{234}Th activities in the MnO_2 cartridges and 1- μm cartridge prefilters were determined by gamma spectrometry using a pure-Ge well detector calibrated for the appropriate geometries using NIST ^{238}U (SRM #4321B) (Buesseler et al. 1992b; Moran et al. 1997; Charette et al. 2001). ^{234}Th activities in the intermediate- and large-particle size classes were determined by direct beta counting of particles resuspended onto the 25-mm GF/F filters using a RISØ Laboratory low-background gas flow proportional counter operated in anti-coincidence mode (Charette et al. 2001). Reported uncertainties in the ^{234}Th data are based on counting statistics. ^{238}U activities were calculated from salinity ($^{238}\text{U} = 0.07081 \times \text{salinity}$) (Chen et al. 1986).

Primary productivity was determined at eight depths by measuring ^{13}C -bicarbonate uptake rates in on-deck incubation simulated in situ experiments (Hama et al. 1983). Depths sampled were chosen to correspond to the 60, 30, 12, 6, 3, 1, 0.5, and 0.2% light penetration depths. Computed hourly, ^{13}C uptake rates were scaled up to daily rates by comparison of integrated irradiance during the incubation period with the total daily value. POC concentrations on GF/F filters were determined using a carbon and nitrogen (CHN) analyzer (Pike and Moran 1997). Dissolved $\text{NO}_2 + \text{NO}_3$ concentrations were analyzed using an autoanalyzer.

Results

The upper 250 m of the stations occupied are characterized by a euphotic zone restricted to the upper ~50–75 m, as evidenced by primary productivity measurements (Fig. 3). Depth profiles of σ_t and dissolved $\text{NO}_2 + \text{NO}_3$ concentration indicate a gradient extending down through the mixed layer to ~100 m (Fig. 3). Particle export of ^{234}Th from the upper 100 m is evident at all stations on the basis of the observed total ^{234}Th deficit (Fig. 3a; average ^{234}Th deficit for all stations indicated by shaded area). Size-fractionated particulate ^{234}Th activities exhibit a subsurface maximum for small (1–10 μm), intermediate (10–53 μm), and large (>53 μm), rapidly sinking size particles. There is progressively more scatter in particulate ^{234}Th activity with increasing particle size. Presumably this reflects the lower abundance of larger size particles and a corresponding greater sampling uncertainty. Intermediate- and large-particle ^{234}Th activities typically represent ~1–15% of small-particle ^{234}Th . Concentrations of POC decrease with depth for all particle size classes, with concentrations in the intermediate- and large-particle size representing ~10% and ~1% of small-particle POC. The $\text{POC}/^{234}\text{Th}$ ratio of the small particles exhibits a slight increase with depth, whereas a marked decrease with depth is evident for intermediate- and larger-size particles. $\text{POC}/^{234}\text{Th}$ ratios are similar in magnitude for both the intermediate and larger particle sizes, and significantly lower than the small-particle $\text{POC}/^{234}\text{Th}$ ratios.

Discussion

In calculating POC export fluxes for the Labrador Sea stations, we also demonstrate quantitatively the sensitivity of

these calculations to the natural variability in the $\text{POC}/^{234}\text{Th}$ ratio and to the choice of depth and method used to calculate the ^{234}Th deficit (Fig. 3). POC export fluxes were calculated using several combinations of $\text{POC}/^{234}\text{Th}$ ratios and depth-integrated ^{234}Th fluxes. Note that these calculations explicitly reproduce many of the published methods used to calculate POC fluxes (see Table 1). We do not consider advective and diffusive transport of ^{234}Th or differences between steady-state and non-steady state conditions because it would have no net effect in comparing the calculated results.

First, ^{234}Th fluxes were quantified by trapezoidal integration of the ^{234}Th deficit from the surface water to the base of the euphotic zone (0–50 m), the base of the mixed layer (0–100 m), and down to 250 m. ^{234}Th fluxes were also calculated by subtracting the average total ^{234}Th activity from the average ^{238}U activity within the 0–50-m and 0–100-m depth range, which was intended to reproduce the vertically integrated (yo-yo) in situ pump-sampling that was conducted in the equatorial Pacific (Buesseler et al. 1995) and Arabian Sea (Buesseler et al. 1998). With respect to calculating $\text{POC}/^{234}\text{Th}$ ratios, the $\text{POC}/^{234}\text{Th}$ ratio in >53- μm particles were calculated at the base of the euphotic zone (50 m), the base of the mixed layer (100 m), and below the mixed layer (250 m). Average $\text{POC}/^{234}\text{Th}$ ratios (>53 μm) were also calculated within the 0–50-m and 0–100-m depth range to reproduce the vertically integrated sampling conducted in the equatorial Pacific (Buesseler et al. 1995). Note that POC concentrations were not obtained from Sta. 9 at 50 m. Our use of $\text{POC}/^{234}\text{Th}$ ratios in >53- μm size-fractionated particles presumes that this fraction is representative of rapidly sinking particles, an assumption also made in a number of previous studies (Buesseler et al. 1995, 1998; Bacon et al. 1996; Charette and Moran 1999; Benitez-Nelson et al. 2001a; Charette et al. 2001), which we note might differ from $\text{POC}/^{234}\text{Th}$ ratios in sediment trap material. Results of these calculations are listed in Table 2 and plotted in Fig. 4.

Our results demonstrate the range in uncertainty in calculating POC export fluxes using different $\text{POC}/^{234}\text{Th}$ ratios and different integration depths and methods for the ^{234}Th flux (Table 2; Fig. 4). Using 0–50-m and 0–100-m depth-integrated ^{234}Th fluxes and $\text{POC}/^{234}\text{Th}$ ratios at 50, 100, and 250 m, the corresponding POC export fluxes range by a factor of ~2–6. Using similar ^{234}Th integration depths and average $\text{POC}/^{234}\text{Th}$ ratios from 0–50 and 0–100 m increases the variability in POC export up to a factor of ~10 because of the inclusion of higher $\text{POC}/^{234}\text{Th}$ ratios from shallower depths (Fig. 3). In addition, the ^{234}Th export ratio (Th-E ratio; Buesseler et al. 1998), defined as the POC export flux divided by integrated primary productivity, also varies significantly for each station depending on the selection of $\text{POC}/^{234}\text{Th}$ ratio and ^{234}Th flux (Table 2). It is also apparent that it is the greater variability in the $\text{POC}/^{234}\text{Th}$ ratio, rather than the ^{234}Th flux, that contributes to the wide range in POC flux (Fig. 4). Overall, our analysis indicates that the natural variability in the $\text{POC}/^{234}\text{Th}$ ratio combined with different criteria used to estimate the depth-integrated ^{234}Th flux can result in an ~2–10-fold uncertainty in the POC export flux.

A further interesting result from these size-fractionated data is the similar POC flux calculated using $\text{POC}/^{234}\text{Th}$ ratios determined in the 10–53- μm - and >53- μm -particle size

Table 1. Summary of published ^{234}Th integration depths; ^{234}Th fluxes, and $\text{POC}/^{234}\text{Th}$ ratios in size-fractionated particulate matter and in sediment trap material, and reported ranges in POC export fluxes.

Location	^{234}Th deep integration depth (m)	^{234}Th flux (dpm m ⁻² d ⁻¹)	$\text{POC}/^{234}\text{Th}^*$		Rationale for selection of $\text{POC}/^{234}\text{Th}$ ratio used to calculate POC flux	Reported POC flux (mmol m ⁻² d ⁻¹)	Reference
			$>0.5\text{--} <1\ \mu\text{m}$	$>53\ \mu\text{m}$			
North Atlantic	35, euphotic zone	1,280–2,610	8–23		35 m, base of euphotic zone (upper limit)	5–41	Buesseler et al. 1992a
North Atlantic (BATS)	96	~250–1,850			150-m trap (lower limit)	5–41	Buesseler et al. 1992a
North East Water Polynya	50 m, euphotic zone <70 m	262–966	13–120		Integrated POC and particulate ^{234}Th	0.4–1.9	Michaels et al. 1994
Equatorial Pacific	100 m, euphotic zone	1,000–3,500	<2–>4	<0.5–>2.5†	0–100-m vertically integrated sample	12–45	Cochran et al. 1995
Equatorial Pacific	120 m, euphotic zone	2,450–3,800	~1.8	0.5–6.5	POC/ ^{234}Th at base of euphotic zone	2, 3–5 (equator)	Buesseler et al. 1995
Equatorial Pacific	100 m, euphotic zone	2,340–3,150	~0.5–4.5	~0.5–4.5	POC flux : Th flux at 150 m	1.9–2.4	Bacon et al. 1996
Bellinghausen Sea	100 m, mixed layer	274–1,557	6.5–37		POC/ ^{234}Th at discrete depths	1–6	Murray et al. 1996
Antarctic	100 m	~3,200	~11–85‡		Average POC/ ^{234}Th in surface water (assumes POC flux = 30–60% of SPM flux)	3.4–6.9	Shimmield et al. 1995
Central Arctic	20–30 m	50–850	5–21§	20–67	Surface (20–30 m) ratio	0.43–0.86 (over 22 d)	Rutgers van der Loeff et al. 1997
Arabian Sea	100 m, depth integrated	1,000–5,500	~1–6	0.7–7.8	POC/ ^{234}Th at 100 m	38 (Chukchi shelf)	Rutgers van der Loeff et al. 1997
Equatorial South Atlantic	100 m, vertically integrated	605	~2–17	~5–50	POC/ ^{234}Th at 100 m	0.3–7 (open ocean)	Moran et al. 1997
South Atlantic	100 m, discrete depth	1,230	~2–17	~5–50	0–100-m vertically integrated sampling	<1–>25	Moran et al. 1997
Northeast Pacific	200 m	200–1,400	~2–14		POC/ ^{234}Th 110 and 220 m	3.2–43	Charette and Moran 1999
Beaufort Sea	50 m	75–626	8.5–12		Integrated POC and particulate ^{234}Th	3.2–43	Charette and Moran 1999
Gulf of Maine	10 m	143–568¶	2–534		Average POC/ ^{234}Th in upper 10 m	2.8–7.1	Charette et al. 1999
Gulf of Maine	50 m	574–1,460#	2–534		Average POC/ ^{234}Th in upper 50 m	0.7–7.4	Moran and Smith 2000
Gulf of Maine	50 m, euphotic zone	~300–900	~0.5–29	~2–300	Base of euphotic zone; 50 m	2.9–66	Benitez-Nelson et al. 2000
Ross Sea	100 m	~200–2,600	~5–80		POC/ ^{234}Th at base of given depth interval	0.3–36	Benitez-Nelson et al. 2000
Iberian Peninsula	50 m	~600–1,000	~5–60		POC/ ^{234}Th at ~10 m	5–25	Charette et al. 2001
Southern Ocean	100 m, below mixed layer	1,800–3,500	3.0–14		POC/ ^{234}Th averaged 80–150 m	7–91	Cochran et al. 2000
North Pacific (HOTS)	150 m	374–2,311¶¶	2.2–5.4	3.6–7.4**	POC/ ^{234}Th at 150 m	1.2–10.4	Benitez-Nelson et al. 2001a

Table 1. Continued.

Location	²³⁴ Th deep integration depth (m)	²³⁴ Th flux (dpm m ⁻² d ⁻¹)	POC/ ²³⁴ Th*		sed. trap	Rationale for selection of POC/ ²³⁴ Th ratio used to calculate POC flux	Reported POC flux (mmol m ⁻² d ⁻¹)	Reference
			>0.5- <1 μm	>53 μm				
North Pacific (HOTS)	150 m	111-1,724#	2.2-5.4	3.6-7.4**		POC/ ²³⁴ Th at 150 m	1.2-10.4	Benitez-Nelson et al. 2001a
North Sea	75 m, euphotic and subeuphotic	357-1,386	11-76			Discrete depths	9.5-48	Foster and Shim-mield 2002
Barents Sea	0-50, euphotic	614-1,549	47-98		3.4-9.2	POC/ ²³⁴ Th at 100 m	29-106	Coppola et al. 2002
South China Sea	100 m	not reported	3.6-21			POC/ ²³⁴ Th at depth of export	5.7	Cai et al. 2002
Antarctic Polar Front	100 m	865	10.2 ± 0.8				8.8	Rutgers van der Loeff et al. 2002
	190 m	1,115					11.3	Rutgers van der Loeff et al. 2002
NW Mediterranean Sea	0-40 m	183-1,985¶	26.8-43.6			POC flux from NSS model and trap POC/ ²³⁴ Th	1.4-9.2	Schmidt et al. 2002
	0-40 m	28-644#						
North Water Polynya	100 m	800-2,400			5-49.5	POC/ ²³⁴ Th at 100 m	5.3-45.4	Amiel et al 2002
Labrador Sea	Variable (see Table 2)			3.8-63		See Table 2	3.1-83	This study

* POC/²³⁴Th ratios in >0.45 to <1 μm were determined by filtration using 0.5-, 0.7- or 1-μm filters (see individual publications for details).

† 0-100-m average value.

‡ Reported as averages for Polar Front (20.9) and Southern Antarctic Circumpolar Current (40).

§ 0.7-53 μm.

|| Both vertically integrated and discrete depth sampling were conducted at one single station.

¶ Non-steady state model.

Steady state model.

** POC/²³⁴Th from 150 m; range represents temporal variation.

Table 2. ^{234}Th integration depths, ^{234}Th fluxes, $\text{POC}/^{234}\text{Th}$ ratios, POC export fluxes, and ^{234}Th -E ratios for the Labrador Sea.

^{234}Th Integration depth (m)	^{234}Th flux (dpm $\text{m}^{-2} \text{d}^{-1}$)	$\text{POC}/^{234}\text{Th}$ size fraction (μm)	$\text{POC}/^{234}\text{Th}$ depth (m)	$\text{POC}/^{234}\text{Th}$ ($\mu\text{mol dpm}^{-1}$)	POC flux (mmol $\text{C m}^{-2} \text{d}^{-1}$)	$\int \text{PP}^*$ (mmol $\text{C m}^{-2} \text{d}^{-1}$)	$\text{Th-E ratio}^\dagger$
Station 9, 55.26°N, 53.98°W							
0–50	963 ± 145	>53	50	n.d.	n.d.	66.9	—
0–50	963 ± 145	>53	100	4.1 ± 0.3	3.9 ± 0.7	—	—
0–50	963 ± 145	>53	250	3.8 ± 0.3	3.7 ± 0.6	—	—
Average 0–50	916 ± 156	>53	Average 0–50	26 ± 3.8	24 ± 5.3	—	—
0–100	1,395 ± 210	>53	100	4.1 ± 0.3	5.7 ± 1.0	—	0.09
0–100	1,395 ± 210	>53	250	3.8 ± 0.3	5.3 ± 0.9	—	0.08
Average 1–100	1,407 ± 285	>53	100	4.1 ± 0.3	5.8 ± 1.2	—	0.09
Average 1–100	1,407 ± 285	>53	Average 0–100	22 ± 3.1	30 ± 7.4	—	0.45
0–250	2,750 ± 410	>53	250	3.8 ± 0.3	10 ± 1.8	—	0.16
0–100	1,395 ± 210	10–53	100	4.4 ± 0.3	6.3 ± 0.4	—	0.09
Range in POC flux (>53 μm) = 3.7–30 mmol $\text{C m}^{-2} \text{d}^{-1}$							
Station 18, 58.22°N, 50.8°W							
0–50	667 ± 100	>53	50	12 ± 1	8 ± 1.4	—	—
0–50	667 ± 100	>53	100	22 ± 9	15 ± 6.5	—	—
0–50	667 ± 100	>53	250	9.1 ± 0.9	6.1 ± 1.1	—	—
Average 0–50	714 ± 129	>53	Average 0–50	37 ± 7.5	26 ± 7.1	—	—
0–100	975 ± 145	>53	100	22 ± 9	21 ± 9.3	—	0.25
0–100	975 ± 145	>53	250	9.1 ± 0.9	8.9 ± 1.6	—	0.11
Average 0–100	1,047 ± 240	>53	100	22 ± 9	23 ± 11	—	0.27
Average 0–100	1,047 ± 240	>53	Average 0–100	36 ± 9.8	38 ± 13	—	0.45
0–250	821 ± 120	>53	250	9.1 ± 0.9	7.5 ± 1.3	—	0.09
0–100	975 ± 145	10–53	100	4.8 ± 0.5	3.1 ± 0.6	—	0.04
Range in POC flux (>53 μm) = 6.1–38 mmol $\text{C m}^{-2} \text{d}^{-1}$							
Station 25, 60.29°N, 48.54°W							
0–50	635 ± 95	>53	50	31 ± 6	20 ± 4.8	—	—
0–50	635 ± 95	>53	100	14 ± 1	8.9 ± 1.5	—	—
0–50	635 ± 95	>53	250	4.8 ± 0.5	3.7 ± 0.7	—	—
Average 0–50	666 ± 99	>53	Average 0–50	63 ± 12	42 ± 11	—	—
0–100	1,110 ± 165	>53	100	14 ± 1	16 ± 2.6	—	0.38
0–100	1,110 ± 165	>53	250	5.9 ± 0.5	6.6 ± 1.1	—	0.16
Average 1–100	1,086 ± 220	>53	100	14 ± 1	15 ± 3.2	—	0.35
Average 1–100	1,086 ± 220	>53	Average 0–100	43 ± 8.1	47 ± 13	—	1.11
0–250	1,495 ± 225	>53	250	5.9 ± 0.5	8.8 ± 1.5	—	0.21
0–100	1,110 ± 165	10–53	100	6 ± 0.3	7.1 ± 1.1	—	0.17
Range in POC flux (>53 μm) = 3.7–47 mmol $\text{C m}^{-2} \text{d}^{-1}$							

* Primary productivity integrated from 0–44 m (St. 9), 0–63 m (St. 18), 0–76 m (St. 25).

† Th-E ratio calculated using POC fluxes determined at 100 and 250 m.

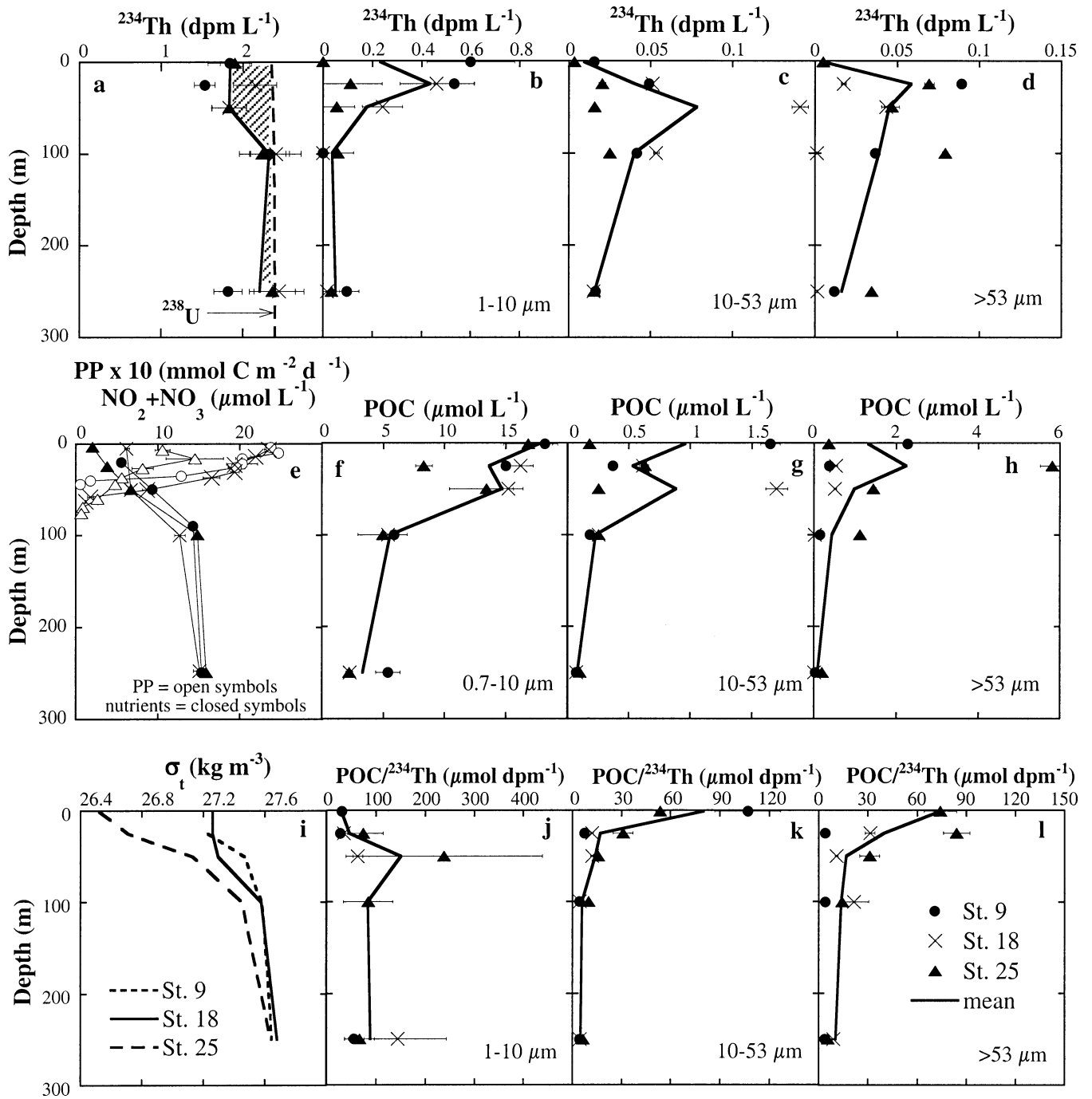


Fig. 3. Depth profiles of (a) total ^{234}Th and ^{238}U activity; (b–d) size-fractionated particulate ^{234}Th activity; (e) primary productivity and $\text{NO}_2 + \text{NO}_3$; (f–h) size-fractionated POC concentrations; (i) σ_t ; and (j–l) size-fractionated POC/ ^{234}Th ratios in the Labrador Sea.

fractions for each station (Table 2). The straightforward explanation is that the POC/ ^{234}Th ratio in each of these particle size classes is remarkably similar with respect to magnitude and depth distribution (Fig. 3), thereby resulting in similar POC fluxes as calculated using Eq. 1. However, although both the intermediate- and large-particle size classes undoubtedly contribute to the total flux, the relative importance of these empirically derived POC fluxes remains unclear.

A key implication is that a similar uncertainty likely exists

for the majority of ^{234}Th -derived POC export fluxes reported for the world ocean (Fig. 1; Table 1). This is not immediately apparent, nor easily determined, from previous studies, which invariably report a narrow range in POC export and Th-E ratio based on POC and ^{234}Th measurement precision (Buesseler 1998). In fact, several open ocean studies have reported that POC/ ^{234}Th ratios typically range by a factor of five or more (Table 1), implying a corresponding uncertainty in the POC flux. Even under optimal conditions, such as in

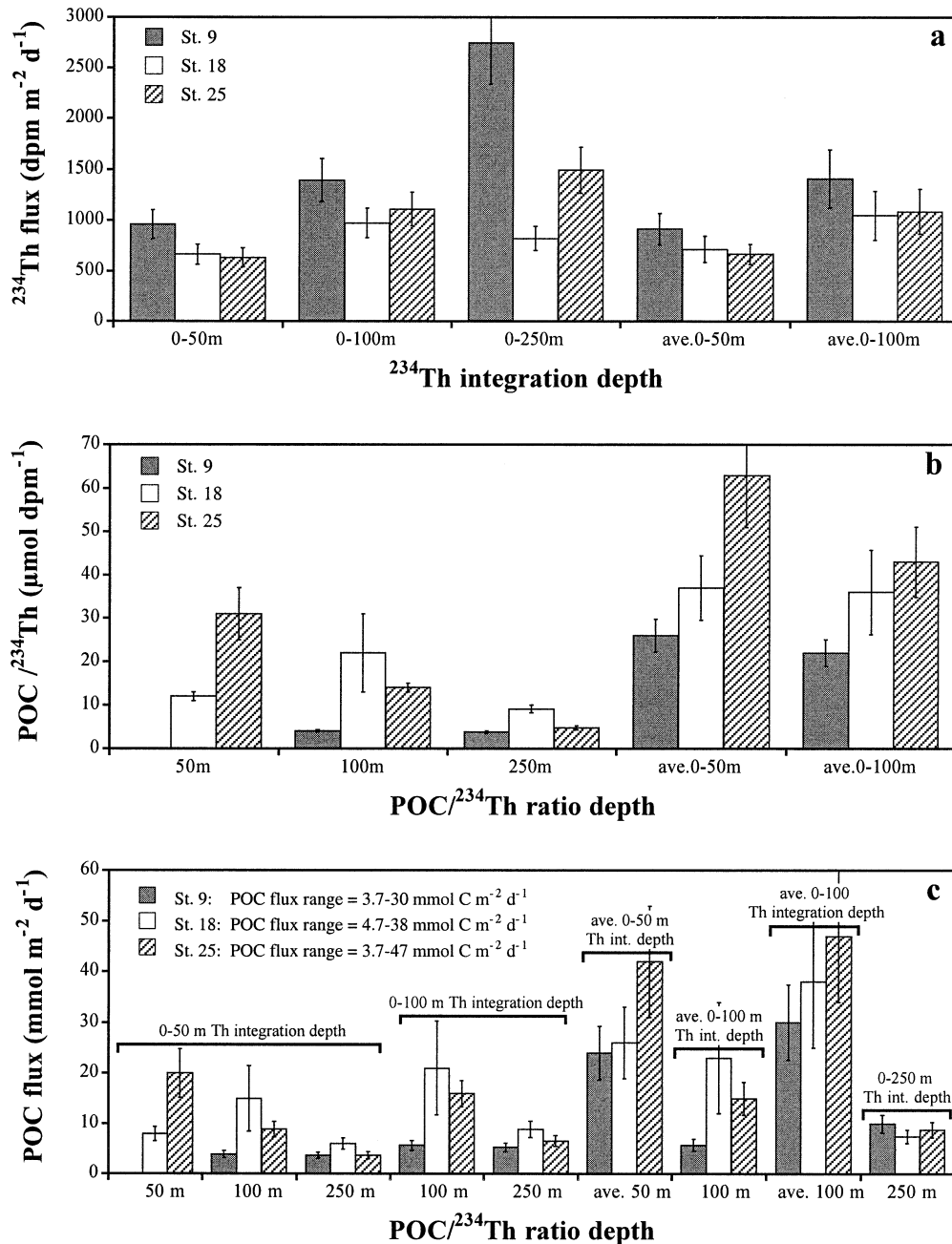


Fig. 4. (a) ^{234}Th fluxes, (b) POC/ ^{234}Th ratios, and (c) POC fluxes from the Labrador Sea. POC fluxes were calculated for different combinations of the depth-integrated ^{234}Th flux and the POC/ ^{234}Th ratio. Note that for ^{234}Th fluxes (panel a), 0–50 m and 0–100 m represent values calculated by integration of the ^{234}Th deficit from the surface water to the base of the euphotic zone (0–50 m) and the base of the mixed layer (0–100 m), whereas ave. 0–50 and ave. 0–100 m represent average values calculated by subtracting the average total ^{234}Th activity from the average ^{238}U activity within the 0–50-m and 0–100-m depth ranges (see text).

the equatorial Pacific, ^{234}Th -derived POC export fluxes from the euphotic zone are expected to vary by at least a factor of two to three (Buesseler et al. 1995; Bacon et al. 1996; Murray et al. 1996). While ambiguous, this uncertainty is comparable to other techniques, such as sediment traps, nutrient and oxygen budgets, and $\delta^{15}\text{N}$ measurements (Buesseler 1991; Michaels et al. 1994; Charette et al. 1999; Ben-

itez-Nelson et al. 2001a). For shelf systems, the observed range in POC/ ^{234}Th ratios is even greater than in the open ocean, potentially increasing the range in POC flux by up to two orders of magnitude. Similar uncertainty can be expected in the application of ^{234}Th to estimate the upper ocean export flux of particulate inorganic carbon (PIC) (Bacon et al. 1996), nutrients (biogenic Si, Buesseler et al. 2001a; Rut-

gers van der Loeff et al. 2002), trace metals (Weinstein et al. 2000), and organic contaminants (Gustafsson et al. 1997).

Improvement in the ^{234}Th method for determining the export flux of POC requires focus on constraining the POC/ ^{234}Th ratio, ideally developing predictive models of this parameter (Burd et al. 2000). A major challenge is the variable gradient in POC/ ^{234}Th ratio with depth, which makes the selection of an appropriate depth to determine the POC/ ^{234}Th ratio ambiguous, using either size fractionation or sediment trap collection methods. Our analysis indicates that using an average POC/ ^{234}Th ratio in the upper ocean can bias the POC flux toward higher values, whereas samples collected deeper in the water column have lower POC/ ^{234}Th ratios and corresponding POC fluxes. Using large-particle POC/ ^{234}Th ratios from deeper in the water column, where there is apparently less variability (Fig. 3), will tend to result in lower and less variable POC export fluxes. There is no theoretical "correct" water column depth, however, since POC/ ^{234}Th ratios will vary with depth as the organic carbon concentration of sinking particles is altered by remineralization and as particulate ^{234}Th continuously undergoes adsorption, desorption, remineralization, and radioactive decay. In addition, recent studies suggest that interaction of ^{234}Th with surface-active acid polysaccharides could account for observed depth variations in POC/ ^{234}Th ratios (Guo et al. 2002; Quigley et al. 2002; Santschi et al. 2003). Additional field and laboratory studies focusing on the interaction between ^{234}Th and surface-active macromolecular organic matter could provide important clues as to the mechanism controlling the natural variability in POC/ ^{234}Th ratios as a function of depth, particle size, and oceanographic regime.

Several recent studies suggest that the POC export flux might be more tightly constrained by combining the ^{234}Th flux with POC/ ^{234}Th ratios determined in material collected with sediment traps (Murray et al. 1996; Charette et al. 1999; Benitez-Nelson et al. 2001a; Coppola et al. 2002), either surface tethered or neutrally buoyant (Buesseler et al. 2000). Particles collected in sediment traps are subjected to sample collection biases, however, including swimmers and bacterial remineralization, which can alter the POC concentration and particulate ^{234}Th activity and hence the POC/ ^{234}Th ratio. It is not known whether size fractionation filtration or sediment traps provide the most representative POC/ ^{234}Th ratio of biogenic particulate matter sinking from the upper ocean. We recommend a systematic, direct comparison of the depth dependence of POC/ ^{234}Th ratios determined using size-fractionated samples collected by large-volume in situ pump filtration, with particulate matter collected by sediment trap.

The accuracy of the ^{234}Th export flux can also be improved, for example, through more detailed sampling using recently developed small-volume analytical techniques (Rutgers van der Loeff and Moore 1999; Benitez-Nelson et al. 2001b; Buesseler et al. 2001b). Nevertheless, improved accuracy in determining ^{234}Th fluxes ideally requires time series (weeks to months) data to constrain the non-steady state that is likely the norm (Minagawa and Tsunogai 1980; Tanaka et al. 1983; Buesseler et al. 1992a; Moran and Buesseler 1993; Benitez-Nelson et al. 2000, 2001a; Kim and Church 2001) and advective and diffusive transport that can redistribute total $^{234}\text{Th}/^{238}\text{U}$ disequilibrium in the upper ocean

(Buesseler et al. 1995; Bacon et al. 1996; Murray et al. 1996; Charette et al. 1999). Although logistically challenging, we recommend an experimental determination of the relative importance of the advective, diffusive, and temporal variations in ^{234}Th and a quantitative analysis of how this translates to variability in the POC export flux.

Finally, the most straightforward improvement in the use of $^{234}\text{Th}/^{238}\text{U}$ disequilibrium to calculate POC export fluxes is a statement of the assumptions used. This should include an explanation of the justification used in selecting the POC/ ^{234}Th ratio and the depth of integration when calculating the ^{234}Th flux. Ideally, the POC export flux should be calculated using various combinations of the POC/ ^{234}Th ratio and ^{234}Th fluxes calculated for the euphotic zone and mixed-layer depths (Table 2), which would provide a range of POC export fluxes and hence a measure of the uncertainty in the reported results.

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